# Cost analysis for the degradation of highly concentrated textile dye wastewater with chemical oxidation H<sub>2</sub>O<sub>2</sub>/UV and biological treatment



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Abstract: The efficiency and cost-effectiveness of  $H_2O_2/UV$  for the complete decolorization and mineralization of wastewater containing high concentrations of the textile dye Reactive Black 5 was examined. Oxidation until decolorization removed  $200-300 \, \text{mg g}^{-1}$  of the dissolved organic carbon (DOC). The specific energy consumption was dependent on the initial dye concentration: the higher concentration required a lower specific energy input on a weight basis ( $160 \, \text{Wh g}^{-1} \, \text{RB5}$  for  $2.1 \, \text{g L}^{-1}$  versus  $354 \, \text{Wh g}^{-1} \, \text{RB5}$  for  $0.5 \, \text{g L}^{-1}$ ). Biodegradable compounds were formed, so that DOC removal could be increased by 30% in a following biological stage. However, in order to attain  $800 \, \text{mg g}^{-1}$  overall mineralization,  $500 \, \text{mg g}^{-1}$  of the DOC had to be oxidized in the  $H_2O_2/UV$  stage. A cost analysis showed that although the capital costs are much less for a  $H_2O_2/UV$  stage compared to ozonation, the operating costs are almost double those of ozonation. Thus, while  $H_2O_2/UV$  can compete with ozonation when the treatment goal only requires decolorization, ozonation is more cost-effective in this case when mineralization is desired. ©  $2006 \, \text{Society}$  of Chemical Industry

**Keywords:** cost analysis; textile dye; Reactive Black 5; hydrogen peroxide/UV; biological process; combination processes

### **NOTATION**

AOPs Advanced oxidation processes

 $C_{\rm d}$  Concentration of RB5 (mg L<sup>-1</sup>)

 $C_{\text{do}}$  Initial RB5 concentration at  $t = 0 \text{ (mg L}^{-1})$  $C_{\text{H}_2\text{O}_2}$  Concentration of hydrogen peroxide (mM)

COD Chemical oxygen demand

 $C_{\rm s}$  Concentration of DOC (mg L<sup>-1</sup>)

 $C_{\rm s,Bio}$  Final DOC concentration in the biological

reactor (mg  $L^{-1}$ )

 $C_{\rm so}$  Initial DOC concentration at t = 0

Dec Decolorization

DOC Dissolved organic carbon (mg  $L^{-1}$ ) E Specific energy consumption (kW h m<sup>-3</sup>)

 $Q_{\rm R}$  Recirculation flow rate (L min<sup>-1</sup>)

RB5 Reactive Black 5

SAC Spectral absorption coefficient (m<sup>-1</sup>)

t Time (min or h)

TOC Total organic carbon (mg L<sup>-1</sup>)  $t_{\text{oxi},1}$  First preoxidation time (min)  $t_{\text{oxi},2}$  Second preoxidation time (min)

 $t_{\text{oxi},3}$  Third preoxidation time (min)

V Reactor volume (L)

 $V_{\rm ex}$  Volume of external vessel (L)

 $V_{\rm uv}$  UV reactor volume (L)

VSS Volatile suspended solid (mg  $L^{-1}$ )

 $\alpha_{\rm dec}$  Degree of decolorization (%)

 $\alpha_{Bio}$  Efficiency of the biological process (mg g<sup>-1</sup>)  $\alpha_{AOP}$  Efficiency of H<sub>2</sub>O<sub>2</sub>/UV process (mg g<sup>-1</sup>)

 $\alpha_{\rm DOC}$  Total efficiency (mg g<sup>-1</sup>)

### INTRODUCTION

The textile industry is well known for its high water consumption (300 L kg<sup>-1</sup> material) and complex wastewater due to the variety of additives and finishing processes. With increasing interest in process water recycling and tighter regulations on the disposal of dyecontaining wastewaters (e.g., German regulations), segregation and separate treatment schemes are becoming important for dye-house wastewaters with high dye concentrations.

