Photocatalytic oxidation of a reactive azo dye and evaluation of the biodegradability of photocatalytically treated and untreated dye

Nevim Genç

University of Kocaeli, Dept. of Environmental Engineering, 41001 0zmit, Turkey

Abstract

The purpose of this study was to investigate the photocatalytic oxidation of a reactive azo dye and determine the improvement in the biodegradability when photocatalytic oxidation was used as a pretreatment step prior to biological treatment. The results obtained from the experiments adding H2O2/TiO2 show that the highest decolorisation rate is provided by the combination of (UV+TiO2+H2O2). The decolorisation efficiencies were 18%, 22%, 34% and 52% in the runs UV, UV+H2O2, UV+TiO2 and (UV+TiO2+H2O2) after approximately 100 min illumination periods, respectively. The decolorisation rate was increased significantly by initially increasing the concentration of TiO2 in the dye solution; however, it was decreased due to the reduced light transmission when the concentration of TiO2 was in excess. The decolorisation rate constant was 0.018 ± 0.002·min⁻¹ in the presence of 1 g·ℓ⁻¹ TiO2 while it was 0.004 ± 0.001·min⁻¹ in the presence of 0.125 g·ℓ⁻¹ TiO2. The results of the obtained oxygen uptake rate measurements in biological activated sludge have shown that the photocatalytically treated dye was easier to degrade than untreated dye. The ability of the activated sludge to degrade glucose was not inhibited in the presence of photocatalytically treated and untreated dye. Also, the biodegradability of photocatalytically treated and untreated dye was investigated via the biological oxygen demand (BOD) test. The results indicated that further degradation of the treated dye may take place by activated sludge in aerobic conditions.

Keywords: azo dye, photocatalytic decolorisation, biodegradability test, activated sludge

Introduction

Photocatalytic oxidation using a semiconductor such as TiO2 as photocatalyst is one of the various advanced oxidation processes used nowadays. As TiO2 is illuminated by light with a wavelength below 380 nm, the photons excite valence band electrons across the band gap into the conduction band, leaving holes behind in the valence band. The hydrogen peroxide absorbs only UV light with wavelengths < 300 nm (Parra et al., 2000). The holes in TiO2 react with water molecules or hydroxide ions (OH⁻) producing hydroxyl radicals (OH). The generation of OH depends on the solution pH.

In alkaline solutions, the generation of the radical OH mainly involves a charge transfer between OH⁻ ions and valence band holes at the photocatalyst surface, whereas at neutral and acidic pH, direct hole oxidation is also possible. Organic pollutants which are adsorbed on the surface of the catalyst will then be oxidised by OH· (Gonçalves et al., 1999).

Photocatalytic oxidation of dyes has been investigated by a number of researchers. Photocatalytic oxidation processes can oxidise a wide variety of toxic and persistent organic compounds to harmless inorganics such as mineral acids, carbon dioxide and water (Dominguez et al., 1998). Also, this process forms some by-products such as halides, metals, inorganic acids and organic aldehydes depending on the initial materials and the extent of decolorisation (Robinson et al., 2001).

The colour of dyes results from conjugated chains or rings which absorb light at visible wavelengths. The UV-degradation can be achieved by the cleavage of conjugated chains (Ma and Chu, 2001).

The biodegradability of azo dyes has also been investigated in the past. Aromatic amines formed by biotic and abiotic conversion processes of azo dye colorants are mostly toxic. The degradability of selected amines which are detected in textile industry wastewaters has been investigated under aerobic and anaerobic conditions as well as abiotic conditions. The results show that the degradation under aerobic conditions proceeds via oxidation of the substituents located on the aromatic ring or on the side-chain (Ekici et al., 2001). The investigated azo dye metabolites are partly stable in the aqueous environment and cannot be efficiently degraded under wastewater plant conditions. Under anaerobic conditions, the azo bond is reductively cleaved, which leads to the formation of substituted aromatic amines some of which are known to be potentially toxic/mutagenic (Bromley-Challenor et al., 2000).

The chemical structures of azo dyes are based on azo benzene and the azo naphthol derivatives. They also exhibit great structural variety, therefore they are not uniformly susceptible to microbial attack. A number of authors have proposed models for the qualitative prediction of azo dye biodegradability. The quantitative relationship between the biodegradability of azo dyes and their chemical structures has been explored, and the probability for rapid aerobic biodegradation has been modeled by Suzuki et al. (2001).

