A study of the photocatalytic degradation of the textile dye CI Basic Yellow 28 in water using a P160 TiO$_2$-based catalyst

VELJKO DJOKIĆ[1], JELENA VUJOVIĆ[1], ALEKSANDAR MARINKOVIĆ[1#], RADA PETROVIĆ[1], DJORDJE JANAĆKOVIĆ[1], ANTONIJE ONJIA[2] and DUŠAN MIJIN[1*#]

[1]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 3503, 11120 Belgrade, Serbia and* [2]*Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia*

Abstract: The photocatalytic degradation of the synthetic textile dye CI Basic Yellow 28 (BY28) in water, using a recently synthesized P160 TiO$_2$-based catalyst, under Osram ultra-vitalux® lamp (300 W) light, was studied. The effects of the operational parameters, such as initial concentration of catalyst, initial dye concentration and pH, were studied. The salt effect (NaCl, Na$_2$CO$_3$, Na$_2$SO$_4$ and NaNO$_3$) was also investigated. It was found that the optimal concentration of catalyst is 2.0 g L^{-1}. A pseudo first-order kinetic model was illustrated using the Langmuir–Hinshelwood mechanism and the adsorption equilibrium constant and the rate constant of the surface reaction were calculated (K_{BY} = 6.126 L mg^{-1} and k_C = 0.272 mg L^{-1} min^{-1}, respectively). The photodegradation rate was higher in weak acidic than in high acidic and alkaline conditions. The presence of CO$_3^{2-}$ ions increased the photodegradation rate while Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ decreased the reaction rate. The rate of photodegradation of BY28 was measured using UV–Vis spectroscopy.

Keywords: TiO$_2$; photocatalysis; pseudo first-order kinetic model; Langmuir––Hinshelwood mechanism; salt effect.

INTRODUCTION

Textile and other synthetic dyes are an important source of environmental contamination due to their large production and usage in the textile and other industries. The majority of these dyes are toxic, mostly non-biodegradable and often resistant to destruction by physicochemical methods, such as chemical precipitation and separation of pollutants, coagulation and elimination by adsorption.[1–3] None of these methods is destructive so they only transfer the contami-

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nation from one phase to another. Therefore, a new kind of pollution is obtained that requires further treatment.

Advanced oxidation processes (AOPs) provide an effective means of rapidly treating compounds with efficient process control.[4] Among the new oxidation methods, heterogeneous photocatalysis appears as a destructive technology leading to the total mineralization of many organic pollutants,[5–8] following the proposed mechanism:
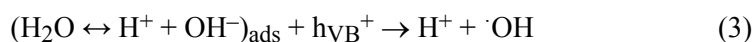
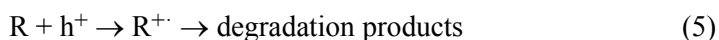a) absorption of efficient photons by titania ($h\nu \geq E_g = 3.2$ eV):

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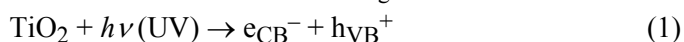
b) oxygen ionosorption:

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

c) formation of $^{\cdot}OH$ by OH^- reaction with photoholes:

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

d) oxidation of the organic reactant *via* successive attacks by $^{\cdot}OH$ radicals:

$$R + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O \tag{4}$$

e) or by direct reaction with holes:

$$R + h^+ \rightarrow R^{+\cdot} \rightarrow degradation\ products \tag{5}$$

As an example of the last process, holes can generate CO_2 according to:

$$RCOO^- + h^+ \rightarrow R^{\cdot} + CO_2 \tag{6}$$
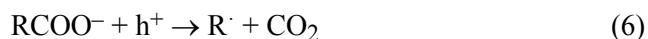
Titanium dioxide is one of the most frequently studied and applied photocatalysts in advanced oxidation processes. Its ability to be activated by means of natural sources (Sun-UV irradiation) as well as its semiconductor properties, chemical and biological inertness, resistance to chemical and photo-induced corrosion, and also its non-toxicity and low price have attracted world wide attention of scientists and engineers for some time.[9] Titanium dioxide can be manufactured using different methods. The most frequently used methods are sol–gel method, hydrothermal processing and gas-phase reaction.[10]

