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SCIENTIFIC PAPER

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PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE CI BASIC YELLOW 28 IN WATER BY UV–A/TIO$_2$

CI Basic Yellow 28 (BY28), commonly used as a textile dye, could be photocatalytically degraded using TiO$_2$ as catalyst and irradiated by UV–A lamp (300 W). However, UV and TiO$_2$ showed no effect on the photodegradation when they were used separately. The effect of some parameters such as initial concentration of catalyst, initial dye concentration, initial NaCl and Na$_2$CO$_3$ concentration, pH and presence of H$_2$O$_2$ on degradation rate of BY28 was examined.

Key words: Textile dye, Basic Yellow 28, Titanium dioxide, Photodegradation, Photocatalysis.

Synthetic dyes are widely used in textile industry. Dye pollutants from the textile industry are an important source of environmental contamination. Major of these dyes are toxic and mostly nonbiodegradable and also resistant to destruction by physico–chemical methods, such as chemical precipitation and separation of pollutants, coagulation, elimination by adsorption [1,2] etc. These methods are not destructive but only transfer the contamination from one phase to another, therefore, a new kind of pollution is obtained which needs further treatment.

Among the new oxidation methods or "advanced oxidation processes" (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants [3–6], following the proposed mechanism:
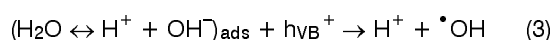
a) absorption of efficient photons by titania (h$\nu \geq$ Eg = 3.2 eV)

$$TiO_2 + h\nu \ (UV) \rightarrow e_{CB}^- + h_{VB}^+ \qquad (1)$$
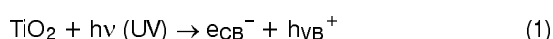
b) oxygen ionosorption

$$(O_2)_{ads} + e_{CB}^- \rightarrow O_2^{\bullet-} \qquad (2)$$

c) neutralization of OH$^-$ groups into OH by photoholes

$$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + {}^\bullet OH \qquad (3)$$

d) oxidation of the organic reactant via successive attacks by $^\bullet$OH radicals

$$R + {}^\bullet OH \rightarrow R^\bullet + H_2O \qquad (4)$$

e) or by direct reaction with holes

$$R + h^+ \rightarrow R^+ \rightarrow degradation \ products \qquad (5)$$

As an example of the last process, holes can generate CO$_2$ according to:

$$RCOO^- + h^+ \rightarrow R^\bullet + CO_2 \qquad (6)$$
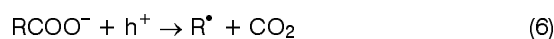
The aim of the present study is to investigate the influence of various parameters on photocatalytic decomposition of textile dye, CI Basic Yellow 28 (BY28), in the presence of TiO$_2$ irradiated by the UV–A light. CI Basic Yellow 28 dye is cationic azo dye which can be also called azomethine dye (–CH=N–) or hydrazone dye (=N–N(H,R)–) (Figure 1). The effect of parameters such as initial concentration of catalyst, initial dye concentration, initial NaCl and Na$_2$CO$_3$ concentration, pH and presence of H$_2$O$_2$ were also studied.
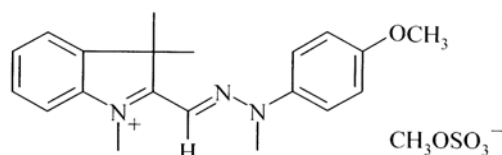

Figure 1. Structure of CI Basic Yellow 28

EXPERIMENTAL

Reagents

The hydrogen peroxide solution (30 %), hydrochloric acid, sodium chloride, sodium carbonate and sodium hydroxide (all p.a.) were obtained commercially, mostly from Fluka. TiO$_2$–Merck Eusolex$^\circledR$ T (anatase modification) was used as received. The textile dye, CI Basic Yellow 28, was obtained from Bezema as a gift (commercial name Bezacryl Goldgelb GL 200) and used without purification. Deionised water was obtained from a Milipore Waters Milli Q purification unit.

Light source

Irradiation was performed in an open flask (100 ml volume) with the sunlamp Osram ULTRA–VITALUX$^\circledR$ 300

W (UV–A) placed 50 cm from the surface of the dye solution.

Procedures

The photodegradation of BY28 was studied by preparing a solution containing known concentration of dye and amount of TiO_2. In a typical experiment, 25 ml of solution was used. Then, lamp was switched on and during the irradiation, agitation was applied and maintained to keep the suspension homogenous, and after an appropriate time of irradiation the suspension was sampled. The concentration of dye was determined by UV–vis spectrophotometer (Shimadzu 1700 UV–vis spectrophotometer) at λ_{max} = 436 nm after centrifugation of a sample. pH of samples was adjusted by adding dilute NaOH and HCl and measured using pH meter (PHM93 reference pH meter, Radiometer Copenhagen, Denmark).