Some studies have shown the utility of photocatalytic oxidation processes as a pretreatment step before a biological treatment for the improvement of biodegradability of toxic and/or non-biodegradable organic substances. The combined photochemical and biological processes were investigated for the destruction of biorecalcitrant herbicides (Parra et al., 2000) and p-nitrotoluene-ortho-sulphonic acid (Pulgarin et al., 1999). The treatability of raw and pretreated wastewater by photocatalytic oxidation was investigated. Results obtained show that the photocatalytic oxidation...
The effect of catalyst and oxidising agent on the photocatalytic dye degradation

TiO$_2$ was used as catalyst and H$_2$O$_2$ was used as oxidising agent. Experiments to examine the effect of the TiO$_2$ and/or H$_2$O$_2$ on the decolorisation rate were conducted under different experimental runs UV, UV+TiO$_2$, UV+H$_2$O$_2$, and UV+TiO$_2$+H$_2$O$_2$ processes in the presence 0.02M H$_2$O$_2$ and TiO$_2$ of 0.75 g l$^{-1}$ at pH = 5. In addition the influence of catalyst amount on decolourisation rate is also investigated. Decolourisation was examined on samples withdrawn periodically during the illumination of a 50 mg l$^{-1}$ dye solution.

Activated sludge experiments

The secondary sludge which was supplied from the wastewater treatment system of the yeast industry was centrifuged at 5 000 r min$^{-1}$ for 5 min and a part of the sediment was diluted with water. The activated sludge which was used in the experiments was not acclimated to the dye.

0.6 g TiO$_2$ was added to 800 ml aqueous solution containing azo dye 50 mg l$^{-1}$ concentration. After photocatalytic treatment samples were centrifuged at 5 000 r min$^{-1}$ for 15 min to separate TiO$_2$. The obtained supernatant was used in the experimental runs. The runs which are listed in Table 1 were investigated to estimate the effect of photocatalytically treated and untreated dye solution on the activated sludge activity. In oxygen uptake rate (OUR) experiments, the samples were poured into a respirometer flask of 105 ml volume. Since the oxygen electrode was covered up to the top of the flask, there was no air transfer to the flask. Dissolved oxygen (DO mg l$^{-1}$) values were recorded until the DO concentration of solution was 1 mg l$^{-1}$.

In Run 1, the activity of the activated sludge was investigated. The biodegradability of photocatalytically treated and untreated dye by activated sludge was determined in Runs 2 and 3, respectively. In Run 4, the activity of the activated sludge was determined by adding glucose which is the substrate of the activated sludge. Glucose is selected because it is the main compound of vital importance which appears in the metabolic pathways of the biodegradation of every organic matter. The inhibition effects on the activated sludge of the photocatalytically treated and untreated dye were investigated in Runs 5 and 6, respectively.

The accuracy and the reliability of the experimental results based on biological degradability were tested using the BOD test.
The change in absorption spectrum with irradiation time during photocatalytic oxidation of the studied azo dye at similar to 275 nm range.

One absorption band of moderate intensity appears near 205 nm and another less intense band appears in the 250 nm range. The UV absorption bands indicate the presence of a benzene ring in an azo dye. The electrons of a benzene ring produce characteristic ultraviolet absorbance in the visible region (Solomons, 1996).

Vinyl groups (CH2=CH-) form conjugate structures such as benzyl, naphtyl and triazinyl within chemical structure of used azo dyes. Aromaticity conjugate structures such as benzyl, naphtyl and triazinyl provide intensive colored because the diazenediyl linkage (-N=N-) brings the two aromatic rings into conjugation. This gives an extended system of delocalised π electrons and allows absorption of light in the visible region (Solomons, 1996).

Absorption bands that indicate the presence of a benzene ring in an azo dye can not be considered as a chromophoric group. It is expressed by Solomons (1996) that the conjugated π electrons of a benzene ring produce characteristic ultraviolet absorption bands that indicate the presence of a benzene ring in an unknown compound. One absorption band of moderate intensity occurs near 205 nm and another less intense band appears in the 250 to 275 nm range.