The aim of the present study was to investigate the influence of various parameters on the photocatalytic decomposition of the textile dye CI Basic Yellow 28 in the presence of a recently synthesized P160 TiO_2-based catalyst[11,12] irradiated under an Osram ultra-vitalux® lamp as the light source. CI Basic Yellow 28 dye is a cationic azo dye that can be also be called an azomethine dye (–CH=N–) or hydrazone dye (=N–N(H,R)–) (Fig. 1). The P160 TiO_2-based catalyst was synthesized by a non-hydrolytic sol–gel process.[11,12] The effects of parameters such as initial concentration of catalyst, initial dye concentration, pH and the presence of salts (NaCl, Na_2SO_4, $NaNO_3$ and Na_2CO_3) were studied.
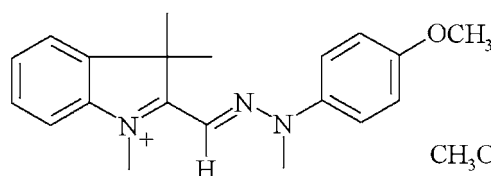
Fig. 1. Structure of CI Basic Yellow 28.

EXPERIMENTAL

Materials

All chemicals used in the investigation were of reagent grade and were used without further purification. Hydrochloric acid, sodium chloride, sodium carbonate, sodium sulfate, sodium nitrate and sodium hydroxide (all *p.a.*) were obtained commercially, mostly from Fluka. P160 TiO_2 was prepared according to a previously procedure published.[11,12] The textile dye, CI Basic Yellow 28, was obtained from Bezema as a gift (commercial name Bezacryl Goldgelb GL 200) and was used without purification. Deionized water was obtained from a Milipore Waters Milli Q purification unit.

Procedures

Irradiations were performed in a glass reactor (cylindrical shape, volume 100.0 mL) with an Osram ultra-vitalux® lamp (mix of lights; UV-A:UV-B = 13.6:3 according to the manu-facturer's specifications) placed 500 mm from the surface of the reaction mixture. The photodegradation of BY28 was studied by preparing a solution containing a known concen-tration of the dye and amount of TiO_2. In a typical experiment, 25 mL of solution was used. Then, the lamp was switched on and during the irradiation, agitation was applied. After an appropriate time of irradiation, as given in the figures, the suspension was sampled. The concentration of dye was determined by UV–Vis spectrophotometer (Shimadzu 1700) at $\lambda_{max} =$ = 436 nm. After filtration, the pH of the samples was adjusted by the addition of dilute NaOH and HCl and measured using pH meter (PHM 93 reference pH meter, Radiometer Copen-hagen, Denmark).

RESULTS AND DISCUSSION

Effect of initial catalyst concentration

The effect of the initial P160 TiO_2 catalyst concentration on the photodegra-dation rate of BY28 is shown in Fig. 2. The photodegradation rate increased with increasing concentration of photocatalyst, reached the highest value at 2.0 g L^{-1} and subsequently decreased. The explanation for this phenomenon is the fact that when all dye molecules are adsorbed on TiO_2, the addition of larger quantities of TiO_2 would have no effect on the photodegradation efficiency. Above this con-centration, light scattering and coagulation of the catalyst particles decreased the reaction rate,[8,13–15] and reduced degradation rate was registered when the con-centration of TiO_2 was increased beyond 2.0 g L^{-1}.

The photodegradation efficiency (X) is given by:

