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Photocatalytic Degradation of Azo Dyes Over Semiconductors Supported on Polyethylene Terephthalate and Polystyrene Substrates

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Abstract:

The discharge of effluents from the textile industry into water bodies has a severe impact on water quality. The photocatalytic degradation of two typical azo dyes used in the textile industry (Acid Brown 83 and Direct Blue 1) was studied using the catalysts titanium dioxide (TiO_2) and zinc oxide (ZnO) supported on polyethylene terephthalate (PET) and polystyrene (PS) substrates. For these dyes, degradation reactions using different initial pH values and supported catalysts were carried out. Adsorption isotherms were obtained and analyzed. No significant statistical differences were found between the use of PET and PS as substrates on degradation rate constants for both dyes. For Acid Brown 83 the highest rate constant was obtained at pH 2.5 using TiO_2. For Direct Blue 1, the rate constant showed a significant difference only between the treatment at pH 2.5 using TiO_2 and the treatment al pH 11.0 using ZnO. The adsorption of both dyes was higher on TiO_2 than on ZnO.

Keywords: Acid Brown 83, Azo dyes degradation, Direct Blue 1, heterogeneous photocatalysis, polymeric supports.

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1 Introduction

Since ancient times, over the history of mankind, humans have used dyes and pigments for art (e.g., rupestrian paintings), for military and religious purposes, among many others [1-4]. The synthetic dye industry emerged in the middle of the19th century and since then the production of synthetic dyes has been increasing continuously in both variety and quantity of dyes. Currently, dyes are used extensively in many fields including the textile, leather, cosmetics and food industries, paper production, and others [5]. It is difficult to quantify the production of dyes but, according to certain authors, the world production of dyes can be estimated in 800 000 tons per year [6]. Taking into account considerations of number as well as the production volume of colourants, azo dyes are the largest group, since they constitute 70% of all organic dyes produced in the world [3]. During the dyeing process, around 10 to 25% of dyes are lost and some 2 to 20% are discharged directly into natural water bodies [7, 8].

The discharge of dye-containing industrial effluents into water bodies has a severe effect on the quality of water. Very low concentrations of dyes (less than 1 ppm) can affect the aesthetic and transparency of water as well as the gas solubility [9]. Since most of the synthetic dyes are very stable to light, temperature and microbial degradation [10], they are considered recalcitrant compounds. Moreover, under certain conditions, some dyes (azo dyes) can release aromatic amines, which are considered as carcinogenic [11]. Therefore, depending on the characteristics of subsequent uses of water containing dye residues (e.g., animal husbandry or human consumption, among others), severe

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consequences for animal and human health could be expected. If untreated or deficiently treated wastewater containing dyes is used for irrigation, important mechanisms in soil involving nitrogen can also be negatively affected [12].

Pelileo is a town in Ecuador known for its textile industries. In this town, most of the industrial untreated (or partially treated) azo dyes-containing wastewaters are discharged directly into the Patate River. Such effluents are difficult to treat using conventional technologies because of their low biodegradability [13]. Therefore, other options should be explored. The heterogeneous photocatalysis is proposed as a feasible technology to treat azo dyes-containing wastewater. This process uses UV radiation (potentially, also solar radiation) and semiconductor oxide catalysts, such as zinc oxide (ZnO) and titanium dioxide (TiO_2), to generate highly oxidant hydroxyl radicals ($^{\bullet}OH$) [14].

Photocatalytic reactions begin when the catalyst absorbs equal or greater energy than its band gap, and an electron in the valence band (vb) is promoted to the conduction band (cb) generating a hole in the valence band, as is shown in equation (1) [15].

$$TiO_2 + hv \rightleftharpoons e^{-}cb\,(TiO_2) + h^{+}vb\,(TiO_2) \quad (1)$$

The valence band hole is strongly oxidant and the conduction band electron is strongly reductant. The electron-hole pairs (e^{-}/h^{+}) can participate in redox reactions with water, organic compounds, hydroxide ions and oxygen in order to oxidize the pollutants [15].