The change in absorption spectrum with irradiation time during photocatalytic oxidation of the studied azo dye at similar conditions (initial dye concentration = 100 mg·l⁻¹, TiO₂ = 1 g·l⁻¹, H₂O₂ = 0.02 M) is shown in Fig. 2. It is observed that this absorbance in the visible spectral region at 580 nm decreased with increasing illumination time, indicating that the azo bonds were broken by the photocatalytic oxidation process. The absorbance peak within the UV region belongs to the aromatic groups. The decrease in absorbance in the UV region is less important than visible region. Can (2003) demonstrated that aromatic ring compounds break only after prolonged illumination time. According to Fig. 2, the UV and visible peaks decreased by 34% and 98% upon 60 min illumination, respectively.

The photodegradation mechanism of the dye is similar to that of any other aromatic compound. Here the possible mechanism is discussed. Both of the dye components have an anionic character. The important substituent in the dye is the sodium sulphonate group (-SO₃Na). The dye is soluble in water due to the presence of -SO₃Na in its structure. In an aqueous solution, the dye ionises into sodium cations and colored sulphonate anions.

### Table 1

Experiments for evaluation of the respiration activity of activated sludge

<table>
<thead>
<tr>
<th>Run</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The mixture (1ml A solution + 1 ml B solution + 4 ml activated sludge) made up to a volume of 105 ml with distilled water.</td>
</tr>
<tr>
<td>2</td>
<td>The mixture (90 ml of photocatalytically treated dye + 1 ml A solution + 1 ml B solution + 4 ml activated sludge) made up to a volume of 105 ml with distilled water.</td>
</tr>
<tr>
<td>3</td>
<td>The mixture (90 ml of photocatalytically untreated dye + 1 ml A solution + 1 ml B solution + 4 ml activated sludge) made up to a volume of 105 ml with distilled water.</td>
</tr>
<tr>
<td>4</td>
<td>The mixture (10 ml of glucose solution + 1ml A solution + 1 ml B solution + 4 ml activated sludge) made up to a volume of 105 ml with distilled water.</td>
</tr>
<tr>
<td>5</td>
<td>The mixture (90 ml of photocatalytically treated dye + 10 ml of glucose solution + 1 ml A solution + 1 ml B solution + 4 ml activated sludge)</td>
</tr>
<tr>
<td>6</td>
<td>The mixture (90 ml of photocatalytically untreated dye + 10 ml of glucose solution + 1 ml A solution + 1 ml B solution + 4 ml activated sludge)</td>
</tr>
</tbody>
</table>

Note: The glucose solution of 10 g·l⁻¹ was used in Runs 4, 5 and 6. The solids content of activated sludge was 16 g·l⁻¹ and 50% of total solid was volatile. Solution A consists of 80 g·l⁻¹ K₂HPO₄, 40 g·l⁻¹ KH₂PO₄, 30 g·l⁻¹ NH₄Cl. Solution B consists of 15 g·l⁻¹ MgSO₄.7H₂O, 0.5 g·l⁻¹ FeSO₄.7H₂O, 0.3 g·l⁻¹ MnSO₄.4H₂O, 2.7 g·l⁻¹ CaCl₂.2H₂O.

### Analysis

Samples were analysed for colour, OUR and BOD. Prior to analysis raw and treated samples were centrifuged at 5 000 r·min⁻¹ for 15 min to separate TiO₂. A Hach DR/2000 spectrophotometer was used to scan and measure the absorbance of the dye solution. The dye concentration was determined by the absorbance at the maximum absorption wavelength (λmax = 622 nm). DO was analysed using WTW Oxi 3000 oxygen meter. OUR (mg·l⁻¹·min⁻¹) was determined by dividing abatement rates in DO to the time. BOD was analysed by Lovibond BOD-Sensor and Inductive Stirring System.

### Results and discussion

Compounds that absorb in the visible spectral region contain at least one chromophoric group such as azo (-N=N-), quinoid carbonyl, nitroso (-NO), nitro-group (-NO₂), carbonyl (>C=O), vinyl group (CH=CH-). For instance, azo compounds are usually intensely colored because the diazenediyl linkage (-N=N-) brings the two aromatic rings into conjugation. This gives an extended system of delocalised π electrons and allows absorption of light in the visible region (Solomons, 1996).