$$X = \frac{c_0 - c}{c_0} \qquad (7)$$

where c_0 is the initial concentration of BY28 in mg L^{-1}, c is the concentration of BY28 at irradiation time t in mg L^{-1}. The effect of the amount of TiO$_2$ on the photodegradation efficiency of BY28 at an irradiation time of 0.5 h is shown in Fig. 3. No decolorization was observed if catalyst or irradiation were applied separately. Complete decolorization was observed after 1 hour of irradiation.
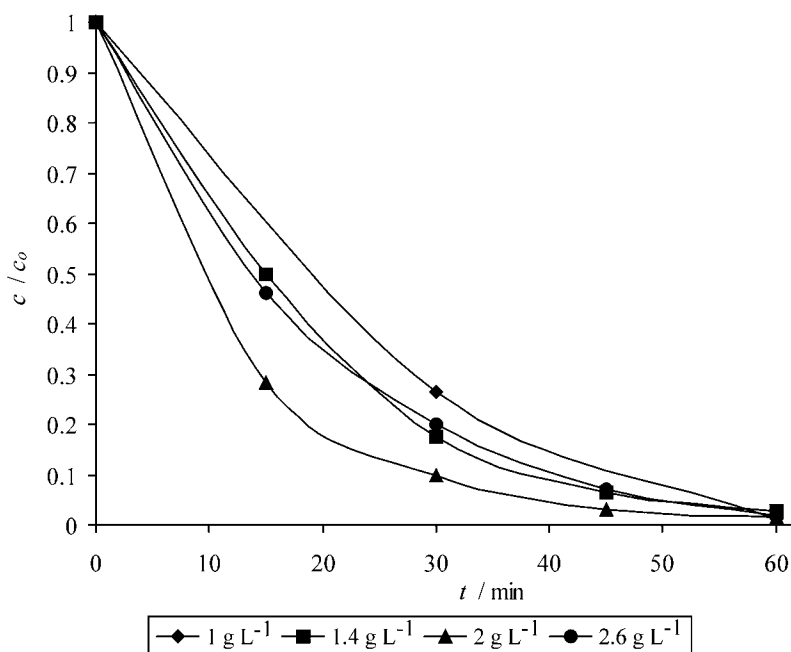

Fig. 2. The effect of the initial concentration of P160 TiO$_2$ on the photodegradation rate of BY28 (dye concentration = 50 mg L^{-1}).
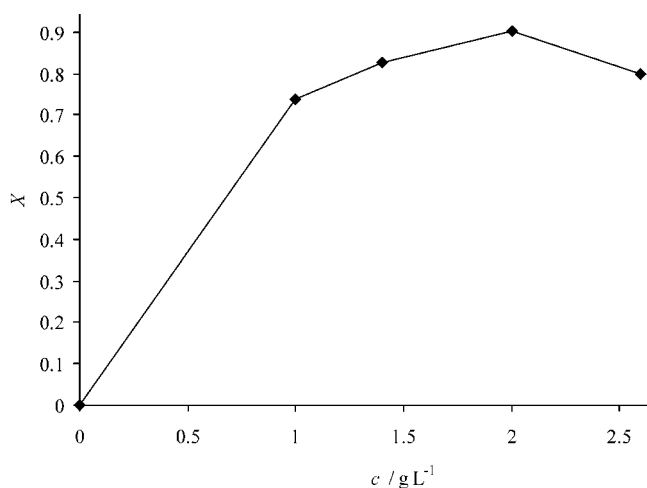

Fig. 3. The effect of the concentration of P160 TiO$_2$ on the photodegradation efficiency of BY28 at an irradiation time of 0.5 h (dye concentration = 50 mg L^{-1}).

