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Photodegradation of azo dye Acid Red 18 in a quartz labyrinth flow reactor with immobilized TiO_2 bed

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Abstract

The photocatalytic oxidation of azo dye Acid Red 18 in water in the quartz labyrinth flow reactor with immobilized catalyst bed was investigated. A commercially available titanium dioxide (Aeroxide® P25, Degussa, Germany) was used as a photocatalyst. The influence of various factors, including reaction mixture flow rate, initial dye concentration and time of the irradiation on the photodegradation of model compound were examined. The reaction rate was affected by the circulation flow rate, particularly when the flow rate was low (i.e. 4.3 dm^3/h). The decomposition rate of Acid Red 18 depended on the initial dye concentration. The rate constants calculated for dye concentrations of 10 and 30 mg/dm^3 amounted to 0.228 and 0.176 h^{-1}, respectively. Not only decolorization but also mineralization was effective in the proposed system. After a total fading of the dye solution, ca. 98% of TOC disappeared when the 10 mg/dm^3 solution was applied and ca. 99% when 30 mg/dm^3 was used. An important advantage of the photoreactor is that no separation of the catalyst is necessary and as a result the size of installation could be minimized and running costs decreased.

Keywords: Titanium dioxide; Azo dye; Photocatalysis; Photocatalyst immobilization; Labyrinth flow reactor

1. Introduction

Color in the effluents from textile or dye industry is a serious environmental problem. Therefore, intensive investigations on novel treatment techniques of these wastewaters have been conducted during the last decades. In general, the methods for the treatment of wastewaters containing dyes can be divided into two main groups [1]: (I) chemical or physical methods of dye removal, which refer to the process called decoloration and (II) dye removal by means of biodegradation. Physical methods of decoloration include different precipitation methods (coagulation, flocculation, sedimentation), adsorption (on activated carbon, biological sludge, silica gel), filtration, reverse osmosis, etc. Among chemical methods of dye removal there are processes such as reduction, oxidation, compleximetric methods, ion exchange and neutralization. Biological treatment can be conducted in the presence or absence of oxygen. Thus it can be distinguished into the aerobic process (revival of biological sludge in aeration basins) and the anaerobic one (decay and rot in stabilising lagoons) [1].

Recently, advanced oxidation processes (AOP) have been widely investigated of which heterogenous photocatalysis has become the most popular. Most studies related to photocatalytic degradation of organic pollutants have been carried out using suspensions of powdered TiO_2 in the treated solution [2–8]. However, from a practical point of view, separation of photocatalyst from the reaction mixture might cause some difficulties. Another disadvantage is an increase in the overall capital and running costs of the plant. Therefore, attempts to immobilize the catalyst on different supports, such as glass [9–15], quartz [15,16], pumice stone [17], stainless steel [12,15,18,19], titanium metal [20], zeolites [21], etc. have been made.

The literature data show that the efficiency of the reactors with immobilized photocatalyst bed could be similar or even

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higher than the efficiency of the reactors with suspended catalyst [11,22–24]. Lin et al. [24] investigated the effectiveness of photodegradation of 1,2-dichlorobenzene in different configurations of photocatalytic reactors, i.e. with catalyst (TiO_2) in suspension or immobilized on a support (polyethylene or quartz). They found that the activity of the immobilized titania is superior to that used as a slurry suspension. The authors concluded that when particles are suspended in water, besides casting shadows, particle aggregation occurs, and inefficient use of light by titania surface results. Moreover, particles of titania immobilized on polyethylene or quartz are more effectively dispersed than powdered titania in suspension. Dijkstra et al. [22,23] also investigated different reactor designs: packed bed reactor (PBR), tubular reactor (TR) and suspended system (SR). Formic acid was applied as a model compound. The authors found that the values of quantum yield for the three systems were comparable. They concluded that it was a remarkable result since the suspended system, in general, has been known to be more efficient than the immobilized one. Similarly, Parra et al. [11] found that the effectiveness of the suspended and supported TiO_2 systems for photocatalytic degradation of atrazine is very similar, indicating that the activity of the TiO_2 is not reduced when it is immobilized on an inert surface like glass. The results presented by Gumy et al. [25] also confirmed that conclusion. The authors showed that the kinetics of disappearance with suspended or fixed TiO_2 are almost similar and linearly correlated with the amount of TiO_2. Moreover, for the same TiO_2 amount, the catalyst fixation does not affect the rate of photodegradation but only the adsorption capacity of TiO_2. Similarly, Mansilla et al. [9] stated that the use of an immobilized catalyst does not significantly reduce the TiO_2 photocatalytic activity, opening the possibility of scaling-up for potential applications.