Biological treatment is usually the most economical wastewater treatment option. However, biological processes alone are not effective for treating dyecontaining effluents. Textile dye wastewater can be decolorized in the anaerobic process, but the intermediates formed may be toxic and scarcely degradable in the aerobic biological process.<sup>3,4</sup> The development of combined chemical–biological processes with the ability to reduce the toxicity and improve the degradability of the dye intermediate compounds can reduce the cost associated with chemical oxidation processes.<sup>5,6</sup>

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Many advanced oxidation processes (AOPs) have been successfully used to decolorize wastewaters with low textile dye concentration ( $<30\,\mathrm{mg}\,\mathrm{L}^{-1}$ ). The UV-driven processes combine the use of UV light with an oxidizer such as ozone,  $\mathrm{H}_2\mathrm{O}_2$  or Fenton's reagent to generate hydroxyl radicals (OH°) which attack organic compounds nonselectively with a high reaction rate. These processes are characterized by high energy consumption and the production of less reactive aliphatic acids. If the goal is to mineralize and not just decolorize the textile dyes, much higher energy consumption is necessary, especially for concentrated dye-baths, or a combination with an aerobic biological process is needed to reduce operating costs.  $^{11}$ 

AOPs have been used to convert a variety of nondegradable compounds to degradable ones by partial oxidation  $^{6,12}$  and further oxidized in a following biological stage. A comparison between the AOPs -  $H_2O_2/UV,\,O_3/H_2O_2,\,$  and  $O_3$  alone – for increasing the biodegradability of low concentrations of disinfection by-products showed that  $H_2O_2/UV$  produced results comparable to  $O_3$  and higher than those obtained by  $O_3/H_2O_2.$  An additional benefit was that  $H_2O_2/UV$  is a much easier process.  $^{12}$ 

An important parameter for increasing biodegradability is the retention time in the oxidation reactor. When treating colored wastewater discharged from the wool-scouring industry with  $H_2O_2/UV$ , the biodegradability of the oxidation products diminished with the extension of the oxidation time. By choosing the best oxidation time, the combined process increased the overall COD removal by 25%.<sup>13</sup>

Substantial reductions in chemical oxidation costs have been reported for combinations with a biological stage. For example, the use of H<sub>2</sub>O<sub>2</sub>/UV combined with a biological stage enhanced the overall COD removal from several biologically pretreated landfill leachates, resulting in an increase from 700 mg g<sup>-1</sup> using H<sub>2</sub>O<sub>2</sub>/UV alone to 850 mg g<sup>-1</sup> using integrated stages with internal recycle.14 Biological oxidation eliminated 460 mg g<sup>-1</sup> of the COD, reducing the energy consumption by 22%. However, the method of the reactor coupling, i.e. with or without internal recycle, has a large influence on the overall costeffectiveness of the process. When ozonation was combined with a biological stage with internal recycle for the treatment of a highly concentrated dye-house wastewater, the ozone consumption was significantly reduced ( $\sim$ 60%). <sup>15</sup> Unfortunately, the internal recycle between the two reactors required solids separation, incurring operation costs which amounted to  $\sim 60\%$ of the ozone production costs, negating the ozone savings.

Furthermore, estimation of the overall costeffectiveness must consider capital as well as operating costs. A major hurdle for ozone treatment is the large investment cost required. A cost estimate for a combined ozone and biological process for treating concentrated dye-baths showed that the one-stage ozone process was less expensive than the combined ozone-biological process, because the reduction in ozone consumption was offset by the additional investment and the personnel costs for biological treatment. In order to avoid these additional costs for a biological treatment stage, it is often argued that chemical oxidation can be used as a pretreatment before discharge to a municipal treatment plant. In this case, criteria to ensure a high removal in the municipal plant must be determined. In both ozonation studies above, oxidation to complete decolorization was not enough.

