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Kinetic of degradation of two azo dyes from aqueous solutions by zero iron powder: determination of the optimal conditions

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ABSTRACT

The textile industry induces one of the main environmental pollution, mainly due to the dyes containing in its effluents. There is therefore a need for their treatment prior to discharge to the environment. The removal efficiency of Acid Red 18 and Acid Red 14 dyes by zero-valent iron were investigated in this study. The effect of some parameters such as pH (3–11), contact time (15–120 min), initial dye concentration (25–100 mg l^{-1}) and initial concentration of iron powder (0.5–2 g l^{-1}) were examined. The results showed that dye removal efficiency increased with increasing contact time and initial concentration of iron powder on the one hand, and decreased for increasing pH and initial dye concentration on the other hand. Experimental data were rather accurately fitted onto both first-order and second-order kinetic models, even if the first-order kinetic model led to higher correlation coefficients. Comparison of the kinetic rate constants showed a low impact of the initial dye concentration and that an acidic pH of 3 was optimal for the removal of Acid Red 14 and Acid Red 18.

Keywords: Iron powder; Batch system; Kinetics; pH; Dyes; Optimal condition

1. Introduction

All over the world, textile industries are a major importance. The main problem of their effluents is the color originating from the use of dyes and pigments [1,2]. Furthermore, colorful effluents are also produced in other industries such as pharmacology and tanning [3]. Many dyes and pigments are being used in industry and the most common are azo dyes, which are characterized by a –N=N– bond. These dyes are widely used in textile dyeing and pigmentation due to their easy application and their lower toxicity than other groups [4–6]. Dyes and pigments have one or several benzene rings and their discharge to the environment can cause many problems due to their toxicity and persistence [7]. There is therefore a need for their treatment, by the use of suitable methods prior to discharge to the environment. Several methods such as biological [8], membrane [9],

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adsorption [10], as well as advanced oxidation processes [11,12], including Fenton-like process have been previously implemented for the treatment of these effluents[13]. Nowadays, the use of zero-valent metals like iron and magnesium is widely investigated. Among the considered metals, zero-valent iron is one of the most often used due to its abundance, cost effectiveness, lack of toxicity, easy removal from reaction solutions and easy reduction [14,15]. At the present time, the use of this metal to remove organic and inorganic pollutants is gaining increasing interest. In recent years, zero-valent iron has been used for the removal of environmental pollutants such as nitrobenzene [16], trichloroethylene [17–19], nitrates [20], EDTA [21], dyes [13,22–26] and phenol [27]. In aqueous solutions, zero-valent iron powder is oxidized (and then settles as precipitate), leading to the production of free electrons, which have the reducing role and hence can reduce organic compounds according to the following reactions [15,28]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (2)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (3)$$

$$2Fe^0 \rightarrow 2Fe^{3+} + 6e^- \quad (4)$$

$$Fe^{2+} + 1/4O_2 + 2.5H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \quad (5)$$

Therefore, during the oxidation of zero-valent iron and also divalent iron to trivalent iron, three electrons are produced. These free electrons can react with atoms of organic compounds such as hydrogen and chlorine, leading to the transformation or the degradation of those organic compounds. Furthermore, as mentioned above trivalent iron produces gelatinous flocks which settle out the pollutants present in the solutions to be treated. Based on the advantages mentioned above regarding iron powder, the main objective of this work was to test zero-valent iron for the degradation of Acid Red 14 and Acid Red 18 and to confirm the relevance of this process to treat azo dyes.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study, including the azo dyes, were purchased from Merck Company (Germany). The maximum sorptive wavelengths were 506 and 515 for AR 14 and AR 18 respectively, according to Merck Company. To adjust the pH, 1 N H_2SO_4 or NaOH was used (model Sartorius Professional Meter PP-50). Iron powder has an approximate particle size of 150 µm with a specific surface area of 2.3 $m^2\ g^{-1}$ (Determined by the BET method). Fig. 1 shows the chemical structure of Acid Red 14 and Acid Red 18.