The aim of the present work was to investigate the possibility of application of the quartz labyrinth flow reactor with immobilized catalyst bed in the removal of azo dye from water. The influence of various factors, including reaction mixture flow rate, initial dye concentration and time of the UV irradiation on the photodegradation of model compound were examined.

2. Materials and methods

Acid Red 18 ($C_{20}H_{11}N_2Na_3O_{10}S_3$) was applied as model azo dye. Chemical structure of the model compound is presented in Fig. 1. The initial concentration of the dye was equal to 10 or 30 mg/dm^3.

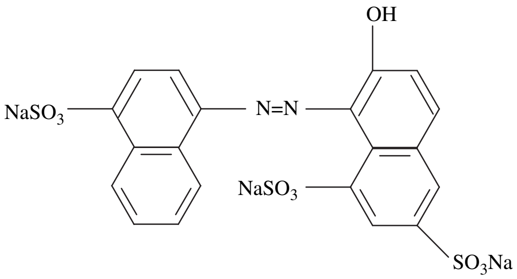

Fig. 1. Chemical structure of Acid Red 18.

A commercially available titanium dioxide (Aeroxide® P25, Degussa, Germany) was used as a photocatalyst. The specific surface area (BET) of the catalyst is ca. 50 m^2/g and the average primary particle size 21 nm (according to the manufacturer).

A laboratory scale apparatus, shown in Fig. 2, was employed in the experiments. The main component of the system was the flow reactor with immobilized catalyst bed. The reactor was built of seven quartz tubes having the following dimensions: length, 300 mm; inner diameter, 16 mm; and outer diameter, 20 mm. The inner surface of the tubes was partly covered with TiO_2 particles, i.e. the catalyst was fixed only to the bottom part of the horizontally positioned tube, as shown in Fig. 3. The total area (A_t) covered with catalyst, determined for one tube, amounted to 6030 mm^2. This value was calculated according to the following equation: $A_t = (l_w(\pi d_{in})/2)$, where l_w is working (i.e. coated with catalyst) length of the tube ($l_w = 240$ mm) and d_{in} is its inner diameter ($d_{in} = 16$ mm).

The photocatalyst particles were fixed to the quartz tubes according to the following procedure. The suspension of TiO_2 in ethanol (5 wt% + 95 wt%, respectively) was sonicated for 1 h with a frequency of 40 kHz. During sonication, the suspension was thermostated at the temperature of 30 °C. The thoroughly cleaned and dried quartz tubes were immersed in such prepared suspension for 30 s and then dried for 10 min at 105 °C. The procedure was repeated twice. After that the tubes were dried at 105 °C for 20 h and then calcinated at 500 °C for 1 h. Before coating with TiO_2 the two ends of the tube were covered with aluminum foil so that the length of the coated area was equal to 240 mm. The tubes were

