TREATMENT OF RECALCITRANT ORGANIC COMPOUNDS IN OIL RECLAIMING WASTEWATER BY OZONE/HYDROGEN PEROXIDE AND UV/TITANIUM DIOXIDE

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ABSTRACT

Refractory organic compounds in samples of a biologically treated oil reclaiming wastewater with a COD of about 300 mg/l were removed by ozonation with or without hydrogen peroxide or by irradiation with UV light in the presence of titanium dioxide in laboratory scale batch experiments. A 5 hrs UV/TiO₂ treatment at pH 3 (energy consumption: about 0.9 kWh/l) resulted in a COD elimination of 70% and an enhanced biodegradability of the organic wastewater constituents. Ozonation was hardly affected by hydrogen peroxide, and a treatment for 47 min (energy consumption about 0.005 kWh/l) led to a COD reduction of about 17% and also to an improved biodegradability. Both processes are suitable for further treatment of biologically oxidized oil reclaiming wastewaters.

KEYWORDS

Oil reclaiming wastewater; ozone; photocatalytic oxidation; residual COD.

INTRODUCTION

Reclaiming of spent oils from different users contributes to environmental protection. In 1986 more than 2 million tons of spent oils were reclaimed in the Federal Republic of Germany, among them 900,000 tons of emulsions and 150,000 tons of other oil-water mixtures (Schmitz, 1990). The aqueous phases resulting from the distillation of emulsions and other oil-water mixtures are wastewaters with high COD loads which have to be treated prior to discharge. Aerobic biological treatment is an appropriate method for the reduction of organic compounds in these wastewaters. However, as there are also refractory organic substances, biological degradation is limited and COD values of these wastewaters can normally not be reduced below 200 mg/l (Gulyas et al., 1991). Tentative treatment in a pilot-scale second stage biology (fixed bed reactor) as well as data from electrochemical respirometer experiments gave evidence that most of the organics of the activated sludge process effluent of the oil reclaiming plant studied in this investigation are recalcitrant.
A couple of techniques are available for the degradative removal of low concentrations of refractory organic constituents of wastewaters: UV/hydrogen peroxide, UV/ozone, Fenton's reagent, gamma-irradiation, irradiation with high energy electron beams, UV irradiation in the presence of semiconductor materials (such as titanium dioxide), ozone, ozone/hydrogen peroxide. In all these processes OH (and other) radicals are formed, which are considered to be the primary active species for those chemical oxidation processes.

For the system UV/titanium dioxide the following mechanisms are discussed (Bahnemann et al., 1991): When titanium dioxide is irradiated by UV light ($\lambda \leq 400$ nm), electrons are transferred from the valence band to the conduction band. The electrons can leave the TiO$_2$ crystal and reduce molecular oxygen which is dissolved in the wastewater to superoxide anion radicals. The corresponding acid of this radical can disproportionate to molecular oxygen and hydrogen peroxide. The generated hydrogen peroxide can be further reduced by additional electrons to hydroxide anions and hydroxyl radicals. On the other hand, the formed defect electrons or holes can diffuse to the surface of the crystal and oxidize water molecules to OH radicals. Organic molecules are either attacked by OH radicals or they are oxidized directly by the holes. In both cases organic radicals are formed which are degraded in further radical reactions. One advantage of this technique is that it can also use solar light in countries with sufficient solar irradiation and thus be a very energy-saving process.

The mechanism of ozonation in aqueous solutions with and without hydrogen peroxide has been described by Staehelin and Hoigné (1982). In aqueous solution ozone reacts with OH$^-$ ions and forms superoxide anion radicals and HO$_2$ radicals. If hydrogen peroxide is present, its anions can generate O$_2^-$ and HO$_2$ radicals by the reaction with dissolved ozone. The formation of HO$_2$ radicals by the reaction of ozone with hydrogen peroxide is about 40 000 times faster than by the reaction of ozone with OH$^-$ ions. Superoxide anion radicals can reduce dissolved ozone to O$_3^-$ radicals which will then form HO$_3$ radicals by the capture of a proton. HO$_3$ radicals release molecular oxygen thus generating OH radicals. Hence, the combination ozone/hydrogen peroxide effectively delivers OH radicals without maintenance of UV lamps.

The potential of three advanced chemical oxidation techniques for removing residual organics from biologically treated wastewater of an oil reclaiming facility was investigated in this study. Our laboratory scale studies included treatment with ozone, ozone/hydrogen peroxide, and UV/TiO$_2$.

**EXPERIMENTAL PROCEDURES**

*Wastewater used for the experiments.* At the treatment plant about 150 to 200 m$^3$ of wastewater results from distillation of oil-water mixtures every day. As a first step the wastewater is collected in equalization tanks. The effluent of these tanks is neutralized and subsequently activated sludge of a publicly owned treatment work is added for adsorption of organics. Then the mixture is flocculated with Fe$^{3+}$ and subdued to flotation. This pretreated wastewater exhibits a COD of 10,000 to 25,000 mg/l and is biologically treated in four parallel aeration tanks of 10 m$^3$ each. The COD of the clarified effluent of the activated sludge process normally is about 300 mg/L. Further chemical characterization of this treated wastewater is given by Gulyas et al. (1994). Two samples of the clarified effluent of the biological stage taken at different times were used for the studies presented here.

*UV irradiation in the presence of titanium dioxide.* Batch UV irradiation experiments were performed with biologically treated effluent. The wastewater (1.5 l) was acidified to pH 3.0 or 4.0, resp., and recirculated as a thin film over TiO$_2$ immobilized on a sloping glass plane (0.6 x 1.2 m; slope 30°) (Bockelmann et al., 1993). Seven UV lamps (40 W each) were adjusted parallel to the glass plane at a distance of 13 cm.