2.2. Batch experiments

Several parameters including pH (3, 5, 7, 9, 11), contact time (15, 30, 45, 60, 75, 90, 105, 120 min), iron powder concentration (0.5, 1, 1.5 and 2 g l^{-1}) and initial dye concentration (25, 50, 75 and 100 mg l^{-1}) were investigated. Stock solutions of 1 g l^{-1} of dye were considered to prepare the working dye solutions. During experiments, only the investigated parameter was modified, with the others kept constants. It should be noted that no significant change of the pH value during the course of experiments was observed. For instance, for the investigation of the pH effect, 50 mg l^{-1} dye solution and 1.5 g l^{-1} zero-valent iron were added to the system which was run at various pH for 120 min contact time. Residual dye concentrations were determined by UV/VIS spectrophotometer (Shimadzo 1700, Japan). Before sample analysis, centrifugation (3000 rpm for 15 min) and filtration were carried out to avoid interference of precipitated $Fe(OH)_3$ (Sigma-301, Germany).

3. Result and discussion

3.1. Model application

Two common kinetic models, first-order and second-order kinetics, were considered to investigate kinetic reaction of Acid Red 14 and Acid Red 18 removal by zero-valent iron. The linear form of the first-order model is expressed as follows:

$$\ln(C_0/C_e) = k_1 t \quad (6)$$

And the linear form of the second order kinetic model is as follows:

$$1/C_e - 1/C_0 = k_2 t \quad (7)$$

where C_0 and C_e (mg l^{-1}) is the pollutant concentrations at initial time t_0 and a given time t; k_1 (l min^{-1});

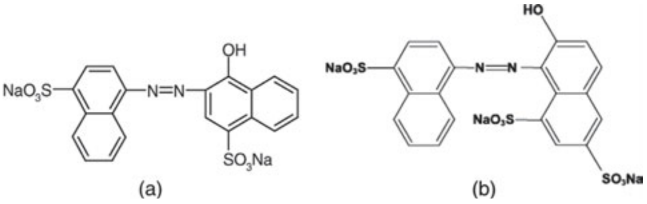

Fig. 1. Chemical structure of Acid Red 18 (a) and Acid Red 14 (b).

k_2 (l mg min^{-1}) is the rate constants for first-order and second-order kinetics, respectively. By plotting the left side of the above equations versus time, one can obtain the value of k from the slope of the curve. Fig. 2 shows the experimental and calculated data for both azo dyes. Linear regression analyses showed that correlation coefficients (r^2) of first-order model were 0.98 and 0.97 and those obtained by the second-order model were 0.87 and 0.95 for Acid Red 14 and Acid Red 18, respectively. First-order model appeared therefore the most appropriate to describe kinetic degradation of Acid Red 14 and Acid Red 18 by zero-valent iron, in agreement with previous reports dealing with the removal of nitrate (Zhen et al. 2010), antibiotic metronidazole [29], 2, 4, 6-trinitrotoluene [30], nitrobenzene [31], Acid Black 24, Reactive Blue 4 and Reactive Black 5 dyes [32–34] by zero-valent iron. The values of first-order rate constants for Acid Red 14 and Acid Red 18 were 0.02 and 0.0077 (l min^{-1}), respectively. The high value of the constant rate for Acid Red 14 illustrated the efficiency of Acid Red 14 degradation by zero-valent iron. Indeed, Dong et al. found that removal of nitrobenzene by zero valent iron followed first-order kinetic model with constant rates of 0.0073 and 0.001 (l min^{-1}) at initial time and after 90 min time-contact, respectively [31]. First-order rate constant was found to be 0.00017 (l min^{-1}) for the removal of Reactive Blue 4 by zero-valent iron[34].