RESULTS AND DISCUSSION

UV–vis spectra changes

The changes in the absorption spectra of BY28 solution during the photocatalytic degradation at different irradiation times are presented in Figure 2. The BY28 textile dye shows a main band with a maximum absorption at 436 nm. The decrease of absorption peak actually indicates a rapid degradation of BY28 dye. Complete discoloration was observed after 3.5 hours of irradiation.
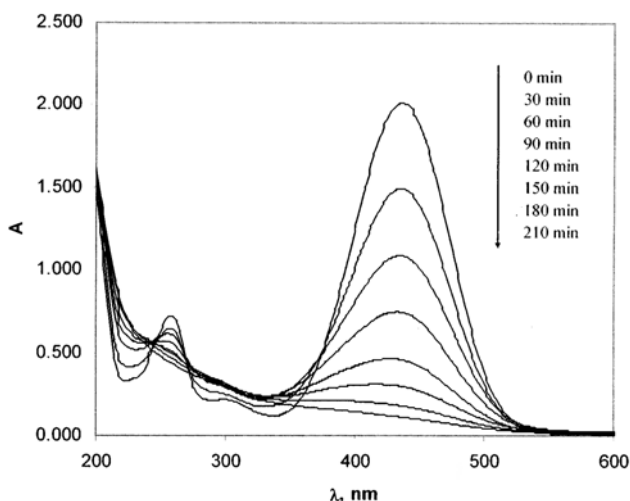

Figure 2. UV–vis spectra changes of BY28 (30 mg/l) in aqueous TiO_2 dispersion (TiO_2 1.2 g/l) irradiated with the sunlamp

Effect of amount of catalyst

The effect of the amount of TiO_2 on the BY28 photodegradation rate was shown in Figure 3. The photodegradation rate increased with increased

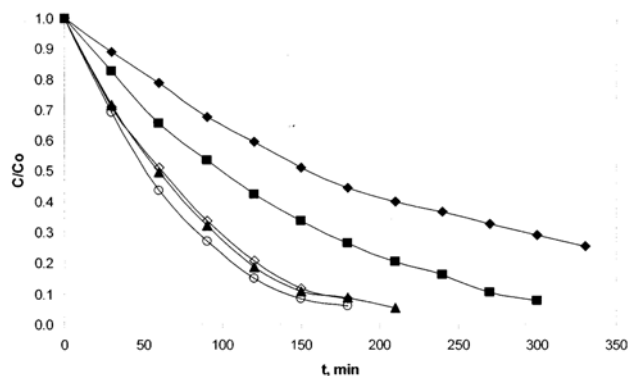Figure 3. Effect of initial concentration of TiO_2 on photodegradation rate of BY28 (dye concentration = 50 mg/l, ♦–0.4 g/l TiO_2, ■–0.8 g/l TiO_2, ▲ –1.2 g/l TiO_2, O –1.6 g/l TiO_2, ◊–2.0 g/l TiO_2)

concentration of photocatalyst, reached the highest value at 1.6 g/l and than decreased. The possible explanation for this phenomenon is the fact that when all dye molecules are adsorbed on TiO_2, the addition of higher quantities of TiO_2 would have no effect on the photodegradation efficiency. The photodegradation efficiency (X) is given by

$$X = \frac{C_o - C}{C_o} \qquad (7)$$

where C_o = initial concentration of BY28 in mg/l, C = concentration of BY28 at irradiation time t in mg/l. Figure 4 shows the effect of the amount of TiO_2 on photodegradation efficiency of BY28 at irradiation time of 3.0 h. Since small changes in photocatalytic efficiency was observed between 1.2, 1.6 and 2.0 g/l of TiO_2, we decided to select the concentration of 1.2 g/l of catalyst as the concentration with the highest efficiency per amount of used catalyst. No degradation effect was observed if catalyst or irradiation were applied separately.
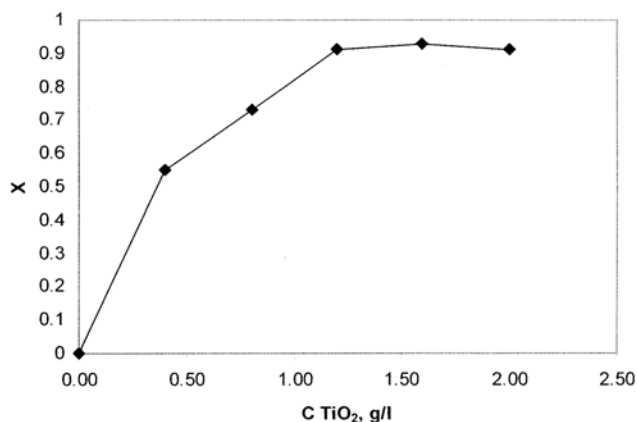

Figure 4. The effect of the concentration of TiO_2 on photodegradation efficiency of BY28 at irradiation time of 3.0 h (concentration of dye 50 mg/l).