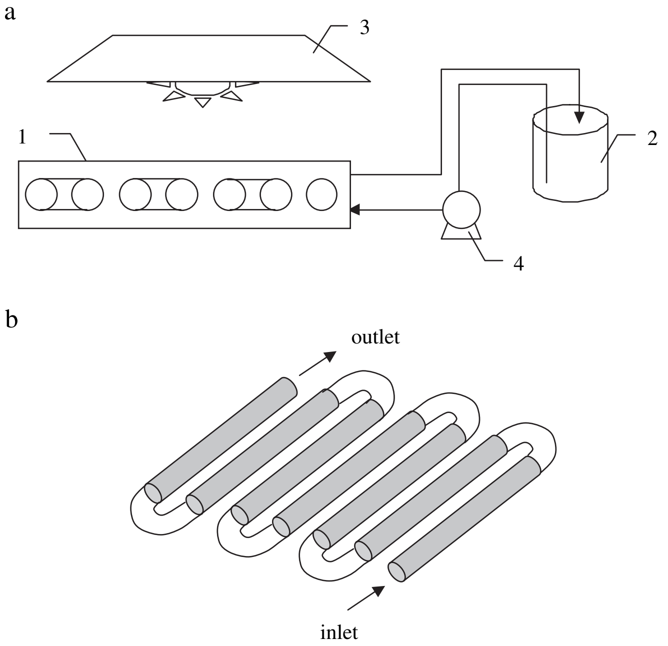

Fig. 2. Schematic diagram of the laboratory installation: (a) side view; 1, quartz labyrinth flow reactor; 2, tank; 3, UV light source; 4, peristaltic pump; and (b) top view of quartz tubes in the reactor.

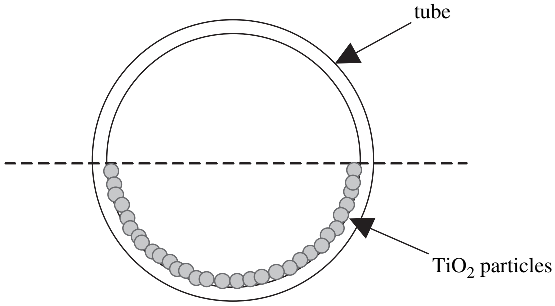

Fig. 3. Schematic diagram of the photocatalyst fixation to the quartz tube.

then placed in a plastic box and connected one another in a manner shown in Fig. 2. Before the photocatalytic experiments were begun the reactor was washed with distilled water in order to remove unfixed catalyst particles. The amount of TiO_2 coated per m^2 of the covered area was ca. 1.45 g/m^2.

The solution circulated in the reactor with the flow rates of 4.3, 14.6 and 26.3 dm^3/h. The photodegradation experiments were conducted for 60 h. The reaction solution was illuminated with a mercury lamp Philips Cleo, emitting UV-A light ($\lambda_{max} = 355$ nm). The UV intensity at the irradiation plate was 141.92 W/m^2. The illumination intensities were measured with an LB 901 radiometer equipped with the PD204AB (Macam Photometrics Ltd) and CM3 (Kipp & Zonen) external sensors. In order to determine the dye degradation rate, samples of the reaction solution were taken every hour during the first 5 h, and then every 5 h. The concentration of the dye was determined by absorbance measurement at 507 nm (Jasco V-530 spectrometer, Japan) in a 1 cm or 5 cm quartz cell, dependent on dye concentration. Total organic carbon (TOC) concentration was measured using the "multi N/C 2000" analyzer (Analytik Jena, Germany). Moreover, total dissolved solids (TDS) content, conductivity (Ultrameter™ 6P, MYRON L COMPANY USA) and pH of the solution were monitored.

3. Results and discussion

No decolorization occurred when an aqueous solution of Acid Red 18 flowed through the labyrinth reactor in the dark and the disappearance of the dye molecules was negligible by direct photolysis. A complete decolorization of Acid Red 18 could only be observed with the simultaneous presence of TiO_2 and UV light. Therefore, it can be stated that in the presence of TiO_2 a true heterogenous catalytic regime takes place.

During the first step of the investigation, the Acid Red 18 solution in concentration of 10 mg/dm^3 was applied. Decomposition was conducted for 60 h. The obtained results are shown in Figs. 4–8.