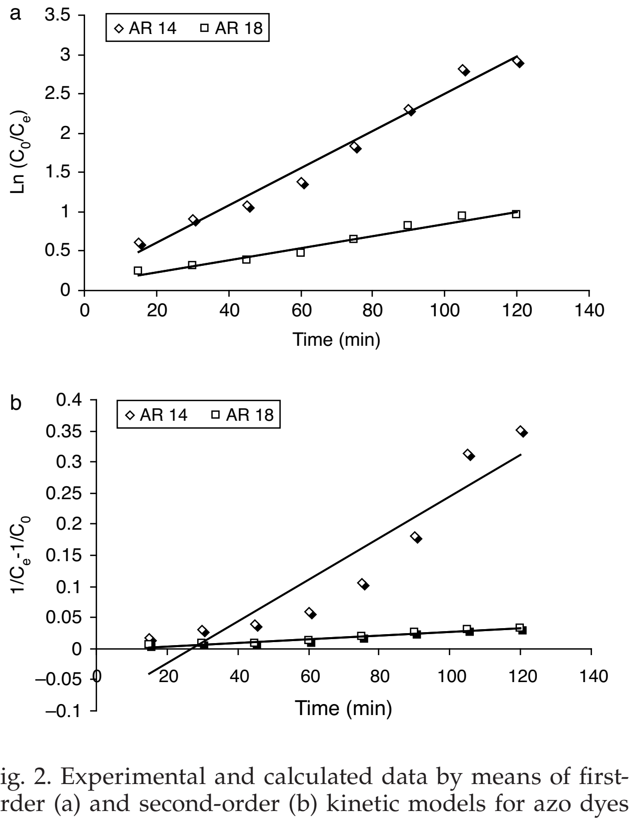

Fig. 2. Experimental and calculated data by means of first-order (a) and second-order (b) kinetic models for azo dyes Acid Red 14 and Acid Red 18.

3.2. Effect of the contact time on dye removal

Fig. 3 shows that increasing the contact time from 15 to 120 min enhanced the removal efficiency until reaching equilibrium after 120 min experiment. In addition, removal yields were higher for Acid Red 14 if compared to Acid Red 18, leading to 94% and 62% removal for Acid Red 14 and Acid Red 18 after 120 min time-contact.

3.3. Effect of pH on dye removal

Fig. 4a shows the effect of pH on removal efficiency and the fitting results by means of first-order kinetic model are displayed in Fig. 4b and c. Dye removal appeared efficient in acidic conditions (pH = 3 – Fig. 4a), leading to about 94% and 90% removal of Acid Red 14 and Acid Red 18 at pH = 3 for a contact time of 120 min; while in alkaline conditions (pH = 11) only 9% and 5% of Acid Red 14 and Acid Red 18 were removed. In addition, high rates of removal were initially recorded, since about 89% and 85% of Acid Red 14 and Acid Red 18 were respectively removed in the first 15 min of experiment. As the initial pH became alkaline (11), the removal efficiency decreased to 14% for the two dyes. The pH had therefore a considerable effect on the efficiency of zero-valent iron powder system. At acidic pH, iron surface kept clean and hence iron reduction continued. In addition, at acidic pH, no precipitation of $Fe(OH)_3$ occurred, allowing an improvement of the production of free electrons and avoiding the formation of precipitate on the surface of iron powder. First-order kinetic rate constants for the two dyes are given in Table 1. Close constant rate values (k_1) were recorded in a pH range from 3 to 7, with an average value of 0.025; while decreasing k_1 values were recorded from 7 to 11. These results demonstrated that the reduction of the two Azo dyes in alkaline conditions required higher amounts of iron powder.

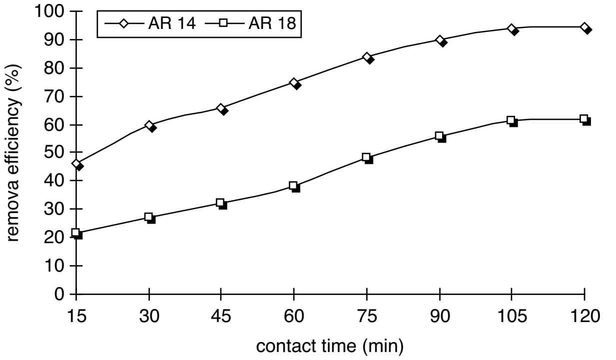

Fig. 3. Effect of the contact time on dye removal efficiency (pH 7, initial dye concentration 50 mg l^{-1}, zero-valent iron 1.5 g l^{-1}).