Although H<sub>2</sub>O<sub>2</sub>/UV represents an alternative to the complexities and high investment costs of ozonation, few studies are available on its combination with biological processes. This paper presents an assessment of the overall removal achieved by combined H<sub>2</sub>O<sub>2</sub>/UV and biological treatment of high concentrations of a common reactive textile dye, as well as a cost analysis of the process. The efficiency of the combined process for treating highly concentrated textile dye wastewater is evaluated based on three criteria: the degree of decolorization and mineralization, as well as energy consumption. First, the results for decolorization and mineralization using the H<sub>2</sub>O<sub>2</sub>/UV process alone and the associated energy consumption are presented for two different dye concentrations. Then the effect of the chemical oxidation time on the combination with the biological process is evaluated. Finally, costs for the oxidation stage are estimated as a function of the degree of mineralization achieved. The costs for H<sub>2</sub>O<sub>2</sub>/UV are compared to those for ozonation.

# **EXPERIMENTAL**Reactors

Oxidation experiments were carried out in a twopart experimental set-up (Fig. 1). The first part was a magnetically stirred photochemical reactor ( $V_{uv}$  = 0.95 L) with a coaxial medium-pressure Hg lamp (TQ 150, 150 W, emission range 200-280 nm; Heraeus Noblelight Company, Kleinostheim, Germany). The UV lamp was inserted into a quartz tube immersed in a cooling jacket. The second part was an external vessel ( $V_{\rm ex} = 2.1$  L) with a variable-speed stirrer and a heat exchanger coil for temperature control to keep the temperature at 25 °C. The total volume of the reactor system including the tubing was 3.8 L. The pH was regulated at the desired value pH =  $7 \pm 0.06$ by dosing 0.5 M NaOH with a membrane pump. The solution was recirculated  $(Q_R = 580 \,\mathrm{Lh^{-1}})$  with a centrifugal pump between the photochemical reactor and the external vessel.

To examine the biodegradability of the chemical oxidation byproducts, 2 L were taken after the appropriate oxidation times and batch experiments carried were made in a glass-stirred tank reactor (V=3 L), liquid volume 2 L). It had a flanged cover with the appropriate openings. Air was introduced through a sparger under the stirrer with a speed of

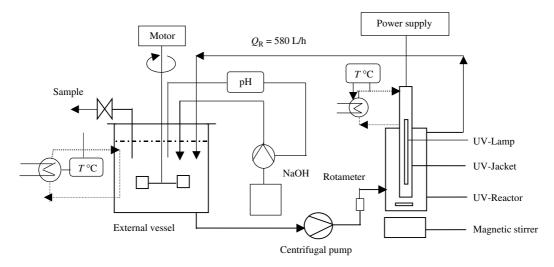


Figure 1. Reactor set-up for oxidation experiments with H<sub>2</sub>O<sub>2</sub>/UV.

320 min<sup>-1</sup>, and the dissolved oxygen concentration was kept between 4 and 6 mg L<sup>-1</sup>. pH was measured regularly and adjusted to pH = 7. The biomass was collected from a sequencing batch reactor, which ran for two months with RB5 oxidative products, and adjusted to 2.0 g VSS L<sup>-1</sup> in the batch reactor. The standard deviation of the biomass concentration in the three oxidation experiments was  $0.096 \, \mathrm{g} \, \mathrm{VSS} \, \mathrm{L}^{-1}$ .

Nutrients and the trace elements required for the microbial growth were added to the intermediates solution according to the ratio of C:N:P, 100:10:1 (w/w/w). The DOC concentration in the aerobic reactor was followed over time. Control experiments using the same bacteria culture to degrade glucose in the presence of the same  $H_2O_2$  concentration were made to ensure biomass viability.