Effect of initial dye concentration

In addition, the effect of the initial dye concentration on the photodegradation rate was studied (Fig. 4). It could be observed that the photodegradation rate of BY28 decreases with increasing initial concentration of dye, since with increasing dye concentration, more and more dye molecules are adsorbed on the surface of the TiO$_2$. Due to the lack of any direct contact between dye molecules with holes or hydroxyl radicals, inhibition occurred. Increased dye concentration also promotes that the dye molecules adsorb light and hence the photons cannot reach the photocatalyst surface; hence the photodegradation efficiency decreases.[5]
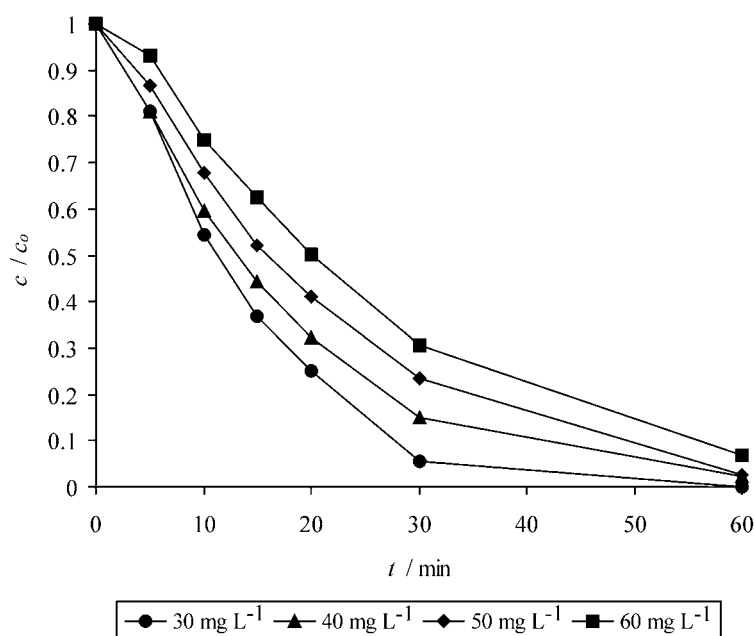

Fig. 4. The effect of the initial dye concentration on the photodegradation rate of BY28 (catalyst concentration = 2.0 g L^{-1}).

The kinetics of the photodegradation rate of most organic contaminants[16] can be well described by pseudo-first order kinetics, which is given by the following equations:

$$\ln\left(\frac{c_0}{c}\right) = kt \tag{8}$$

$$c = c_0 e^{-kt} \tag{9}$$

where c_0, c and t are as given above and k is the pseudo-first order rate constant.

Heterogeneous photocatalytic reaction can be successfully analyzed using the modified Langmuir–Hinshelwood (L–H) kinetic expression.[14,16–18] The rate

of oxidation of BY28 by a surface reaction is proportional to the surface coverage of BY28 on the P160 TiO_2, assuming that BY28 is adsorbed stronger on the catalyst surface than the intermediate products. The effect of the initial BY28 concentration c_0 on the initial BY28 degradation rate r is given in the form of Eqs. (10) and (11):

$$r = \frac{K_{BY}k_C c}{1 + K_{BY}c_0} = kc \qquad (10)$$

$$\frac{1}{k} = \frac{1}{K_{BY}k_C} + \frac{c_0}{k_C} \qquad (11)$$

where K_{BY}, k_C, and k are the Langmuir–Hinshelwood adsorption equilibrium constant, the rate constant of photodegradation surface reaction and the rate constant of the initial BY28 photodegradation reaction, respectively. At the investigated concentrations, *i.e.*, concentrations up to 60 mg L^{-1}, the applicability of L–H equation for the photocatalytic degradation was confirmed by the linear plot ($R = 0.9716$) obtained by plotting the reciprocal of the rate constant ($1/k$) against the initial dye concentration c_0 (Fig. 5). The values of K_{BY} and k_C were found to be 6.126 L mg^{-1} and 0.272 mg L^{-1} min^{-1}, respectively.
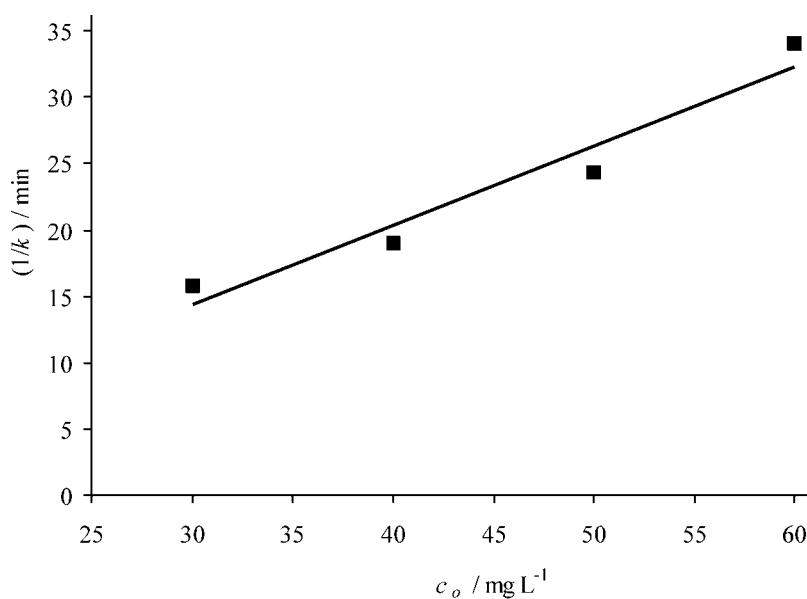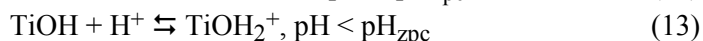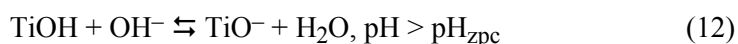