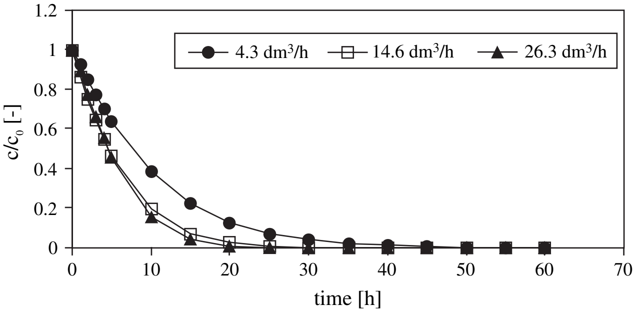

Fig. 4. Changes of Acid Red 18 concentration in time for different solution flow rates; initial dye concentration: 10 mg/dm^3.

Fig. 4 presents changes of dye concentration in time at different solution flow rates. For the lowest circulation rate applied (i.e. 4.3 dm^3/h), the dye concentration at the end of the process was very low (i.e. 0.004 mg/dm^3); however, a complete decolorization of the solution was not obtained. For the flow rates of 14.6 and 26.3 dm^3/h, the effectiveness of dye decomposition was higher—the solution faded completely after 40 and 35 h, respectively. It can be observed (Fig. 4) that the decolorization rate was significantly lower at 4.3 dm^3/h than in the case of the other two flow rates. The course of changes of dye concentration at 14.6 and 26.3 dm^3/h was to each other. During the initial 10 h of the process performance, the model dye was decomposed for ca. 61%, 80% and 85% for solution flow rates of 4.3, 14.6 and 26.3 dm^3/h, respectively.

The fading of the solution was associated with cleavage of azo linkage in dye molecule. Azo dyes are characterized by nitrogen to nitrogen double bonds (−N=N−) that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene or naphthalene rings). The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band [21]. The cleavage of −N=N− bonds leads to the decolorization of dyes.

The UV–vis spectra recorded during photodegradation of model dye are presented in Fig. 5. The spectrum of dye before photodegradation ($t = 0$ h) exhibits four main peaks at the wavelengths of 507, 330, 245 and 215 nm. The absorption in the visible region can be attributed to chromophore containing azo linkage, whereas the bands observed in the UV region can

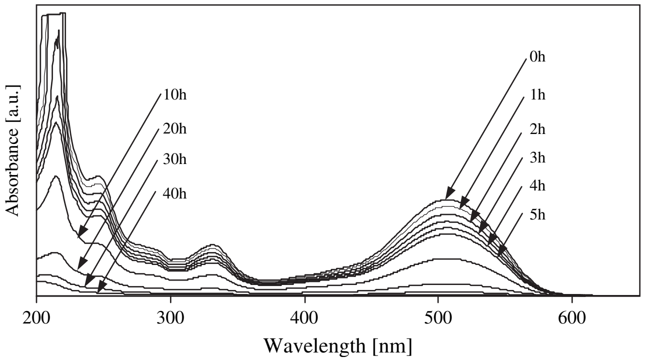

Fig. 5. Changes in the UV–vis spectra of Acid Red 18 during photodegradation; initial dye concentration: 10 mg/dm^3; solution flow rate: 4.3 dm^3/h.

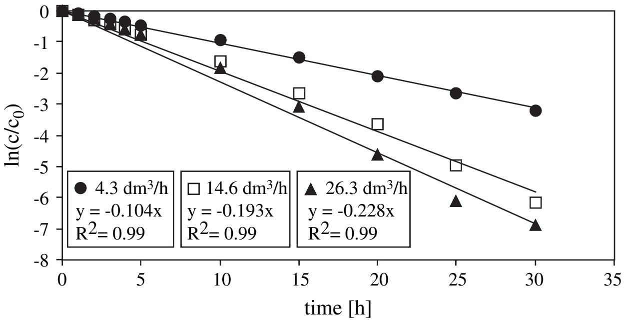

Fig. 6. Rate constants of Acid Red 18 decomposition for different solution flow rates; initial dye concentration: 10 mg/dm^3; time of the process performance: 30 h.

be assigned to aromatic (naphthalene) rings substituted with SO_3^- and OH groups, which are present in Acid Red 18 molecule [26,27] (Fig. 1). It can be observed that during irradiation not only a rapid decolorization of the dye, but also significant degradation of the aromatic structure proceeds.