## Reagent and analytical methods

The diazo reactive dye C.I. Reactive Black 5 was obtained as a commercial product (520 mg g<sup>-1</sup> dye), from DyStar, Germany. It was hydrolyzed in an aqueous solution of 0.1 M NaOH at boiling point for 20 min to simulate the dying process.<sup>17</sup> Samples were taken periodically during the runs, filtered (0.2 µm cellulose acetate; Sartorius, Göttingen, Germany) and diluted if necessary. The dye concentration  $(C_d)$ was measured with a spectrophotometer (UV-1202; Shimadzu, Kyoto, Japan) at wavelength  $\lambda = 583 \, \text{nm}$ . Dissolved organic carbon (DOC) was measured using a DIMA-TOC100 (Dimatec, Essen, Germany).  $300 \,\mathrm{g} \,\mathrm{L}^{-1}$  analytical-grade hydrogen peroxide (Merck, Germany) was used. Residual hydrogen peroxide concentration  $C_{H_2O_2}$  was determined photometrically according to the methods reported by Masschelein et al. 18

The biomass concentration was determined as total volatile suspended solids (VSS) in triplicate for each experiment.

The efficiencies of the AOP oxidation ( $\alpha_{AOP}$ ) and biodegradation processes ( $\alpha_{Bio}$ ) were calculated in terms of DOC removal degree for each process based

on the initial DOC concentration of the wastewater  $C_{so}$ , so that the overall efficiency of the combined system can be calculated by the summation of the oxidation efficiency and the biological efficiency:

$$\alpha_{\text{DOC}} = \alpha_{\text{AOP}} + \alpha_{\text{Bio}} = \frac{C_{\text{so}} - C_{\text{s,Bio}}}{C_{\text{so}}}$$
 (1)

where  $C_{\rm s,Bio}$  is the final DOC concentration. The degree of decolorization  $\alpha_{\rm dec}$  was calculated for the UV/H<sub>2</sub>O<sub>2</sub> stage based on the initial dye concentration  $C_{\rm do}$ .

A cost analysis of a chemical oxidation stage for  $H_2O_2/UV$  versus ozonation was made for a segregated wastewater containing  $2\,\mathrm{g}\,\mathrm{L}^{-1}$  RB5,  $0.45\,\mathrm{g}\,\mathrm{L}^{-1}$  DOC with a flow rate of 50 L  $h^{-1}$ . A  $H_2O_2$  concentration of  $6\,\mathrm{kg}\,\mathrm{m}^{-3}$  was used. Operating cost of ozonation process is based on an ozone dose of  $8\,\mathrm{g}\,O_3\,\mathrm{g}^{-1}$  DOC,  $^{16}$  assuming that ozone will be applied at pH = 5; the cost of adjusting pH was neglected. The investment was depreciated over 5 years with an interest rate of 5% and operated  $300\,\mathrm{days}$  per year. Since the biological stage would be the same for both, only the costs for the chemical oxidation stage were considered.

# RESULTS AND DISCUSSION Chemical oxidation

The first step of this work was to examine the ability of the  $\rm H_2O_2/UV$  process to completely mineralize wastewater containing a high concentration of RB5. Figure 2 shows how the RB5 concentration fell sharply over radiation time. In contrast, the DOC and  $\rm H_2O_2$  concentrations decreased slowly at first, falling more rapidly only after decolorization was achieved. It also shows the decrease in the spectral absorption coefficient at 260 nm (SAC), which was used as an indicator for aromaticity. As can be seen in Fig. 2, by the time the color was removed ( $\sim$ 270 min), approximately  $300 \, {\rm mg \, g^{-1}}$  DOC removal was also achieved. This could be increased with an extension of

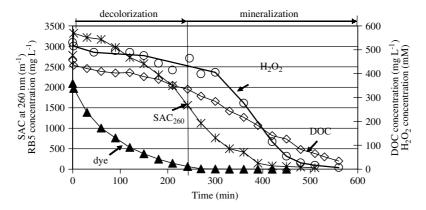


Figure 2. Relationship between decolorization, DOC removal,  $H_2O_2$  concentrations and spectral absorption coefficient at 260 nm during mineralization of Reactive Black 5 by  $H_2O_2/UV$ .  $C_{do}=2.1\,\mathrm{g\,L^{-1}}$ ,  $C_{H_2O_2}=530\,\mathrm{mm}$ , pH=7 and  $T=25\,^{\circ}\mathrm{C}$ .

radiation time and as long as hydrogen peroxide was available for generating enough OH° to proceed with the degradation reaction; e.g. at 560 min, 920 mg g<sup>-1</sup> of the DOC was removed.