Effect of initial dye concentration

The effect of initial dye concentration on photodegradation rate was also studied (Figure 5). As can be concluded, there is a decrease in photodegradation rate of BY28 with increased initial concentration of dye. With an increase of dye concentration, more and more dye molecules are adsorbed on the surface of TiO_2. This fact contributes to inhibition effect of the reaction of dye molecules with holes or hydroxyl radicals, due to the lack of any direct contact between them. Increased dye concentration also promotes that the dye molecules adsorb light and hence the photons can not reach the photocatalyst surface causing that the photodegradation efficiency decreases [4].
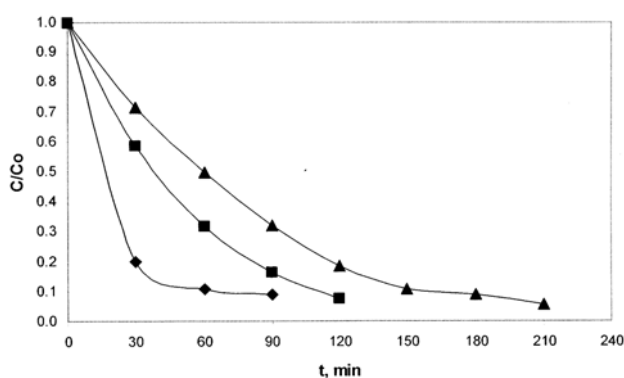

Figure 5. Effect of initial dye concentration on photodegradation rate of BY28 (dye concentration = ♦−10 mg/l, ■−30 mg/l, ▲ −50 mg/l at 1.2 mg/l of TiO_2)

Effect of pH

It is well known that pH value has an influence on the rate of degradation of some organic compounds in photocatalytic processes [7,8]. Photodegradation of BY28 was studied at three different pH values (2.5, 5.2 and 10.0). The pH was adjusted by addition of HCl (2.5) or NaOH (10.0). The third value is pH of pure dye solution in deionised water. The obtained results (Figures 6 and 7) imply that the initial photodegradation rate is highest in alkaline solution and lowest in acidic solution. Added OH^- ions favor the photodegradation as they can react with holes and produce $^\bullet OH$ [2]:

$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + {}^\bullet OH \qquad (8)$$
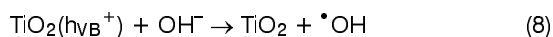
When OH^- ions are consumed, pH falls and the photodegradation efficiency slows down so after 3 hours it's slower than pure dye solution (Figure 7).

In acidic solution photocatalytic degradation is probably due to the formation of $^\bullet OH$ [9] but in lesser extent:

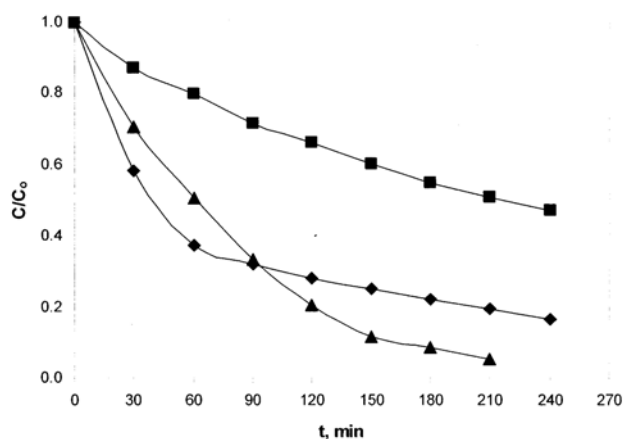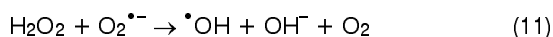$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \qquad (9)$$

$$HO_2^\bullet \rightarrow O_2 + H_2O_2 \qquad (10)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^\bullet OH + OH^- + O_2 \qquad (11)$$