Fig. 5. Linear transformation of the L–H type expression.

Effect of pH

Since pH value has an influence on the rate of photodegradation of some organic compounds in photocatalytic processes,[13,19,20] the photodegradation of

BY28 at four different pH values (3.3, 5.2, 6.7 and 8.7) were studied. The second value is the pH of the pure dye solution in deionized water.

It is known that the amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst. The zero point charge for TiO_2 (pH_{zpc}) is 5.0–6.0, and above this value, the TiO_2 surface is predominantly negatively charged (TiO^-) (Eq. (12)).[18] The surface of the catalyst is positive below pH 6.0, and as the pH decreases, the functional groups are protonated ($TiOH_2^+$), and the proportion of the positively charged surface increases (Eq. (13)):[8]

$$TiOH + OH^- \leftrightarrows TiO^- + H_2O, \ pH > pH_{zpc} \tag{12}$$

$$TiOH + H^+ \leftrightarrows TiOH_2^+, \ pH < pH_{zpc} \tag{13}$$

It was found that the initial photodegradation rate was higher at 5.2 than in more acidic or alkaline solutions (Fig. 6). Since BY28 is cationic dye, one would expect that the reaction rate would be higher at pH values above pH_{zpc} since in this pH range, the TiO_2 surface is negatively charged and the affinity of the dye molecules should be higher, as was reported earlier for TiO_2-Merk Eusolex® T (anatase modification). When TiO_2-Merk Eusolex® T was used, the initial photodegradation rate was highest in alkaline solutions and lowest in acidic solutions.[21] This behavior of the P160 catalyst could be probably be explained by different surface structure obtained by the non-hydrolytic sol–gel process.[12]
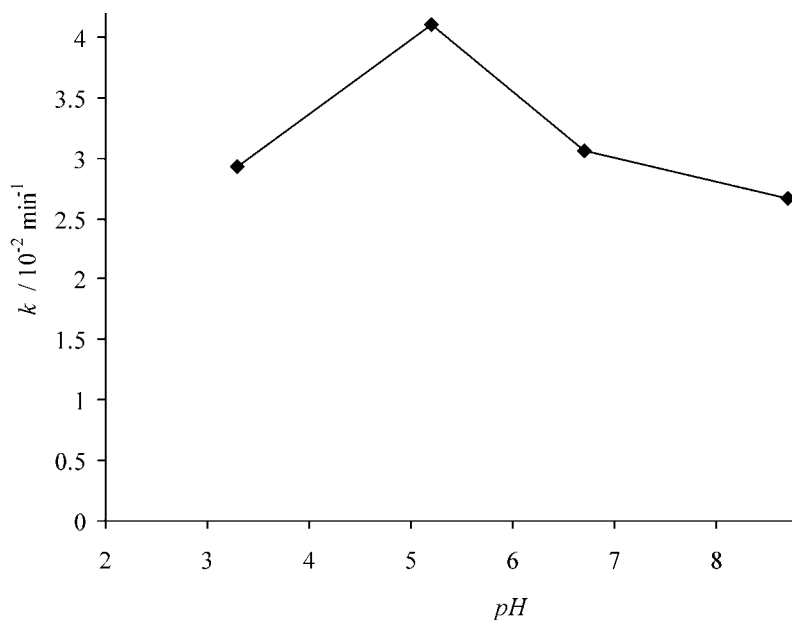

Fig. 6. The effect of pH on the photodegradation rate of BY28 (dye concentration =50 mg L^{-1}, catalyst concentration = 2.0 g L^{-1}).