In order to compare the course of the photodecomposition of Acid Red 18 at different flow rates, the apparent rate constants were calculated. It is known from the literature [28] that the photocatalytic oxidation of organic pollutants follows the pseudo-first order kinetics. This kind of the reaction can be represented as follows:

$$-dc/dt = kc, \quad (1)$$

and after integration:

$$c = c_0 \exp(-kt), \quad (2)$$

where c_0 is the initial concentration of dye, c is the concentration of dye after time t of photocatalytic decomposition and k is a rate constant related to the reaction properties of the solute, which depends on the reaction conditions, such as reaction temperature and the pH of the solution. [28]. The rate constants k were obtained from the linear transforms $\ln(c/c_0) = f(t)$, as shown in Fig. 6. Due to the fact that at the highest flow rate applied the solution was decolorized after 30 h of irradiation, the rate constants were calculated for a 30 h period to make it easier to compare the results between different circulation rates.

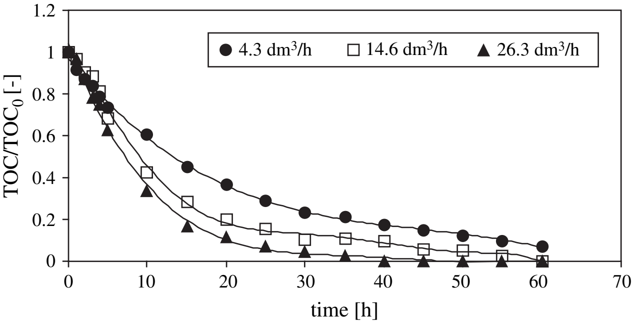

Fig. 7. Changes of total organic carbon (TOC) concentration in time for different solution flow rates; initial dye concentration: 10 mg/dm^3; initial TOC concentration: 4.0 mgC/dm^3.

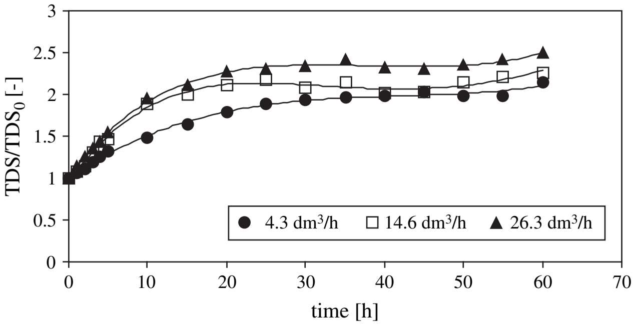

Fig. 8. Changes of total dissolved solids (TDS) concentration in time for different solution flow rates; initial dye concentration: 10 mg/dm^3; initial TDS value: 9.4 ppm.

The obtained results might suggest that the external mass transfer resistance exists in the discussed system, as the reaction rate (Fig. 6) depends on the circulation flow rate, particularly when the flow rate is low (i.e. 4.3 dm^3/h). The external mass transfer resistance can be reduced to a minimum by increasing mixing of fluid through stirring or increasing the circulating flow rate of the reaction medium [29]. It was found (Fig. 6) that the constant k calculated for the flow rate of 4.3 dm^3/h was about twice lower than that for the other two flow rates, i.e. 14.6 and 26.3 dm^3/h (0.104 h^{-1} vs. 0.194 h^{-1} and 0.228 h^{-1}, respectively). During photocatalytic oxidation, organic substrates follow the steps of diffusion, adsorption, and reaction [30]. For the highest flow rates applied, it can be supposed that mass transport towards catalyst surface was beneficial to mass diffusion, therefore the rate constant k was less affected by the flow rate. On the other hand, when the flow rate of 4.3 dm^3/h was used, mass diffusion was a limiting factor of the examined process.

