

Kinetic degradation of acid blue 9 through the TiO₂/UV advanced oxidation process.

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Abstract

In recent years, advanced oxidation processes have brought significant improvements to the treatment of waste water with recalcitrant, toxic and/or colored compounds. Textile and tanning industries produce considerable volumes of wastewater colored by several kinds of dyes; acid blue 9 is one of the dyes used by these industries that is frequently found in their wastewater.

The objective of the present work is to evaluate the degradation of acid blue 9 using titanium dioxide activated with UV light. The degradation tests were performed in a fully-mixed heterogeneous reactor.

In order to analyze the behavior of the degradation reaction, three series of tests were considered: in the first series, the concentration of the catalyst was kept constant at 150 mg L⁻¹ and the initial dye concentration was varied from 20 – 60 mg L⁻¹; in the second series, the initial dye concentration was kept constant at 40 mg L⁻¹ and the catalyst concentration was varied from 150 to 600 mg L⁻¹; in the third series, both the concentration of the dye (20 - 80 mg L⁻¹) and that of the catalyst (150 – 600 mg L⁻¹) were varied simultaneously while always keeping a constant dye/catalyst ratio of 1:7.5.

The results show that the dye acid blue 9 can be completely degraded by the TiO₂-UV advanced oxidation processes, and that the initial concentrations of catalyst and dye affect the kinetics and order of reaction. Reaction time increases exponentially when the initial dye concentration is increased linearly, showing first order reaction kinetics. When the catalyst concentration is increased linearly, the reaction time decreases exponentially.

The simultaneous increase of catalyst and dye increases the reaction time linearly, with pseudo-first-order kinetics in the first two tests (low concentration) and changing to ½ order in the last two tests (high concentration). All the tests show zeroth-order degradation kinetics with respect to the Chemical Oxygen Demand (COD), with an organic load removal of up to 97%.

Keywords: Initial concentrations, Reaction kinetic, Reaction order, Titanium dioxide and Advanced Oxidation Processes.

1. Introduction

Textile and leather tanning industries use considerable volumes of water for their manufacture processes, and consequently produce a considerable amount of wastewater. Water consumption per tonne of finished product is in the broad range of 25 to 250 m³, depending on the type of process, type of material to be tanned, type of dye and type of the additives used (Chacón et al, 2006). Synthetic dyes are commonly used in dyeing processes and are in general the greatest pollutants found in wastewaters (Muruganandham et al, 2004). It is estimated that a worldwide total of 140,000 tonnes of different synthetic dyes in aqueous streams are released to the environment every year by different industries (Chacon et al, 2006; Behnajaday et al, 2006; Konstaninou et al, 2004). The adverse effects of these synthetic dyes on the environment include an increase of the color and toxicity of the waters, death of fish and zooplankton, general affectation of ecosystems, and widespread aesthetic damage (Azbar et al 2004; Sponsa, 2006; Pokhrel et al, 2004). These effects are persistent because the pollutants in wastewater streams in general have low biodegradability; it is because of this that biological processes are usually unsuccessful in removing dyes (Muruganandham et al, 2006 and Azbar et al, 2004). Much research effort in recent years has been focused on the need of treatment systems which make it possible to slow down or eliminate the adverse effects on the water bodies that receive tinted wastewater. This research has produced significant advances in advanced oxidation processes (AOPs) for the degradation of colored compounds. (Behnajaday et al, 2006; Mahmoodi et al, 2005; Konstantinou et al, 2004; Stilidy et al, 2003; Wawrzyniak et al, 2006 Arslan et al, 2000). Equivalent progress has not been seen, however, in the development of process engineering that considers the initial reaction conditions, process variables, reactor engineering and quantum yield that affect the kinetic oxidation of organic substances (Cabrera et al, 2000; Romero et al, 1997).

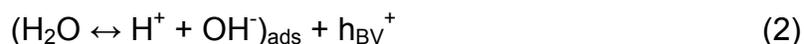
The present work means to evaluate the impact that the initial concentrations of dye and catalyst have on the kinetics and order of the degradation reaction. Acid blue 9 was selected for this work because it is used in the dyeing of various materials and can be found in the wastewater of the textile, tanning and food industry.