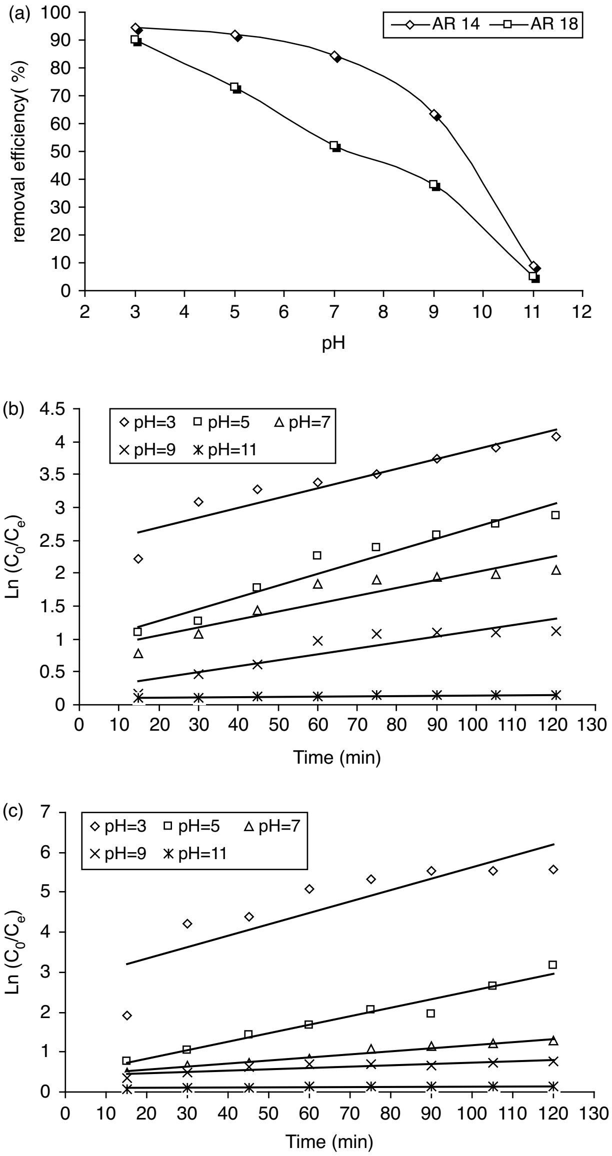

Fig. 4. Effect of pH on dye removal efficiency (initial dye concentration 50 mg l^{-1}, iron powder 1.5 g l^{-1}, contact time 120 min) (a); experimental and calculated data by means of first-order kinetic model for AR 14 (b) and AR18 (c).

Table 1
Parameters of first-order kinetic model for experimental runs carried out at various pHs

AR14	k_1 (l min^{-1})	r^2	AR18	k_1 (l min^{-1})	r^2
pH = 3	0.028	0.88	pH = 3	0.022	0.83
pH = 5	0.025	0.94	pH = 5	0.021	0.95
pH = 7	0.022	0.84	pH = 7	0.020	0.96
pH = 9	0.009	0.84	pH = 9	0.003	0.81
pH = 11	0.003	0.94	pH = 11	0.001	0.93

3.4. Effects of the amount of iron powder on dye removal

Increasing the amount of iron powder has a positive impact on dye removal (Fig. 5a). Indeed, dye removal by iron powder occurred at the surface of the medium, and hence an increment of metal dosage led to more available active surface. In addition, the number of free electron producing active sites increased with the amount of iron powder, leading to an improvement of the removal efficiency. For a metal dosage of 0.5 g l^{-1}, removal yields were 39% and 31% and reached 90% and 67% for a metal dosage of 2 g l^{-1} for Acid Red 14 and Acid Red 18, respectively. As shown in Fig. 5b, the value of k_1 increased for increasing initial iron mass.

3.5. Effect of the initial dye concentration

Fig. 6a shows a decrease of dye removal efficiency for increasing dye concentrations, as it was expected for a constant mass of metal. Indeed, in iron powder system, a given amount of reactant can remove a given amount of pollutant. As shown from Fig. 6b and c, experimental results clearly followed a first-order kinetic model, and the corresponding parameters are collected in Table 2.

