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 H_2O_2/TiO_2 show that the highest decolorisation rate is provided by the combination of ($UV+TiO_2+H_2O_2$). The decolorisation efficiencies were 18%, 22%, 34% and 52% in the runs UV, $UV+H_2O_2$, $UV+TiO_2$ and ($UV+TiO_2+H_2O_2$) after approximately 100 min illumination periods, respectively. The decolorisation rate was increased significantly by initially increasing the concentration of TiO_2 in the dye solution; however, it was decreased due to the reduced light transmission when the concentration of TiO_2 was in excess. The decolorisation rate constant was $0.018 \pm 0.002 \cdot min^{-1}$ in the presence of $1\ g \cdot \ell^{-1}$ TiO_2 while it was $0.004 \pm 0.001 \cdot min^{-1}$ in the presence of $0.125\ g \cdot \ell^{-1}$ TiO_2. 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 TiO_2 as photocatalyst is one of the various advanced oxidation processes used nowadays. As TiO_2 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 a wavelength < 300 nm (Parra et al., 2000). The holes in TiO_2 react with water molecules or hydroxide ions (OH^-) producing hydroxyl radicals ($\cdot OH$).The generation of $\cdot OH$ depends on the solution pH. In alkaline solutions, the generation of the radical $\cdot OH$ 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 $\cdot OH$ (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).

☎+902623355559; fax:+902623351168; e-mail: ngenc@kou.edu.tr
Received 12 January 2004; accepted in revised form 25 May 2004.

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

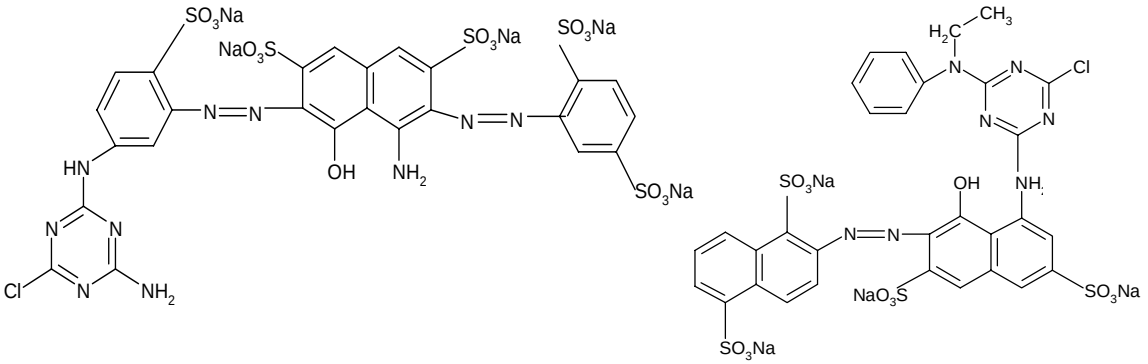

Figure 1
The chemical structure of the azo dye mixture

process was more efficient in the removal of pollutants for pretreated wastewater (Balciolu and Arslan, 1998).

It is also possible to envisage incomplete photocatalytic degradation to detoxify wastewater. The products of partial oxidation and their concentrations may be sufficiently innocuous as to be permissible for discharge or for further biological treatment. However, it is very difficult to identify all the intermediary products *en route* to complete mineralisation. Toxicity testing of photocatalytically treated wastewater is therefore necessary, particularly when incomplete degradation is envisaged. The respiration rate measurements in activated sludge can be used as a measure of the toxicity of photodegradation products (Manilal et al., 1992).

The purpose of this study was to investigate the photocatalytic oxidation of azo dye and determine the improvement in the biodegradability when photocatalytic oxidation was used as a pretreatment step prior to biological treatment.

Materials and methods

Materials

The reactive azo dye (CIBACRON NAVY P-2R-01) was obtained from Ciba Specialty Chemicals. This reactive dye was used without further purification. The azo dye used is the mixture of a sulphonated dye with two azo groups (at the ratio of 10 to 20%) and a sulphonated dye with mono azo groups (at the ratio of 1 to 5%). The chemical structure of the dye mixture is given in Fig. 1. TiO_2 was obtained from the Merck Company. According to the information obtained from the Merck Company, the crystal form of TiO_2 is anatase. H_2O_2 was obtained from Riedel-deHaën 30% (w/w). All other chemicals were analytical grade (AR).

Experimental equipment

Experiments were performed in an open batch system (total volume 1 000 mℓ). The total suspension volume in the system was 800 mℓ. The dye solution contained in a flask was placed on a magnetic stirrer to keep the catalyst powder suspended. An Osram-Vitaluks UV-lamp with a power of 300 W was used as the light source. Maximum emission peaks in spectral distribution of the used light source are between 300 nm and 600 nm wavelength. The main emission intensity is approximately 750, 530, 600 and 340 $mW \cdot m^{-2}$ per 1 000 lux for 350 nm, 425 nm, 540 nm and 560 nm, respectively.