Figure 6. Effect of pH on photodegradation rate of BY28 (dye concentration = 50 mg/l, pH = ■−2.5, ▲ −5.2, ♦−10.0, at 1.2 g/l of TiO_2)
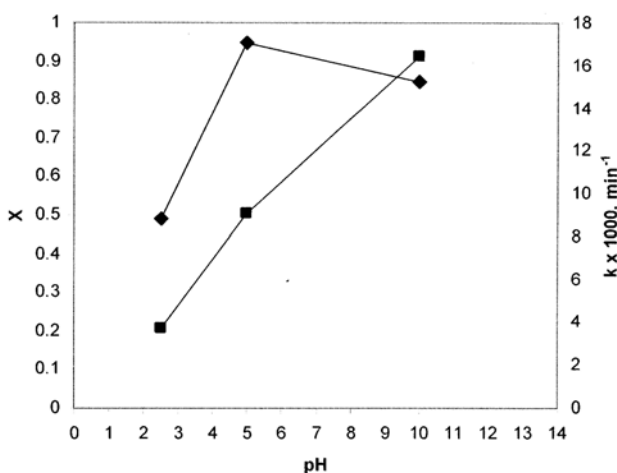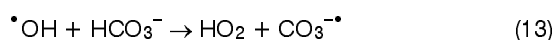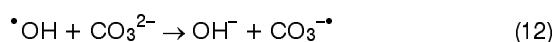

Figure 7. Effect of pH on photodegradation efficiency and initial photodegradation rate of BY28 (♦ − photodegradation efficiency, ■ − initial photodegradation rate)

Effect of Na_2CO_3

Sodium carbonate is the common auxiliary used in textile processing. It is mainly used to adjust the pH of the dyeing bath. Therefore the wastewaters from the dyeing operation contain considerable amount of carbonate ions. We studied the effect of very high quantities of sodium carbonate. The obtained results are shown in Figure 8. Photodegradation in the presence of sodium carbonate (1–10% w/v) was slower in comparison to the reaction without sodium carbonate. Contrary to expectations, the increase in carbonate concentration resulted in an increase in photodegradation rate. Generally, the presence of sodium carbonate decreases the reaction rate due to the hydroxyl scavenger property of carbonate ions [10]:
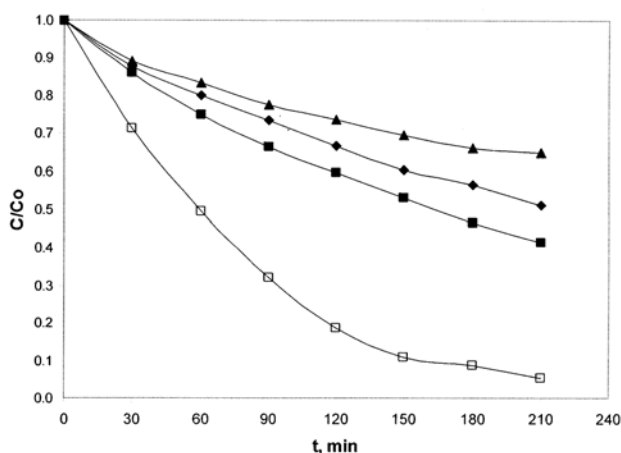
$$^\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet} \qquad (12)$$

$$^\bullet OH + HCO_3^- \rightarrow HO_2 + CO_3^{-\bullet} \qquad (13)$$

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Figure 8. Effect of Na_2CO_3 concentration on photodegradation rate of BY28 (dye concentration = 50 mg/l, Na_2CO_3 concentration = ∀–0 %, 7–1 %, Λ–5 %, !–10 %, at 1.2 g/l of TiO_2)

On the other hand, the obtained results indicate that the higher concentration of carbonate ions might favor the formation of OH^- ions, thus promoting the reaction [11]:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \qquad (14)$$

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- \qquad (15)$$
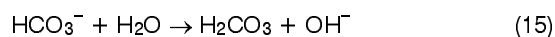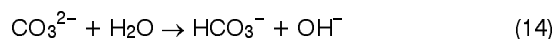
Effect of NaCl