It should be emphasized that decolorization of the solution does not provide complete data on the azo dye degradation. Therefore, other parameters such as TOC, TDS, conductivity and pH should be monitored. Fig. 7 presents the effectiveness of mineralization of Acid Red 18 determined on the basis of changes of TOC concentration. The most significant TOC degradation took place within the initial 10 h of irradiation and amounted to ca. 66%, 57% and 40% at the solution flow rates of 26.3, 14.6 and 4.3 dm^3/h, respectively. It can also be observed that, similar to the case of decolorization, the lowest efficiency of dye mineralization was at the lowest flow rate applied. A complete TOC removal was found after 60 h of irradiation at the flow rate of 14.6 dm^3/h and after 40 h at 26.3 dm^3/h. In case of 4.3 dm^3/h, the TOC concentration determined at the end of the process amounted to 0.3 mg/dm^3. From the obtained results it was also found that after a total decolorization of the Acid Red 18 solution ca. 90% of TOC has disappeared when the flow rate of 14.6 dm^3/h was used and ca. 98% when the process was conducted at 26.3 dm^3/h. This means that not only decolorization but also mineralization is effective in the proposed system.

Another parameter indicating the rate of the dye photodecomposition could be the TDS content. The TDS parameter includes all the dissolved species present in water, i.e. inorganic ions (e.g. bicarbonates, sulfates, nitrates, ammonia, etc.), CO_2 and all manner of organic compounds. Fig. 8 presents changes of TDS concentration in time for photocatalytic decomposition of Acid Red 18.

In case of the dye concentration of 10 mg/dm^3 that is now being discussed, the initial concentration of TDS in the solution amounted to ca. 9.4 ppm and after 60 h of the process performance it reached the value of ca. 19, 22 and 24 ppm for the flow rates of 4.3, 14.6 and 26.3 dm^3/h, respectively. The initial conductivity (data not shown) amounted to ca. 15 μS/cm, whereas after 60 h of photodecomposition the value of this parameter was about 30, 34 and 37 μS/cm for the flow rates of 4.3, 14.6 and 26.3 dm^3/h, respectively. The most significant increase of both TDS and conductivity took place within the initial 10 h of irradiation. This is consistent with the data of TOC degradation (Fig. 7) and could suggest that at the beginning of irradiation of Acid Red 18 solution in the presence of TiO_2 a significant number of lower molecular compounds are formed. It can also be observed (Fig. 8) that the least increase of TDS content took place in case of the lowest solution flow rate applied. This might result from the lowest decomposition rate of the dye under these conditions. On the other hand, an increase of the recirculation rate resulted in an increase of the TDS value; therefore, it can be supposed that the number of the intermediate products formed increased with increasing flow rate. During the initial hours of the irradiation, the course of changes of TDS concentration was similar at 14.6 and 26.3 dm^3/h, suggesting that during this time the effect of the flow rate was not very significant. However, the degradation of the intermediate products formed during the photodecomposition of the dye was probably much more affected by the hydrodynamic conditions than in case of degradation of the dye itself. Thus, at the highest flow rate, as the mass transfer was more effective, more efficient decomposition of organics leading to the formation of final products such as CO_2, H_2O and inorganic ions (HCO_3^-, NH_4^+, NO_3^- and SO_4^{2-}) took place. As a result, higher TDS and conductivity values (Fig. 8) as well as complete TOC removal (Fig. 7) were obtained. When the flow rate of 14.6 dm^3/h was applied, a complete mineralization was obtained at the end of the irradiation (Fig. 7), thus the TDS content was lower than at 26.3 dm^3/h.

Another parameter monitored was pH of the solution. Fig. 9 presents changes of pH during photodegradation of Acid Red 18 ($c_0 = 10$ mg/dm^3) as a function of the irradiation time. It can be observed that the pH of the solution decreased rapidly at the initial stages of the experiment, dropping from 5.9 at $t = 0$ to ca. 4.6, 4.4 and 4.3 at $t = 10$ h for the flow rates of 4.3, 14.6 and 26.3 dm^3/h, respectively. Then, the pH remained constant, reaching at the end of the experiment a value of 4.6 at 4.3 dm^3/h and 4.3 at both 14.6 and 26.3 dm^3/h. The initial drop of the pH indicated the formation of acid products, mainly that of CO_2 from oxidation of the carbon part of the dye, H_2SO_4 originating from the three sulfonate groups (Fig. 1) and, to a lesser extent, from the transient formation of aliphatic acids [27].