The mechanism proposed for this heterogeneous photocatalysis is the *in situ* production of a high energy OH^o radical, which ruptures organic molecules through proton capture (reactions 1, 2 and 3). This is followed by the formation of peroxy radicals and their subsequent oxidation to CO₂, water and oxidized inorganic molecules (reactions 4 and 5, respectively) (Konstantinou et al, 2004; Azbar et al, 2004; Stilidy et al, 2003; Chun-Hsin et al, 2006).

Absorption of photons by TiO₂:



Production of the OH^o radicals:



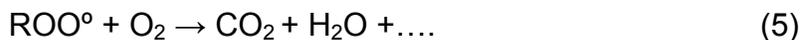
Oxidation of organic compounds through attacks by OH° radicals:



Formation of the peroxy radicals:



Oxidation of peroxy radicals to CO_2



2. Methodology

2.1 Materials

The dye blue acid 9 has a molecular weight of 792.84 and chemical formula $\text{C}_{37}\text{H}_{34}\text{N}_2\text{O}_9\text{S}_{32}\text{Na}_{32}$, and is identified with the number 42090 in the color index catalog. It was used in the degradation tests without any treatment, and its structure is shown in Figure 1.

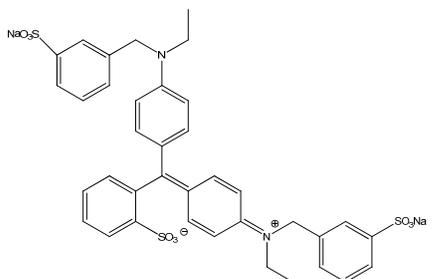


Figure 1. Structure of acid blue 9

Untreated Degussa P-25 TiO_2 powder was the catalyst used in this study. This catalyst had a particle diameter between 20 and 30 nm, purity greater than 97%, surface area of $50 \text{ m}^2/\text{gr}$, pore diameter between 20 and 200 Å , and an anatase/rutile ratio of 80/20 (Mahmoodi et al, 2005; Stilidy et al, 2003).

Oxygen was supplied using three nozzles at the bottom of the reactor and a flow rate of 0.5 L min^{-1} . This flow rate supplied oxygen for the oxidation of the dye and the dispersion of catalyst in the suspension.

The light source used to trigger the photo-oxidation processes was a Tecnolite UV-lamp, model F6T5BLB with 6 watts of nominal power and a maximum emission of 5.0 mW/cm^2 at 365 nm.

2.2 Photoreactor

A vertical, tubular, heterogeneous and completely mixed reactor was used for the photodegradation tests and is presented in Figure 2. The UV source is located in the center of the reactor, which has a reaction volume of 0.2 L. The dye degradation takes place in the annular space formed between the lamp and the reactor walls.

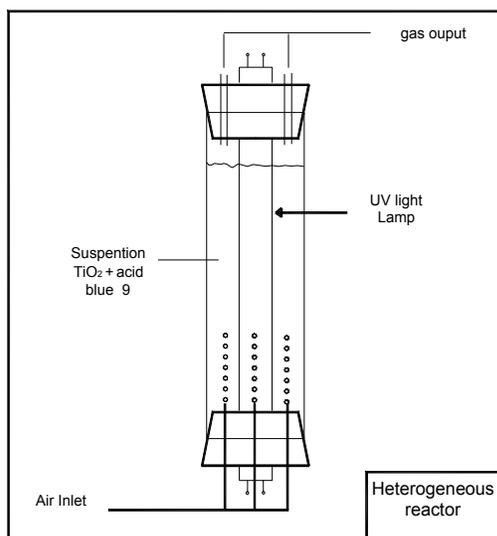


Figure 2. The heterogeneous reactor.