The SAC of the mixture depends on both the dye concentration as well as the hydrogen peroxide concentration. The initial SAC of RB5 alone was  $2785 \,\mathrm{m}^{-1}$  (for  $C_{do} = 2.1 \,\mathrm{g} \,\mathrm{L}^{-1}$ ), and when  $H_2 O_2$  was added the SAC of the mixture increased to 3320 m<sup>-1</sup>; i.e., the contribution of H<sub>2</sub>O<sub>2</sub> to the SAC value is  $\sim 16\%$ . After the first 40 min of the oxidation a small decrease was observed, which ran parallel to the DOC and H2O2 curves. Thereafter it fell faster than both curves as the oxidation proceeded. This indicates that the aromatic rings of RB5 were converted to aliphatics before being converted to CO<sub>2</sub>. These results agree with those reported by Galindo et al., 19 who found that at the end of the decolorization of a mono azo dye AO52 less than  $300 \,\mathrm{mg}\,\mathrm{g}^{-1}$  of the stoichiometric amount of carbon dioxide was produced. The oxidation of the dye was initiated by the attack of the electrophilic OH° upon an electron-rich site, e.g. the amino group or near the azo nitrogen atoms. The aromatic ring was completely converted to colorless aliphatic compounds without significant carbon loss. The mineralization occurred due to destruction of the aliphatic intermediates as radiation continued.

The decomposition of H<sub>2</sub>O<sub>2</sub> during the decolorization process was extremely slow (Fig. 2). Only  $120\,mg\,g^{-1}$  of the  $H_2O_2$  was consumed during decolorization, accompanied by  $300 \text{ mg g}^{-1}$  DOC removal. This low consumption of H<sub>2</sub>O<sub>2</sub> has been also observed by Shu et al.7 during the decolorization of many azo dyes at low concentration. In contrast, for the same time period after the color was removed, 840 mg g<sup>-1</sup> of the  $H_2O_2$  was consumed, reaching  $920\,mg\,g^{-1}$ DOC removal. The higher rate of decomposition of H<sub>2</sub>O<sub>2</sub> after decolorization may be coupled with the decreasing SAC of RB5 and its intermediates. Because aromatic compounds absorb UV radiation between 200 and 260 nm, they compete with H<sub>2</sub>O<sub>2</sub> for the UV radiation. The opening of the aromatic rings leaves more radiation to be absorbed by H<sub>2</sub>O<sub>2</sub>, accelerating its decomposition.

Thus, if decolorization is the treatment goal, the majority of the  $H_2O_2$  added can still remain in the solution. With the goal of  $900\,\mathrm{mg\,g^{-1}}$  DOC mineralization,  $\sim\!960\,\mathrm{mg\,g^{-1}}$  of the  $H_2O_2$  will be consumed.