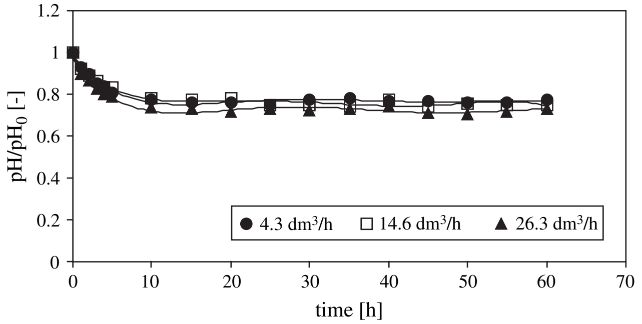

Fig. 9. Changes of pH in time for different solution flow rates; initial dye concentration: 10 mg/dm^3; initial pH value: 5.9.

In the second step of the investigation, the effect of the initial Acid Red 18 concentration on the decomposition of the dye in the labyrinth flow reactor was determined. A solution recirculation rate of 26.3 dm^3/h was selected on the basis of the previously described experiments as the most beneficial one. The initial dye concentration amounted to 10 and 30 mg/dm^3. The obtained results are presented in Figs. 10 and 11.

During the initial 5 h of irradiation, concentration of Acid Red 18 decreased for ca. 55% and 40%, for $c_0 = 10$ and 30 mg/dm^3, respectively (Fig. 10). The solution faded completely after 45 h of irradiation when the Acid Red 18 concentration of 30 mg/dm^3 was used and after 35 h when 10 mg/dm^3 was applied (Fig. 10). The rate constants calculated for the initial 30 h of the process performance amounted to 0.228 and 0.176 h^{-1} for dye concentration of 10 and 30 mg/dm^3, respectively. The obtained results indicate that the decomposition rate of Acid Red 18 depends on the initial dye concentration. This is consistent with the literature data [31–33]. An increase of the initial dye concentration results in an increase of the amount of dye adsorbed on the catalyst surface, affecting the catalytic activity of the photocatalyst. Moreover, at higher dye concentrations the path length of photon entering into the dye solution is decreased. In such a case, a significant amount of UV light might be absorbed by the dye molecules rather than by the catalyst and, as a result, the catalytic efficiency of the system could be reduced.

Fig. 11 presents changes of TOC concentration in time. It can be observed that the shape of both curves is different indicating much faster TOC disappearance in case of lower dye concentration applied. In case of the initial dye concentration of 10 mg/dm^3, TOC decreased linearly during the initial 10 h of irradiation, reaching the value of 1.3 mg/dm^3. During decomposition of Acid Red 18 in the solution containing 30 mg/dm^3, a linear decrease of TOC concentration up to 30 h was observed and during this time TOC content was reduced to 1.5 mg/dm^3. After a total decolorization of the Acid Red 18 solution, ca. 98% of TOC has disappeared when the 10 mg/dm^3 solution was applied and ca. 99% when 30 mg/dm^3 was used. From the obtained results it can be concluded that both decolorization and detoxification are very effective in the system investigated.