*Treatment with ozone and ozone/hydrogen peroxide.* The biologically treated oil reclaiming wastewater for ozonation experiments was sampled at another time than that used for UV experiments. COD removal by ozonation was studied in a stirred vessel (batch mode) without and with hydrogen peroxide (initial hydrogen peroxide concentration 65 mg/l). The vigorously stirred aqueous phase (800 ml) was purged with oxygen containing 48 mg/l ozone (flow: 100 ml/min) using a glass frit. In the absence of hydrogen peroxide the sample was treated for a period of 47 min, in the experiment using hydrogen peroxide the duration of
Ozonation was 35 min. Ozone concentrations in the inlet and in the off-gas were determined by an ozone analyzer and the consumed amount of ozone was calculated from these data.

**Analytical procedures.** Removal of the organic pollutants was evaluated by COD or TOC analysis. The influence of chemical oxidation on modifying the organic constituents to biodegradable compounds was examined in electrochemical respirometers by inoculation with activated sludge isolated from a pilot-scale domestic wastewater aeration tank. Identification of organic constituents of the wastewater used for photocatalytical oxidation was performed by GC/MS of dichloromethane extracts of wastewater samples before and after treatment with UV/TiO₂ and is described elsewhere (Gulyas et al., 1994).

**RESULTS AND DISCUSSION**

In both photocatalytical oxidation experiments (pH 3 and pH 4) about 50% of the TOC was removed after an irradiation period of 5 hrs. COD was reduced from 333 mg/l to 98 mg/l (treatment at pH = 3) or to 115 mg/l (treatment at pH 4), resp. Decolorization of the samples was achieved after a shorter period, however, indicating removal of humic substances. The biological degradation of organic constituents in the neutralized irradiated wastewater samples was tested in an electrochemical respirometer (Fig. 1a). Part of the organics of the UV/TiO₂-treated wastewater were susceptible to biodegradation, while the original sample was only poorly degradable. During a period of five days the biological oxygen consumption of the samples treated at pH 3 and 4 was 26 mg/l (26.5% of COD) and 21 mg/l (18.3% of COD), resp., while the untreated effluent of the activated sludge process exhibited an oxygen consumption of only 11 mg/l (3% of COD).

In the wastewater irradiated for 5 hrs in the presence of TiO₂ at pH 3 ten organic substances were identified or at least related to classes of compounds (Tabl e 1). Except for a not exactly characterized phthalic acid ester all the analyzed compounds had not been detected in the original sample (for identified compounds in the untreated effluent of the activated sludge process see Gulyas et al., 1994). One can assume that an almost complete chemical modification of the organic compounds took place during treatment with UV/TiO₂ and that the modified compounds were biodegradable to a higher extent. Further substances detected in the gas chromatogram exhibited too low concentrations for MS identification.

**TABLE 1. Organic Compounds Identified by GC/MS in a Biologically Treated Oil Reclaiming Wastewater Which Had Been Irradiated by UV in the Presence of TiO₂ at pH 3**

<table>
<thead>
<tr>
<th>[alkylated phenol derivative]</th>
<th>[phthalic acid ester]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[acetyl-oxo-derivative of butanone]</td>
<td>phthalic acid diethylester</td>
</tr>
<tr>
<td>phthalic acid anhydride</td>
<td>[noncharacterized acetyl derivative]</td>
</tr>
<tr>
<td>acetic acid methylester</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>1,2-ethanediol-monoacetate</td>
<td>1,2,5-thiadiazole</td>
</tr>
</tbody>
</table>

In the ozonation experiments a biologically treated oil reclaiming wastewater sample with a COD of 316 mg/l was used. If 1 mol ozone is assumed to be equivalent to 1 mol COD, the ozone dose was substoichiometric (about 18% of the COD of the biologically treated wastewater). This addition of ozone resulted in a reduction of about 17% of the COD. Addition of hydrogen peroxide did not markedly influence the COD removal (ozone dosage was about 17% of initial COD; COD elimination: 17.7%). After ozonation, part of the recalcitrant organics were susceptible to biodegradation (Fig. 1b). In the samples treated only with ozone, the oxygen consumption by microorganisms was 43 mg/l (16.3% of COD) after 120 hrs. Oxygen consumption of the sample treated with O₂H₂O₂ was 37 mg/l (14.2% of COD). Hydrogen peroxide did not affect the results indicating either that radical mechanisms were not significant or that hydrogen peroxide was formed during ozonation.
Energy consumption was about 0.9 kWh/l during UV/TiO₂ treatment and about 0.005 kWh/l during ozonation (generation of 1 g ozone requires about 20 Wh). However, a comparison of the results presented here is difficult, because two wastewaters sampled at different times were used for the different treatment experiments. Assuming that the chemical composition of the wastewater will not greatly influence the treatment efficiency it can be calculated that the experiments consuming more energy (UV/TiO₂) lead to a higher COD elimination (70%) than the ozonation (COD elimination 17%). But COD elimination is not proportional to energy consumption.

In conclusion we are confident that both techniques, ozonation as well as UV irradiation in the presence of TiO₂, are suitable for removal of refractory COD from wastewaters. Both methods can also be used as intermediate stages for modifying recalcitrant organic constituents to form substances susceptible to aerobic biodegradation. Because the chemical reactions are not predictable, it is advisable to prove that no new toxic substances have been formed during the treatment.

REFERENCES