2.3 Experimental procedure

The oxidation kinetics were evaluated through an experimental design based on three series of tests, as shown in Table 1. In the first series (tests 1, 2 and 3) the concentration of the catalyst was kept constant at 150 mg L^{-1} and the dye concentration was varied from 20 to 60 mg L^{-1} . In the second series (tests 2, 5, 6 and 7) the dye concentration was kept constant at 40 mg L^{-1} and the catalyst concentration was varied from 150 to 600 mg L^{-1} . In the third series (tests 1, 5, 8 and 9) the dye and catalyst concentration were both varied simultaneously, always keeping the dye/catalyst ratio constant at 1:7.5. This experimental design was established based on two considerations: a) the dye concentration in the discharged waters has a wide range of variation and b) the average representative dye concentration in the wastewater of the textile industry is in the order of 40 mg L^{-1} (Behnajaday et al, 2006; Sponza, 2006).

Table 1. Experimental design

Concentration of acid blue 9 (mg L^{-1})	Concentration of TiO_2 (mg L^{-1})			
	150	300	450	600
20	Test 1			
40	Test 2	Test 5	Test 6	Test 7
60	Test 3		Test 8	

The degradation tests were performed with maximum lamp intensity, and aliquots of the solution were taken every 30 minutes until the color disappeared. Each sample was allowed to stand for 24 hours so that the catalyst settled and the sample solution could be analyzed for dye concentration.

2.4 Analysis of samples

The degradation of the samples was evaluated through Chemical Oxygen Demand (COD) and absorbance (A) analyses. The quantity of organic matter reported in the COD analysis includes the amount of dye remaining after every evaluation interval, plus the intermediate substances generated during dye degradation. The concentration of chromophore groups was determined by measuring the absorbance of the dye at 365 nm.

The absorbance determination was performed with a Perkin Elmer spectrophotometer, model lambda 10; DQO was determined using a model 45600 Hach digestion reactor and a model DR/2000 Hach spectrophotometer. The methodology used for COD evaluation was Hach's Method 8000, which is approved by the US Environmental Protection Agency (USEPA-1980).

$$\text{Degradation} = \frac{COD_0 - COD}{COD_0} \quad (6)$$

$$\text{Discoloration} = \frac{A_0(635nm) - A(635nm)}{A_0(635nm)} \quad (7)$$

3. Results and discussion

3.1 Dye degradation kinetics

Complete removal of the chromophore groups was achieved in all tests, as well as oxidation of 97% of the dye molecule in some cases. The results and the analysis of each series of tests are shown here.

3.1.1 The effect of increasing dye concentration (first series, tests 1, 2, 3)

Figures 3 and 4 show the decrease in color intensity as a function of reaction time in tests 1, 2 and 3. The results show that complete color elimination was reached after 2, 4 and 7 hours with kinetic constant values of 1.87, 1.08 and 0.62 h⁻¹ for dye concentrations of 20, 40 and 60 mg L⁻¹, respectively. These constants correspond to the pseudo-first-order kinetic model, which has been used in various occasions to evaluate the reaction order of the degradation of several azo-type dyes (Chacón

et al, 2006; Muruganandham et al, 2006; Behnajaday et al, 2006; Mahmoodi et al, 2005 and Stilidy et al, 2003).

Linearly increasing dye concentration logarithmically reduces reaction kinetics and exponentially increases the total degradation time. This effect is attributed to the following two conditions: a) there is an increase of the concentration of the colorant to be degraded and, b) there is a simultaneous increase in the amount of UV light absorbed by the dye, which decreases transmittance and the number of photons that collide with catalyst molecules. As a consequence, fewer hollow-electron pairs are produced and a greater reaction time is needed to produce the OH^0 radicals needed for degradation of the dye. These effects have been reported by other researchers (Cabrera et al, 2000; Romero et al, 2000, Cheng-Hsin et al, 2006).

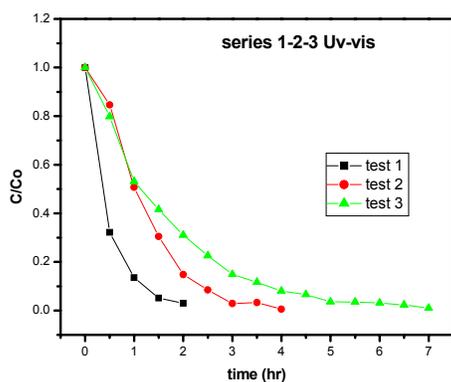


Figure 3. Decrease of the dye concentration as a function of time, first series.