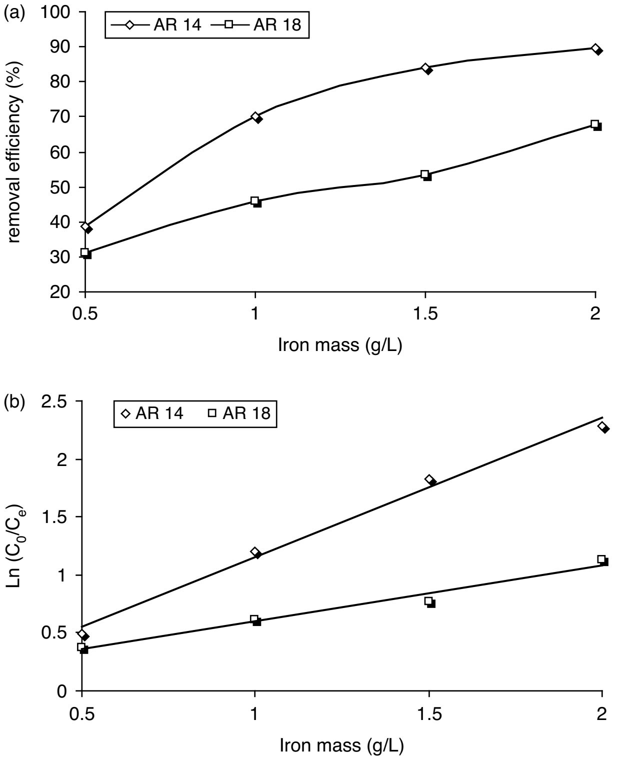

Fig. 5. Effect of the amount of iron powder on dye removal (pH 7, initial dye concentration 50 mg l^{-1}, contact time 120 min); removal efficiency (a), as well as experimental and calculated data by means of first-order kinetic model for AR14 and AR18 (b).

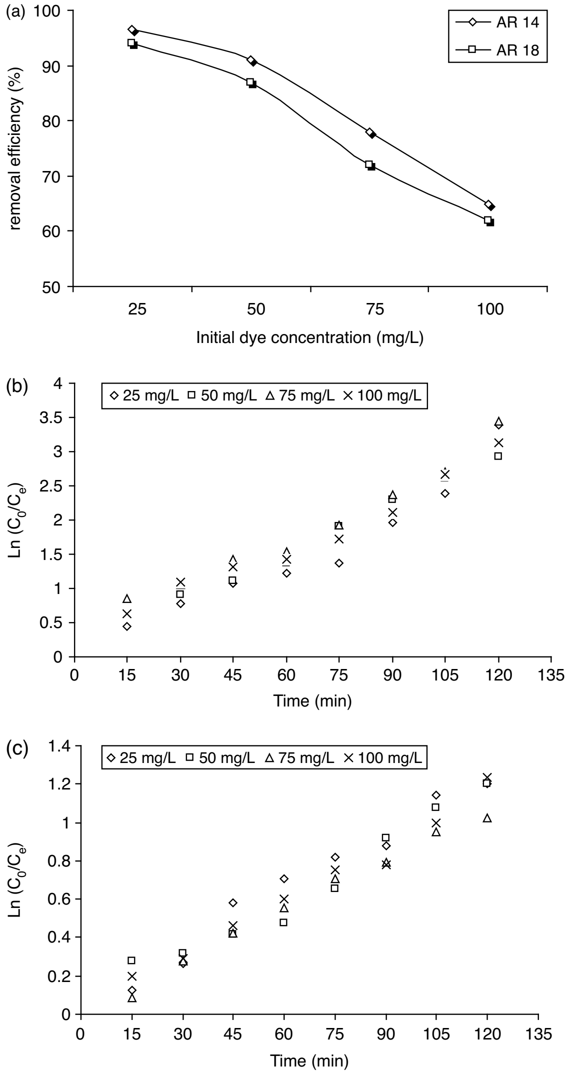

Fig. 6. Effects of the initial dye concentration on the removal efficiency (a) (pH = 7, iron powder 1.5 g l^{-1}, contact time 120 min), as well as the experimental and calculated data by means of first-order kinetic model for AR14 (b) and AR18 (c).

Table 2
Parameters of first-order kinetic model for experimental runs carried out at various initial dye concentrations

	Acid Red 14		Acid Red 18	
C_0 (mg l^{-1})	k_1 (l min^{-1})	r^2	k_1 (l min^{-1})	r^2
25	0.025	0.91	0.01	0.97
50	0.023	0.98	0.009	0.96
75	0.023	0.96	0.009	0.96
100	0.022	0.96	0.009	0.97

Only a weak impact of the initial dye concentration on the k_1 values was recorded, since the decrease was very low, leading to mean values of 0.023 ± 0.001 and 0.00925 ± 0.0005 (l min^{-1}) for the k_1 values for AR14 and AR18, respectively.