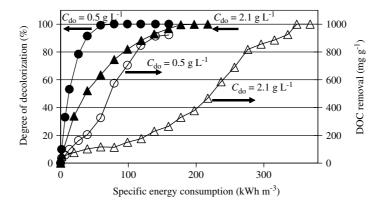
A further treatment goal to be considered is the use of as little energy as possible for the decolorization and mineralization. The energy required to treat textile wastewater is dependent on the wastewater composition as well as the treatment target, e.g. degree of decolorization ( $\alpha_{dec}$ ) and mineralization ( $\alpha_{DOC}$ ) desired. Figure 3 shows the removal efficiencies that were achieved as a function of the specific energy consumption kW h m<sup>-3</sup> for wastewater containing two different initial RB5 concentrations: 0.5 and  $2.1\,\mathrm{g\,L^{-1}}$ . The specific energy required for complete decolorization and  $850 \,\mathrm{mg}\,\mathrm{g}^{-1}$  DOC removal was 177 and  $335 \, kW \, h \, m^{-3}$  for 0.5 and  $2.1 \, g \, L^{-1}$ , respectively. In contrast, if the energy consumption is calculated per weight of dye removed, the specific energy consumption decreases from 354 to 160 W h g<sup>-1</sup> RB5 as the concentration is increased (Fig. 4).

These values for high concentrations compare very favorably to that found for the decolorization of a very low concentration of dye (76.7 kW h m<sup>-3</sup> and 402 W h g<sup>-1</sup> dye for 20 mg L<sup>-1</sup> of Acid Black 1).<sup>10</sup> A possible explanation for the higher energy requirement at lower concentrations is that more energy is spent on radical recombination reactions at the lower dye concentrations, which are not useful for the oxidation reaction.

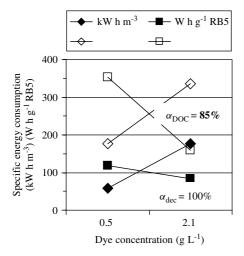
In summary, almost complete mineralization of RB5 with  $\rm H_2O_2/UV$  at high concentrations required high energy consumption, although the specific energy consumption (based on weight of dye treated) decreased as concentration increased. The combination of  $\rm H_2O_2/UV$  and an aerobic biological process was investigated next to reduce the energy consumption for the treatment goal of mineralization.

# Combination with biological treatment

The biodegradability of the oxidation products for three different oxidation times was tested in an aerobic activated sludge reactor. Since aerobic treatment



**Figure 3.** Degree of decolorization and DOC removal as a function of specific energy consumption for wastewater containing two different concentrations of RB5.  $C_{do} = 2.1 \,\mathrm{g\,L^{-1}}$ ,  $C_{so} = 460 \,\mathrm{mg\,L^{-1}}$  DOC,  $C_{do} = 0.5 \,\mathrm{g\,L^{-1}}$ ,  $C_{so} = 125 \,\mathrm{mg\,L^{-1}}$  DOC, pH = 7 and  $T = 25 \,^{\circ}\mathrm{C}$ .



**Figure 4.** Comparison of specific energy consumption per volume of treated wastewater (kW h m $^{-3}$ ) and per unit weight of treated dye (W h g $^{-1}$  RB5) for total decolorization and 850 mg g $^{-1}$  DOC removal of two different dye concentrations.

cannot decolorize the dye, the first end point was when 93% of the color was removed ( $\Delta t_{\rm oxi,1} = 240$  min,  $\alpha_{\rm DOC} = 23\%$ ). The second end point was at 97% decolorization, which was reached at  $\Delta t_{\rm oxi,2} = 360$  min and  $\alpha_{\rm DOC} = 34\%$ . The third end point was after

complete decolorization, at  $\Delta t_{\text{oxi},3} = 420$  min and  $\alpha_{\text{DOC}} = 47\%$ .

Figure 5 shows the decrease in the normalized RB5 concentration  $C_{\rm d}/C_{\rm do}$  and the DOC concentration of the RB5 during the three different oxidation periods: 240, 360, and 420 min, respectively. After each point the RB5 intermediates were introduced into the biological reactor for further oxidation.

The DOC concentration  $C_s$  of the metabolites decreased over time in the biological reactor (Fig. 6). The slight increase in the DOC concentration at the start of each experiment may have been caused by lysis products of the mixed culture used. Control experiments using the same bacteria culture with glucose in the presence of the same  $H_2O_2$  concentration demonstrated the activity of the biomass. Independent of the oxidation time, approximately  $140-150 \, \text{mg} \, \text{DOC} \, \text{L}^{-1}$  of the residual DOC was biodegradable.