Experimental procedure

Experimental studies were performed to estimate the photocatalytic oxidation of an azo dye solution and the biodegradability of the photocatalytically treated and untreated dye solution. The tests were carried out at room temperature (approximately 291±2°K).

The effect of catalyst and oxidising agent on the photocatalytic dye degradation

TiO_2 was used as catalyst and H_2O_2 was used as oxidising agent. Experiments to examine the effect of the TiO_2 and/or H_2O_2 on the decolorisation rate were conducted under different experimental runs UV, UV+TiO_2, UV+H_2O_2 and UV+TiO_2+ H_2O_2 processes in the presence 0.02M H_2O_2 and TiO_2 of 0.75 $g \cdot \ell^{-1}$ at pH = 5. In addition the influence of catalyst amount on decolorisation rate is also investigated. Decolorisation was examined on samples withdrawn periodically during the illumination of a 50 $mg \cdot \ell^{-1}$ 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 $r \cdot min^{-1}$ 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 $mg \cdot \ell^{-1}$ concentration. After photocatalytic treatment samples were centrifuged at 5 000 $r \cdot min^{-1}$ 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 $mg \cdot \ell^{-1}$) values were recorded until the DO concentration of solution was 1 $mg \cdot \ell^{-1}$.

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.

TABLE 1
Experiments for evaluation of the respiration activity of activated sludge

Run	Content
1	The mixture (1mℓ A solution + 1 mℓ B solution + 4 mℓ activated sludge) made up to a volume of 105 mℓ with distilled water.
2	The mixture (90 mℓ of photocatalytically treated dye + 1mℓ A solution + 1 mℓ B solution + 4 mℓ activated sludge) made up to a volume of 105 mℓ with distilled water.
3	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.
4	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.
5	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)
6	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)

Note: The glucose solution of 10 $g \cdot \ell^{-1}$ was used in Runs 4, 5 and 6. The solids content of activated sludge was 16 $g \cdot \ell^{-1}$ and 50% of total solid was volatile. Solution A consists of 80 $g \cdot \ell^{-1}$ K_2HPO_4, 40 $g \cdot \ell^{-1}$ KH_2PO_4, 30 $g \cdot \ell^{-1}$ NH_4Cl. Solution B consists of 15 $g \cdot \ell^{-1}$ $MgSO_4.7H_2O$, 0.5 $g \cdot \ell^{-1}$ $FeSO_4.7H_2O$, 0.3 $g \cdot \ell^{-1}$ MnSO4.H_2O, 2.7 $g \cdot \ell^{-1}$ $CaCl_2.2H_2O$.

Analysis

Samples were analysed for colour, OUR and BOD. Prior to analysis raw and treated samples were centrifuged at 5 000 $r \cdot min^{-1}$ for 15 min to separate TiO_2 . 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 ($mg \cdot \ell^{-1} \cdot min^{-1}$) was determined by dividing abatement rates in DO to the time. BOD was analysed by Lovibond BOD-Sensor and Inductive Stirring System.

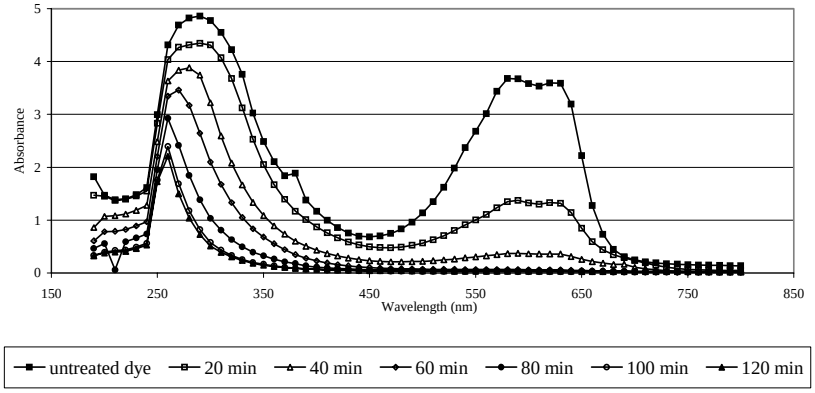

Figure 2
Spectral changes observed for the azo dye solution upon irradiation (initial concentration: 100 $mg \cdot \ell^{-1}$, TiO_2: 1 $g \cdot \ell^{-1}$, H_2O_2 : 0.02M, pH: 5)

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 ($-NO_2$), carbonyl (>C=O), vinyl group (CH_2=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).