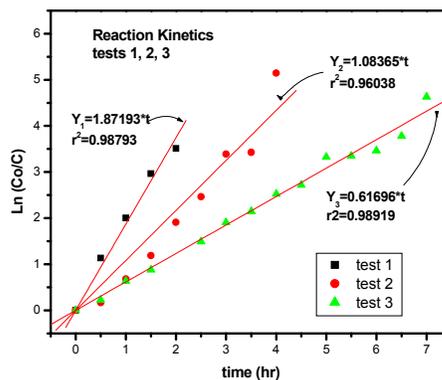


Figure 4. Rate of disappearance of the chromophore groups, first series.

The organic matter oxidation levels reached after total elimination of the dye were 97%, 64% and 78%, with rate constants of 43.13, 17.83, and 11.10 $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$ for tests 1, 2 and 3, respectively, as is shown in Figures 5 and 6. It can be observed that the reaction is of zeroth-order for COD which means that a limit condition is reached from the energetic standpoint (Blanco et al, 2001).

The difference found in the reaction order is explained by the fact that even though the OH^0 radical is non-selective, the organic dye molecule has bonds of different energies which cause the molecule to be broken at different rates in different sites. This is the case of the chromophore group, which has a low bond energy (March, 1992) and therefore breaks at a high rate. This is reflected in the fast disappearance of the color (reaction 3) in the first steps of the reaction (see Figure 3). The oxidation of the organic molecules (to which the measurable COD is proportional) requires reactions 4 and 5, which makes the reaction slower; the reaction is also linear as a result of the non-selectivity of OH^0 .

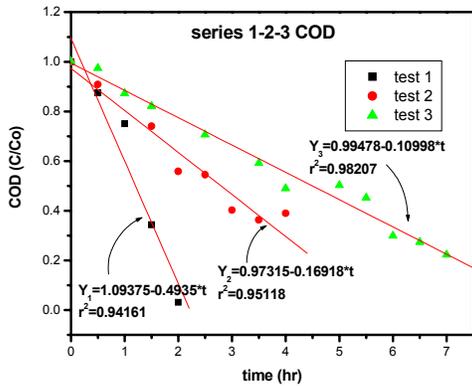


Figure 5. Decrease of organic matter (COD) in the solution as a function of time, first series.

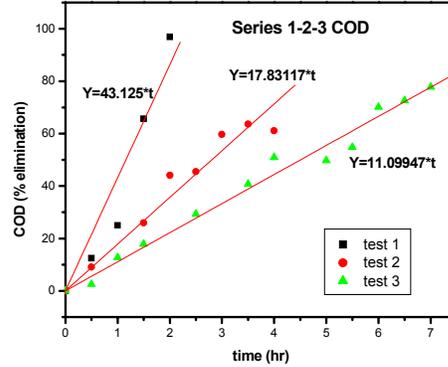


Figure 6. Percentage elimination of COD, first series.

3.1.2 The effect of increasing catalyst concentration (second series, tests 2, 5, 6, 7)

Figures 7 and 8 show the behavior of color degradation as a function of time in tests 2, 5, 6 and 7 with a constant dye concentration of 40 mg L^{-1} and a variable TiO_2 concentration. The results show that complete elimination of the color was reached after 4.0, 2.5, 2.0 and 1.5 hours, with rate constants of 1.08, 1.69, 2.54 and 2.81 h^{-1} for catalyst concentrations of 150, 300, 450 and 600 mg L^{-1} , respectively. As in the first series of tests, the rate constants were obtained by means of pseudo-first-order models. Increasing catalyst concentration increased reaction rate and decreased the reaction time needed for total elimination of the dye. This effect occurs because a greater number of photons are absorbed by TiO_2 and a greater concentration of OH° radicals is therefore available for the degradation of the dye.

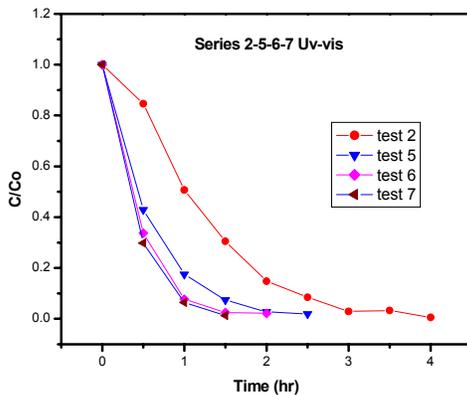


Figure 7. Decrease of dye concentration as a function of time, second series.