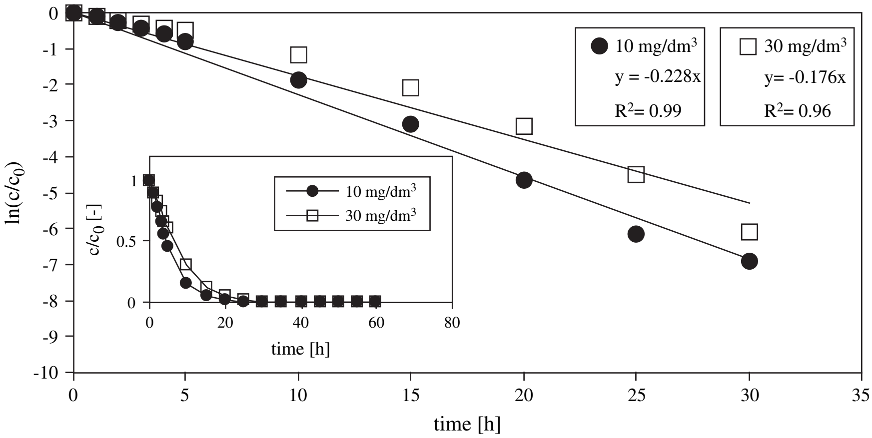

Fig. 10. Changes of Acid Red 18 concentration in time for different initial dye concentrations; solution flow rate: 26.3 dm^3/h.

The TDS content at the end of the process (data not shown) amounted to 71.7 ppm in case of 30 mg/dm^3 and 23.6 ppm in case of Acid Red 18 solution in the concentration of 10 mg/dm^3. It can be noticed that when the dye concentration increased three times, the amount of inorganic species formed (TOC at the end of the process was equal to 0 mg/dm^3) was also about three times higher.

The pH of the reaction mixture after 60 h of irradiation of the 30 mg/dm^3 dye solution amounted to 3.9 and was lower in comparison with the 10 mg/dm^3 Acid Red 18 solution (pH 4.3). This could be associated with the amount of acid products originating from the mineralization of the dye (CO_2) as well as from sulfonate groups (Fig. 1), the concentration of which was higher at higher dye concentration.

4. Conclusions

It was found that azo dye Acid Red 18 could be successfully decomposed in the quartz labyrinth flow reactor with immobilized photocatalyst bed.

The reaction rate was affected by the circulation flow rate, particularly when the flow rate was low (i.e. 4.3 dm^3/h). The rate constant k of the photodecomposition of Acid Red 18 ($c_0 = 10$ mg/dm^3) calculated for the 4.3 dm^3/h was about twice lower than for the other two flow rates, i.e. 14.6 and 26.3 dm^3/h (0.104 h^{-1} vs. 0.194 h^{-1} and 0.228 h^{-1}, respectively).

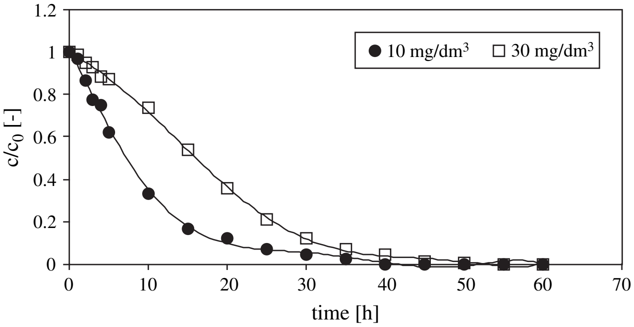

Fig. 11. Changes of TOC concentration in time for different initial dye concentrations; solution flow rate: 26.3 dm^3/h.

The obtained results indicated that the decomposition rate of Acid Red 18 depended on the initial dye concentration. The rate constants calculated for initial 30 h of the process performance amounted to 0.228 and 0.176 h^{-1} for dye concentrations of 10 and 30 mg/dm^3, respectively.

It was found that not only decolorization but also mineralization was effective in the proposed system. After a total decolorization of the Acid Red 18 solution, ca. 98% of TOC has disappeared when the 10 mg/dm^3 solution was applied and ca. 99% when 30 mg/dm^3 was used.

The pH of the solution decreased rapidly at the initial stages of the experiment, and then remained constant. The initial drop of the pH indicated the formation of acid products, originating from the 3 sulfonate groups, and the transient formation of aliphatic acids.

The presented quartz labyrinth flow reactor with immobilized photocatalyst bed could be successfully applied for the purification of wastewaters containing azo dyes. An important advantage of the photoreactor is that no separation of the catalyst is necessary and as a result the size of installation could be minimized and running costs decreased.

Acknowledgements

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