Aromaticity conjugate structures such as benzyl, naphtyl and triazinyl within chemical structure of used 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 $mg \cdot \ell^{-1}$, TiO_2 = 1 $g \cdot \ell^{-1}$, H_2O_2= 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 groups ($-SO_3Na$). The dye is soluble in water due to the presence of $-SO_3Na$ in its structure. In an aqueous solution, the dye ionises into sodium cations and colored sulphonate anions. Sulphonic

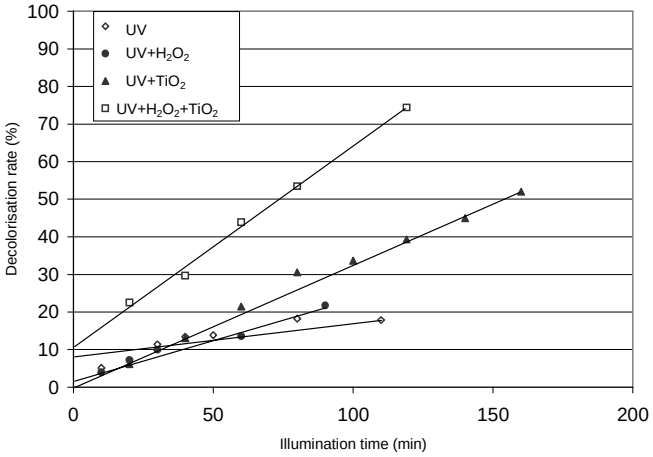

Figure 3
Decolorisation rate of a 50 mg·ℓ$^{-1}$ dye solution under UV irradiation (TiO_2: 0.75 g·ℓ$^{-1}$, H_2O_2: 0.02M, pH: 5)

groups linked to naphthalene and a benzene ring can be removed during the photocatalytic process, and converted into sulphate ions (Wang, 2000). The chloride group 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 chloride and the phenyl and ethyl groups connected to the triazine ring is likely. Ionic species produced upon photocatalytic oxidation under conditions similar to those used for this azo dye were analysed by Can (2003). Ion concentrations were determined as 5.2 mg·ℓ$^{-1}$ and 27 mg·ℓ$^{-1}$ for $SO_4^{=}$, 9.3 mg·ℓ$^{-1}$ and 12.8 mg·ℓ$^{-1}$ for Cl^-, 0.7 mg·ℓ$^{-1}$ and 2.2 mg·ℓ$^{-1}$ for NH_4^+-N and 0.02 mg·ℓ$^{-1}$ and 1.2 mg·ℓ$^{-1}$ for NO_2^--N, respectively, in untreated and treated dye solution. In the course of photo-oxidation, the amine group is converted into NH_4^+ and NO_2^-.

A naphthalene ring is more stable than a benzene ring and the main primary intermediate formed by photo-oxidation of benzene is phenol. The pathway and the produced intermediates in the photocatalytic oxidation of phenol were reported by Chen et al. (2002).

The effect of catalyst and oxidising agent on the photocatalytic dye degradation

The effect of TiO_2 and H_2O_2 on the colour removal upon photo-oxidation is shown in Fig. 3. Direct UV light irradiation was insufficient to decolorise this dye. The addition of H_2O_2 as oxidant together with the UV light was more effective for colour removal. However, the colour removal in the experiment ($UV+TiO_2$) was much more efficient. This is attributed to the adsorption of the dye molecules on the surface of the catalyst, where the water molecules adsorbed on the surface of the catalyst generate ·OH radicals efficiently. In the presence of H_2O_2, the UV light induces the formation of ·OH radicals from H_2O_2. H_2O_2 absorbs only the UV light with a wavelength <300 nm (Parra et al., 2000):

$$H_2O \xrightarrow{h\nu} 1/2\ H_2 + {\cdot}OH$$

$$H_2O_2 \xrightarrow{h\nu(\lambda<300nm)} 2{\cdot}OH$$

Combination of TiO_2 and H_2O_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 $UV+H_2O_2+TiO_2$. The decolorisation efficiencies were 18%, 22%, 34% and 52% in the runs UV, $UV+H_2O_2$, $UV+TiO_2$ and $UV+TiO_2+H_2O_2$ processes after approximately 100 min of illumination period, respectively. The fact that the decolorisation efficiency is higher with ($UV+H_2O_2+TiO_2$) than with ($UV+H_2O_2$) 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 decolorisation obtained in the ($UV+H_2O_2+TiO_2$) series which is higher than in the series ($UV+H_2O_2$) (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. (I).

$$\ln\left(\frac{C_t}{C_0}\right) = -k.t \qquad (1)$$

where:

C_0 and C_t are the dye concentrations at times 0 and t, respectively

k is the pseudo first-order rate constant (time^{-1}).

The effect of TiO_2 concentration on the decolorisation was investigated in the run ($UV+H_2O_2+TiO_2$). 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·ℓ$^{-1}$ TiO_2 concentration, while it was 0.004·min^{-1} in the presence of 0.125 g·ℓ$^{-1}$ 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 (Gonçalves 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 ($UV+H_2O_2$) the zero-order rate constant determined from the slope of plot 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