Although the intermediate products of RB5 introduced to the biodegradation process after the three different oxidation times were different in concentration and most probably in chemical structure, the reduction in DOC obtained in the biological reactor is almost the same in all three cases:  $\sim\!300\,\mathrm{mg\,g^{-1}}$  of the initial DOC (Fig. 7). Since more

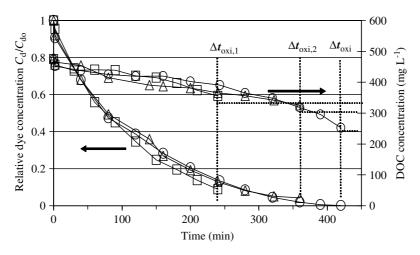
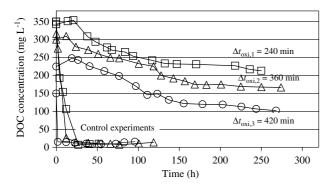


Figure 5. Variation of the relative dye concentration  $C_{\rm d}/C_{\rm do}$  and DOC concentration of RB5 at by  $H_2O_2/{\rm UV}$  at three different oxidation time intervals,  $C_{\rm do}=2.1\pm0.025\,{\rm g\,L^{-1}}$ ,  $C_{\rm so}=470\,{\rm mg\,L^{-1}}$  DOC,  $C_{H_2O_2}=543\pm4\,{\rm mm}$ , pH = 7, and  $T=25\,{\rm ^{\circ}C}$ .



**Figure 6.** Aerobic degradation of intermediates of RB5 formed by the partial oxidation with  $H_2O_2/UV$  for three different oxidation times,  $C_{\text{Bo}} = 2.0 \pm 0.1 \text{ g VSS L}^{-1}$ .

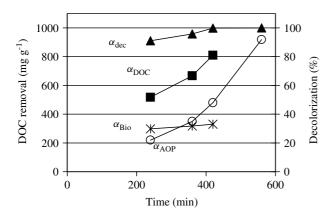


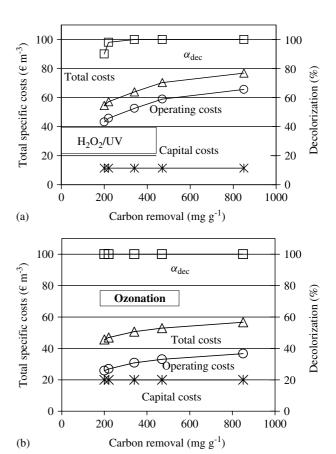
Figure 7. The efficiencies of the  $H_2O_2/UV$ -biological processes as a function of the oxidation time.

DOC was removed at the longer oxidation times, the total DOC removal increased from  $500\,\mathrm{mg\,g^{-1}}$  at  $240\,\mathrm{min}$  to  $800\,\mathrm{mg\,g^{-1}}$  at  $420\,\mathrm{min}$ . Apparently, with the extension of the oxidation time, the available OH° radicals react nonselectively with the degradable and nonbiodegradable compounds, resulting in a steady amount of biodegradable compounds discharged to the biological process.

The biological stage reduced the oxidation time necessary to achieve a certain degree of DOC removal. Biological treatment after decolorization increased the DOC removal from  $200-300\,\mathrm{mg\,g^{-1}}$  to  $50-60\,\mathrm{mg\,g^{-1}}$ . However, in order to achieve high DOC removal, e.g.  $800\,\mathrm{mg\,g^{-1}}$ , almost  $500\,\mathrm{mg\,g^{-1}}$  of the DOC had to be removed by chemical oxidation first. This means that if the  $H_2O_2/UV$  process is used as a pretreatment before discharge to a biological in-plant or municipal facility, the oxidation time should be extended  $\sim 20\%$  over that needed to reach decolorization in order to ensure a high degree of dye mineralization. If the treated water is to be recycled, an evaluation of the application is necessary to determine the concentrations of DOC and  $H_2O_2$  that can be tolerated.