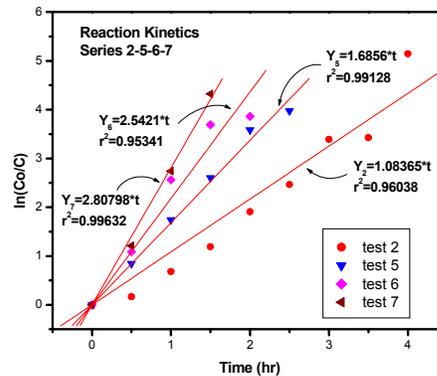


Figure 8. Rate of disappearance of the chromophore groups, second series.

A linear increase in catalyst concentration exponentially decreases the total degradation time, a condition which allows one to infer that there is a catalyst concentration after which the changes in reaction rate are not significant. This

effect was observed in Tests 6 and 7, which have rate constant values of 2.54 h^{-1} and 2.81 h^{-1} , respectively.

Regarding the COD for this series, it can be observed that the maximum oxidation levels of organic matter in tests 2, 5, 6 y 7 were 64%, 75%, 97% and 95%, with rate constants of 17.83 , 28.96 , 49.51 , $46.89 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$, respectively (Figures 9 and 10). As was also observed for color elimination in this series, reaction time decreases exponentially with increasing concentration and the degradation rates for tests 6 and 7 are very similar (49.51 and $46.89 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$).

The exponential decrease in reaction time that follows the increase in catalyst concentration can be attributed to the increased number of particles inside the reactor, a condition which causes the absorption of UV light to happen very close to the lamp surface and generates a shadow effect on the particles further away from the light source. This creates zones of different catalytic activity within the reactor.

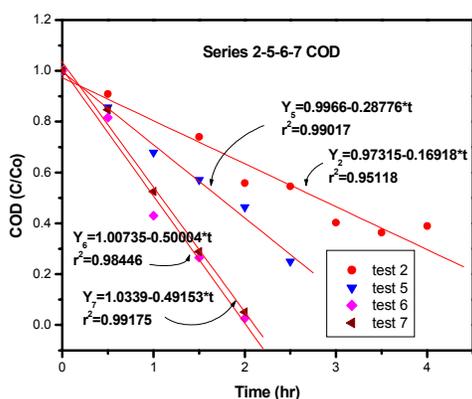


Figure 9. Decrease of organic matter (COD) in the solution as a function of time, second series.

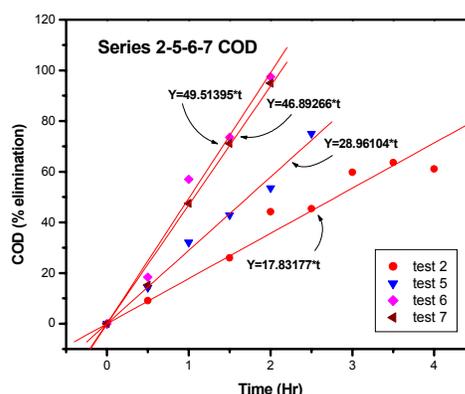


Figure 10. Percentage of elimination of COD, second series.

3.1.3 The effect of simultaneously increasing catalyst and dye concentrations

Figures 11 and 12 show the degree of dye elimination as a function of reaction time and the kinetic constants of the third series, which contains tests 1, 5, 8 and 9. The results show that complete color elimination was reached after 2, 2.5, 3 and 3.5 hours in tests 1, 5, 8 and 9, respectively. These results indicate that a simultaneous increase in dye and catalyst concentration linearly increases reaction time.