Salt effect of the photodegradation rate of BY28

Salt effect on photodegradation of organic pollutants was frequently investigated due to the possibility of the adsorption of inorganic anions onto the photocatalyst surface. This adsorption results in decreasing of number of the holes and ·OH radicals, and reaction rate decrease.[14,22] The presence of different inorganic ions ($SO_4{}^{2-}$, $HSO_4{}^-$, $PO_4{}^{3-}$, $CO_3{}^{2-}$, $HCO_3{}^-$, Cl^-, $NO_3{}^-$, *etc.*) present in surface and ground waters leads to decreasing photodegradation effectivity due to their scavenging properties.[22]

The salt effect on the photodegradation of BY28 was studied using sodium salts, *i.e.*, sodium chloride, sodium carbonate, sodium sulfate and sodium nitrate (Fig. 7). Sodium chloride along with sectional wastes is usually present in the effluent of textile mills. The decrease of the photodegradation rate of BY28 in the presence of sodium chloride (20 mM) could be explained by the hole scavenging properties of chloride ions:[22]

$$Cl^- + h_{VB}{}^+ \rightarrow Cl^{\cdot} \tag{14}$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2{}^{-\cdot} \tag{15}$$

The formed chloride anions block the surface sites that are normally available at the TiO_2/dye solution interface for adsorption and electron transfer and so inhibited the degradation process. A similar effect of sodium chloride on the photodegradation rate of BY28 was observed when TiO_2-Merk Eusolex® T was used.[21]
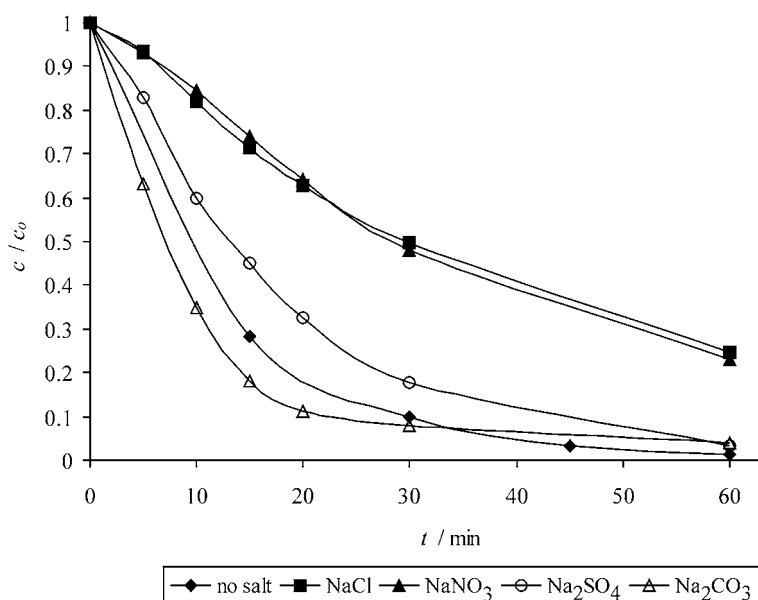

Fig. 7. Salt effect (20 mM) of on the photodegradation rate of BY28 (dye concentration = 50 mg L^{-1}, catalyst concentration = 2.0 g L^{-1}).

Sodium carbonate is mainly used in the textile industry to adjust the pH of the dyeing bath. Therefore, the wastewaters from the textile industry contain considerable amounts of carbonate ions. As can be seen from Fig. 7, the photodegradation in the presence of sodium carbonate (20 mM) was faster in comparison to the reaction in its absence. The obtained results indicate that carbonate ions might favor the formation of OH$^-$ ions, thus promoting the degradation reaction:[23]

$$CO_3{}^{2-} + H_2O \rightarrow HCO_3{}^- + OH^- \tag{16}$$

$$HCO_3{}^- + H_2O \rightarrow H_2CO_3 + OH^- \tag{17}$$
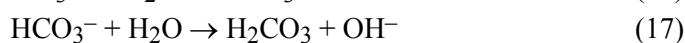
A similar effect of sodium carbonate on the photodegradation rate of BY28 was observed when TiO$_2$-Merk Eusolex$^®$ T was used.[21]