# Cost analysis

Treatment costs for a segregated wastewater with a high dye concentration  $(2 g L^{-1})$  using the  $H_2O_2/UV$  process were evaluated and compared to ozonation



**Figure 8.** Comparison of specific treatment costs for the chemical oxidation stage alone as a function of the degree of carbon removal for (a)  $H_2O_2/UV$  and (b) ozone.

based on an ozone dose of 8 g O<sub>3</sub> g<sup>-1</sup> DOC.<sup>16</sup> Since the biological stage would be the same for both, only the costs for the chemical oxidation stage were considered. Although the capital costs for an H<sub>2</sub>O<sub>2</sub>/UV unit are relatively low compared to an ozone unit (Fig. 8a, b), the energy costs for the UV radiation are higher than the ozone production costs. The cost required for pretreatment before discharging to a biological process (complete decolorization and  ${\sim}500\,\text{mg}\,\text{g}^{-1}$  mineralization) is  ${\sim}74~\text{€}\,\text{m}^{-3}$  for  $H_2O_2/UV$  versus  $54 \in m^{-3}$  for ozonation. The figures show the sensitivity of the processes to the changes in treatment efficiency requirements. A high DOC removal efficiency of  $\sim 850 \,\mathrm{mg}\,\mathrm{g}^{-1}$  could be achieved for both processes with only a small increase in the costs ( $\sim$ 3  $\in$  m<sup>-3</sup>), whereas a reduction in the treatment objectives to only decolorization (90% decolorization and 200 mg g<sup>-1</sup> mineralization) lowers the total costs sharply for H<sub>2</sub>O<sub>2</sub>/UV and very little for ozone, bringing them to comparable values: 52 versus  $45 \in m^{-3}$ .

Comparison of only the operating costs shows that those of ozonation are almost half those for  $H_2O_2/UV$ . The long oxidation times for  $H_2O_2/UV$  cause high energy costs. Since most of the radiation from the medium-pressure UV lamp is emitted at wavelengths where the  $H_2O_2$  has no absorption, improved UV technology is needed to increase the energy efficiency. A high-efficiency UV lamp is needed

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with improved spectral output that provides high energy at wavelengths at which  $H_2O_2$  has a high absorbance, a long useful life, and a low cost.

Furthermore, continued research on the combination of  $\rm H_2O_2/UV$  and biodegradation with internal recycle is recommended to assess whether increases in overall biodegradability can be achieved similar to those discussed in the introduction. A biological stage with fixed biomass would reduce the biomass separation costs, thereby reducing overall costs.

### **CONCLUSIONS**

Complete decolorization and a high degree of mineralization were achieved with  $H_2O_2/UV$  for high concentrations of Reactive Black 5. The specific energy required as kWh g<sup>-1</sup> dye for decolorization and mineralization decreased as the dye concentration increased. Dilution of concentrated dye-baths should be avoided before treatment with  $H_2O_2/UV$ . Since most of the radiation from the medium-pressure UV lamp is emitted at wavelengths where  $H_2O_2$  has no absorption, improved UV technology is needed to increase the energy efficiency.

The addition of a biological stage can reduce energy costs to achieve a high degree of mineralization. Biodegradable compounds are formed during oxidation of RB5; however, the contribution of the biological process to the overall efficiency was independent of the oxidation time. The biological stage removed about  $300\,\mathrm{mg\,g^{-1}}$  of the initial DOC. The combination of  $\mathrm{H_2O_2/UV}$  with biological treatment reduced the specific cost ( $\mathrm{\leqslant m^{-3}}$ ) at least 30%.

Nevertheless, the cost analysis showed that, while  $H_2O_2/UV$  can compete with ozonation when the treatment goal only requires decolorization, ozonation is more cost-effective when mineralization is desired.

### **ACKNOWLEDGEMENT**

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