3.6. Degradation mechanism

As indicated in the Introduction part, the main mechanism of zero-valent iron system for the removal of organic compound is oxidation-reduction. As reported in the literature, oxidation of iron powder produces free electrons. Such electron attack organic matter and modify its structure. The main target of free electrons in dye degradation is the azo bond (N=N), leading to a colorless solution. In such conditions, other compounds such as aniline may be formed, which also need to be treated. Several methods are available for this purpose, including among others adsorption, biological and advanced oxidation processes. However, with oxidation of Fe^0–Fe^{3+}, $Fe(OH)_3$ flocks can form which may allow by-products removal. Many researchers proposed such mechanism for the removal of azo compounds by zero-valent iron. Feng et al. investigated the removal of the azo dye Reactive red 2 by iron powder, and the mechanism proposed by these authors involved decomposition of azo bonds

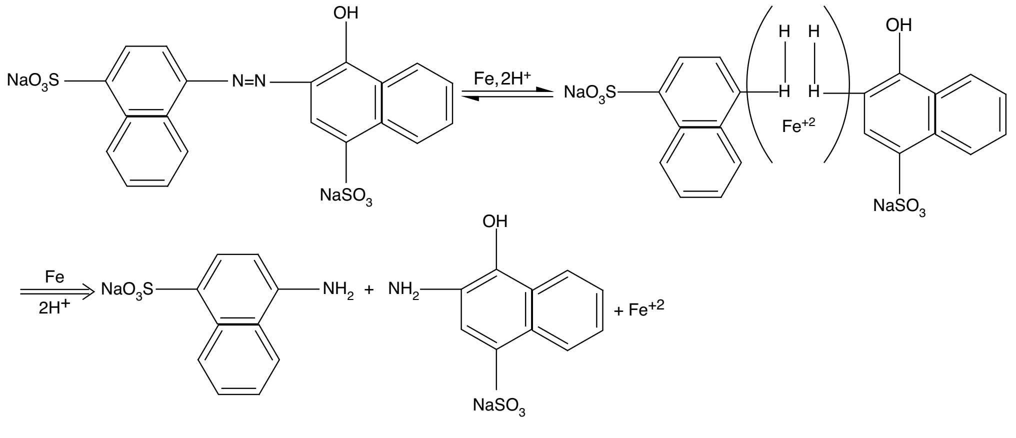

Fig. 7. Degradation route of Acid Red 14.

by free electrons produced on metallic iron surface [35]. The main pathway involved in the removal of methyl orange by the Fenton process using zero-valent metallic iron is the decomposition of the azo bond by free electrons produced during metallic iron erosion (Devi et al., 2008). Furthermore, such mechanism has been proposed by researchers for other zero-valent metals such as the removal of Reactive black 5 by magnesium–palladium system [36], showing that the main route for RB5 discoloration is the attraction of free electrons by azo bonds. According to the above comments, a degradation pathway is proposed and illustrated in Fig. 7 for Acid Red 14. It should be noted that the same degradation mechanism also occurs for Acid Red 18 (not shown).

4. Conclusions

The removal of Acid Red 14 and Acid Red 18 was investigated by zero-valent iron powder, which proved its efficiency in batch experiments. Dye removal increased for increasing contact time and zero-valent iron mass, while it decreased for increasing pH and initial dye concentration. Kinetic modeling showed that both dyes obeyed first order kinetic model. The degradation rate constants decreased from 0.028 to 0.003 and from 0.022 to 0.001 (l min^{-1}) for Acid Red 14 and Acid Red 18 for pH increasing from 3 to 11. Based on the examination of the degradation rate constants, it appeared that the optimal pH was 3 for both dyes. The initial dye concentration had only a very weak effect on the degradation rate constant, which decreased only from 0.025 to 0.022 and from 0.01 to 0.009 (l min^{-1}) for increasing initial dye concentrations from 25 to 100 mg l^{-1}, for AR14 and AR18 respectively.

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