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groups linked to naphthalene and a benzene ring can be removed during the photocatalytic process, and converted into sulphate ions (Wang, 2000). The triazine ring is linked to the triazine ring. Cleavage of the chloride group depends on its position in the molecular structure. The triazine ring and the groups connected to it are stable to photo-oxidation. Hequet et al. (2001) reported that atrazine is converted to hydroxyatrazine by breaking the C-Cl bond upon UV irradiation. On account of this, the cleavage of the chlorate group is likely. Ionic species produced upon photocatalytic oxidation of chloride and the phenyl and ethyl groups connected to the triazine ring upon UV irradiation. Combination of TiO$_2$ and H$_2$O$_2$ is necessary to obtain a high colour removal within a short illumination period in the photo-oxidation process. The maximum colour removal efficiency was observed for the combination UV+H$_2$O$_2$+TiO$_2$. The decolorisation efficiencies were 18%, 22%, 34% and 52% in the runs UV, UV+H$_2$O$_2$, UV+TiO$_2$ and UV+TiO$_2$+H$_2$O$_2$ processes after approximately 100 min of illumination period, respectively. The fact that the decolorisation efficiency is higher with (UV+H$_2$O$_2$+TiO$_2$) than with (UV+H$_2$O$_2$) shows that TiO$_2$ acts as a photocatalyst. Dye molecules are oxidised by OH radicals on the surface of the catalyst and within the bulk of the solution. This was confirmed by the efficiency of decolarisation obtained in the (UV+H$_2$O$_2$, TiO$_2$) series which is higher than in the series (UV+H$_2$O$_2$) (Fig. 3). It is explained by Fujishima et al. (2000) that photocatalytic degradation can take place at a distance of as much as 500 µm away from the TiO$_2$ surface and of the reaction rate decreasing with distance. In addition, they show that both oxidation and reduction reactions can take place on the illuminated TiO$_2$ surface.

**Effect of the amount of catalyst on the colour removal**

Assuming pseudo first-order reaction kinetics for photocatalytic oxidation process (low initial concentration of pollutant) the decolorisation rate constant was determined from Eq. (1).

\[
\ln \left( \frac{C_t}{C_0} \right) = -k_t t
\]

where:

- $C_t$ and $C_0$ are the dye concentrations at times 0 and $t$, respectively
- $k_t$ is the pseudo first-order rate constant (time$^{-1}$).

The effect of TiO$_2$ concentration on the decolorisation was investigated in the run (UV+H$_2$O$_2$, TiO$_2$). The decolorisation rate constants determined from the slopes of plots of ln($C_t/C_0$) vs. time, which were given in Table 2. Accordingly the colour removal rate was increased significantly by increasing the amount of catalyst. Highest decolorisation rate constant was obtained as 0.018 min$^{-1}$ in the presence of 1 g TiO$_2$, while it was 0.004 min$^{-1}$ in the presence of 0.125 g TiO$_2$. When all the dye molecules are adsorbed on TiO$_2$, no improvement was achieved by adding more catalyst as suggested by some authors (Gonzalves et al., 1999). It is suggested that this decrease is due to an increased opacity of the suspension in the excess of TiO$_2$ particles (Fig. 4).

The photo degradation of the dye fits zero-order kinetics in catalyst-free solution and first-order kinetics in the presence of TiO$_2$ (Shourong et al., 1997). However, a number of authors also explain that the reaction in catalyst-free solution fits first-order kinetics (Silva and Faria, 2002). In this study, in the run of (UV+H$_2$O$_2$) the zero-order rate constant determined from the slope of (C$_t$-C$_0$) vs. time was 0.0022 min$^{-1}$ (the correlation coefficient, $R=0.9765$). However, the first-order rate constant was 0.0024 min$^{-1}$ ($R=0.9751$). The correlation coefficient measures the relation between the decolorisation rate and time. Despite the difference between the calculated R value is negligible, it is more true to say that the reaction in catalyst-free solution fits first-order kinetics. In a photo-oxidation process, the driving force is the amount of photons absorbed by water or on the catalyst surface. The decolorisation rate depends on initial dye concentration because the higher UV absorbance of the dye enables more photolysis. The dye removal rate depends on the initial dye concentration for the amount of the absorbed light increases in direct proportion to the dye concentration to a particular extent. The amount of light