The photodegradation in the presence of sulfate anions was slower in comparison to the reaction without salt. Sulfate anions change the distribution of BY28 between the solution and the P160 TiO$_2$ surface and/or react with the positive holes ($h_{VB}{}^+$) and hydroxyl radicals ($^·$OH):[24]

$$SO_4{}^{2-} + h_{VB}{}^+ \rightarrow SO_4{}^{-•} \tag{18}$$

$$SO_4{}^{2-} + OH^• \rightarrow SO_4{}^{-·} + OH^- \tag{19}$$

The presence of $SO_4{}^{2-}$ leads to formation of $SO_4{}^{-•}$, which is less reactive than $^•$OH and $h_{VB}{}^+$ and thus the photodegradation rate of BY28 is hindered.

Finally, the effect of sodium nitrate was studied (Fig. 7). Although some authors have reported that nitrate anions can increase the photodegradation rate,[25] in the present study, a strong inhibition of the photodegradation of BY28 was observed due to the possible blockage of the active sites on the TiO$_2$ surface by nitrates.

CONCLUSIONS

The behavior of recently synthesized P160 TiO$_2$-based catalyst in the photodegradation of CI Basic Yellow 28 was studied. It was shown that complete decolorization could be achieved in 60 min using a catalyst concentration 2.0 g L^{-1}. The obtained results indicated that the photodegradation rate of BY28 was affected by the initial dye concentration, pH and the presence of salts. The Heterogeneous photocatalytic reaction was analyzed using the modified Langmuir–Hinshelwood kinetic expression, and the rate constant of the photodegradation surface reaction and the rate constant of initial BY28 photodegradation reaction were calculated. The values K_{BY} and k_C were found to be 6.126 L mg^{-1} and 0.272 mg L^{-1} min^{-1}, respectively.

И З В О Д

ПРОУЧАВАЊЕ ФОТОКАТАЛИТИЧКЕ ДЕГРАДАЦИЈЕ ТЕКСТИЛНЕ БОЈЕ CI BASIC YELLOW 28 У ВОДИ КОРИСТЕЋИ P160 КАТАЛИЗАТОР НА БАЗИ TiO$_2$

ВЕЉКО ЂОКИЋ[1], ЈЕЛЕНА ВУЈОВИЋ[1], АЛЕКСАНДАР МАРИНКОВИЋ[1], РАДА ПЕТРОВИЋ[1], ЂОРЂЕ ЈАНАЋКОВИЋ[1], АНТОНИЈЕ ОЊИА[2] и ДУШАН МИЈИН[1]

[1]*Технолошко–металуршки факултет Универзитета у Београду, Карнегијева 4, Београд и* [2]*Институт за Нуклеарне науке Винча, Универзитет у Београду, Београд*

У раду је проучавана фотокаталитичка деградација синтетске текстилне боје CI Basic Yellow 28 у води, користећи недавно синтетисани катализатор на бази P160 TiO$_2$, и Osram ultra-vitalux® лампу (300 W). Проучаван је утицај различитих параметара на реакцију, као што су: почетна концентрација катализатора, почетна концентрација боје, присуство соли (NaCl, Na$_2$CO$_3$, Na$_2$SO$_4$ и NaNO$_3$) и pH. Утврђено је да је оптимална концентрација катализатора 2,0 g L^{-1}. Користећи Langmuir–Hinshelwood механизам одређене су равнотежна адсорпциона константа и константа брзине површинске реакције (K_{BY} = 6,126 L mg^{-1} и k_C = 0,272 mg L^{-1} min^{-1}). Брзина реакције је већа у слабо киселој средини у поређењу са јако киселом или базном средином. Присуство CO$_3^{2-}$ повећава брзину реакције фотодеградације док је Cl$^-$, SO$_4^{2-}$ и NO$_3^-$ смањују.

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