Tests 1 and 5, which were analyzed previously, are pseudo-first-order reactions. Tests 8 and 9 present pseudo-half-order reactions with kinetic constants of 4.65 and $4.1 \text{ (mg L}^{-1}\text{)}^{0.5} \text{ hr}^{-1}$, respectively. A decrease of the reaction order can be attributed to the decrease in light intensity (Chacón et al, 2006; Behnajaday et al, 2006; Konstantinou et al, 2004) that comes from manipulating a variable light source or from the natural variation in radiation intensity that comes from using sunlight. Nevertheless, the change of the reaction order in this project is attributed to the combined effect of the energy blocking between the catalyst particles closer

to the light source (an effect first observed in the second series of tests) and the increase in the number of molecules that must be degraded with the same light intensity (effect observed in the first series of tests).

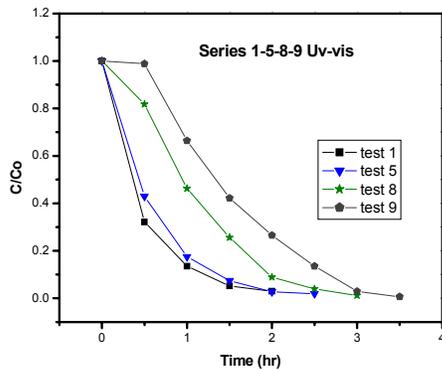


Figure 11. Decrease of dye concentration as a function of time, third series.

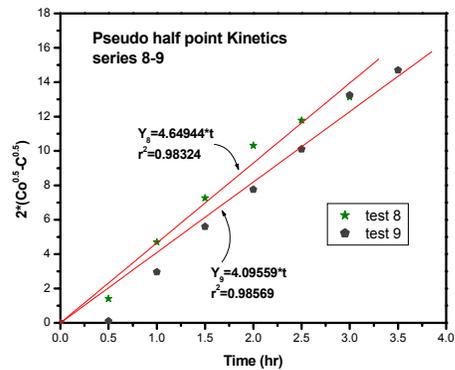


Figure 12. Rate of disappearance of the chromophore groups, third series.

As in the previous series of tests, the COD (Figures 13 and 14) presents a zeroth-order reaction order, with rate constants values of 43.13, 28.96, 26.14, and 17.96 $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$ and maximum organic matter oxidation levels of 97%, 75%, 96% and 89% for tests 1, 5, 8 and 9, respectively.

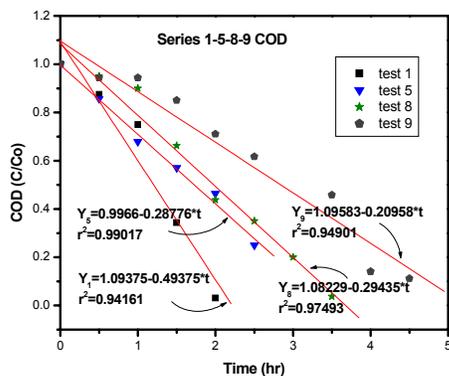


Figure 13. Decrease of the organic matter (COD) in the solution as a function of time, third series.

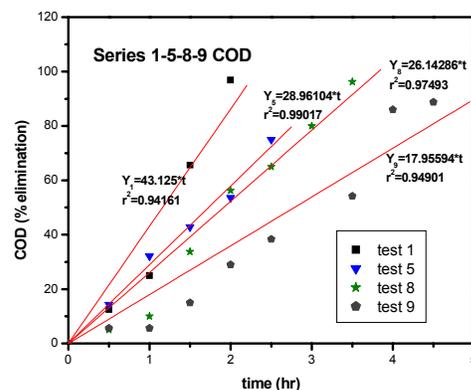


Figure 14. Percentage elimination of COD, third series.

4. Conclusions

- The chromophore groups of acid blue number 9 can be completely eliminated by the advanced oxidation process using suspensions of TiO₂ and artificial UV light.
- The initial concentrations of acid blue 9 and catalyst affect the order and kinetics of the reaction.
- The reaction rates for dye elimination in this process are mostly of first order.
- For high concentrations of dye (60, 80 mg L⁻¹) and catalyst (450, 600 mg L⁻¹), the reaction was of half order.
- The maximum level reached for the degradation of the dye molecule was 97%.
- The degradation kinetics of the dye were of zeroth-order.
- An increase in dye concentration increases the reaction time exponentially.
- An increase in the catalyst concentration decreases the reaction time exponentially.

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