Another common inorganic ion, i.e. chloride ion as sodium chloride was employed to study photodegradation rate of BY28. Sodium chloride is usually the effluent along with sectional wastes of textile mills. The influence of different concentrations of sodium chloride (1–10% w/v) on photodegradation rate of BY28 is plotted in Figure 9. The decrease of photodegradation of dye in presence of chloride ions is due to the hole scavenging properties of chloride ions [10]:
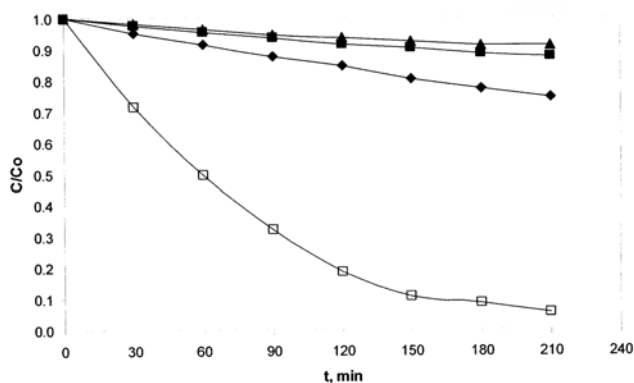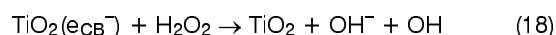
$$Cl^- + h_{VB}^+ \rightarrow Cl^\bullet \qquad (16)$$

$$Cl + Cl^- \rightarrow Cl_2^- \qquad (17)$$

This is an example of competitive inhibition where reaction of dye molecules with the holes will compete with this reaction. While chlorine radicals are forming slowly, they are converted into chloride anions instantly. Surface site normally available at the TiO_2/dye solution interface for adsorption and electron transfer from the dye can be blocked by anions such as chloride which are not oxidisable but yet effective inhibitors for detoxification process.

Effect of H_2O_2

One possible way to increase the reaction rate is to increase the concentration of hydroxyl radicals becouse these species are widely considered to be promoters of photocatalytic degradation [12–16]. This could be attributed to the increase in the concentration of hydroxyl radical by the following reactions [12]:

$$TiO_2(e_{CB}^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH \qquad (18)$$

$$O_2^{\bullet -} + H_2O_2 \rightarrow OH^- + {}^\bullet OH + O_2 \qquad (19)$$

$$H_2O_2 + h\nu \rightarrow 2\,{}^\bullet OH \qquad (20)$$

In this paper we wanted only to investigate the effect of H_2O_2 by conducting experiments using solely H_2O_2 in the phodegradation reaction as well as experiments with H_2O_2 and TiO_2 using relatively high concentration of H_2O_2. The obtained results were compared to the experiments where only TiO_2 was used (Figure 10). The initial photodegradation rate of BY28 was highest when H_2O_2 and TiO_2 were used, but after 3.5 hours similar photodegradation efficiency was achieved in all experiments.

When the reaction with H_2O_2 and TiO_2 is concerned, an inhibition effect was observed in comparison to the reaction with only TiO_2, after the initial period of the degradation.

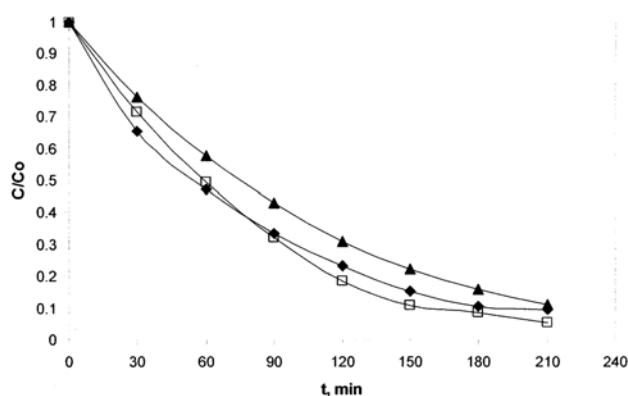*Figure 9. Effect of NaCl concentration on photodegradation rate of BY28 (dye concentration = 50 mg/l, NaCl concentration = ∀–0 %, Λ–1 %, !–5 %, 7–10 %, at 1.2 g/l of TiO_2)*

Figure 10. Effect of H_2O_2 on photodegradation rate of BY28 (dye concentration = 50 mg/l, 7–only H_2O_2 (2.2 % v/v), Λ–H_2O_2 and TiO_2, ∀–only TiO_2, at 1.2 g/l of TiO_2)

CONCLUSION

Photodegradation of CI Basic Yellow 28 is only efficient if the UV/TiO_2 process is applied while in the absence of the irradiation or TiO_2 no photodegradation was detected. The obtained results indicated that the photodegradation rate of BY28 was affected by the initial dye concentration, pH and the concentration of TiO_2. The presence of NaCl and Na_2CO_3 led to inhibition of the photodegradation process. The presence of higher concentration of H_2O_2 initially increases the BY28 photodegradation rate, but after prolonged irradiation time the inhibition effect was observed.

ACKNOWLEDGMENT

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