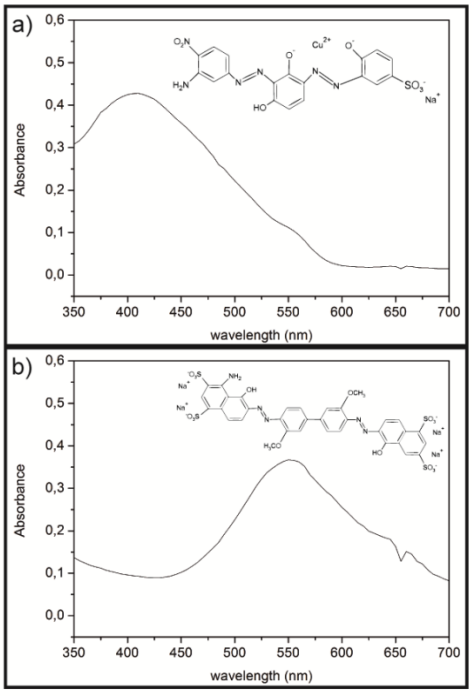

Figure 1: Chemical structures and UV – Vis absorption spectrum of an aqueous solution 50 ppm of the azo dyes: a) Acid Brown 83, AB83, and b) Direct Blue 1, DB1

The catalyst can be used in a suspension or supported over a wide variety of materials. If it is in a suspension, the main disadvantage is the loss of catalyst, and the requirement of a filtration system. Therefore, the catalyst immobilization on different supports is a good way to avoid these problems. In fact, several studies concerning the immobilization of photocatalysts on a variety of substrates were reported in the past. Barka et al. [16] used nonwoven natural and synthetic fibers coated with TiO_2 as catalyst for the degradation of the dye patent blue V. Mounir et al. [17] reported the discoloration of water using TiO_2 immobilized on cellulose fibers, with and without carbon fibers. Other rigid supports for TiO_2, such as glass, quartz and stainless steel, were tested in the past [18, 19]. Substrates for the immobi-

lization of ZnO were also studied. For instance, the deposition of ZnO on glass and ceramic substrates was reported by Akyol and Bayramoglu [20]. In addition, the preparation of a substrate based on ZnO nanoparticles deposited on paper and its antibacterial activity were reported [21].

Plastics have been also considered as materials for the immobilization of photocatalysts. For this purpose, reports about the use of polythene, polypropylene, poly(tetrafluoroethylene), polymethylmethacrylate and others, can be found in the scientific literature [22-26]. Among other plastic supports that can be used, polyethylene terephthalate (PET) and polystyrene (PS) have a lot of advantages such as, their capability to be recycled, low weight, and UV radiation resistance. Additionally, in contrast to some supports like glass, the immobilization process on polymers requires only low energy and can be carried out at room temperature [26-28].

Titanium dioxide, TiO_2 is one of the most used catalysts worldwide. It has two different crystalline phases, anatase and rutile, which play an important role in the photocatalytic process. It was reported that anatase allows a higher methyl orange dye removal than rutile [29]. Zinc oxide, ZnO can also be used and there are reports on the efficient removal of Rhodamine B and Red 27 [30, 31].

In this work, TiO_2 and ZnO supported on PET and PS were tested as photocatalysts for the degradation of two commonly used azo dyes: Acid Brown 83 (Figure 1a) and Direct Blue 1 (Figure 1b). The effects of the substrate (PET and PS), the catalyst (TiO_2 and ZnO) and the initial pH value on the degradation rates of these azo dyes were evaluated. The results presented in this work can be used for the design of reactors for wastewater treatment. In addition, the information provided in this article contributes with data for future studies on the feasibility of applying this technology in Ecuadorian textile industries for wastewater treatment.

2 Experimental and methods

2.1 Reagents

Commercial PET and PS food containers were employed as supports. The catalysts zinc oxide (ZnO, size of grain 20 nm, 99.5%) and titanium dioxide (TiO_2, size of grain 15 nm, 99% anatase), were purchased from Nanostructured and Amorphous Materials, Inc. (USA). The azo dyes, Acid Brown 83 (AB83, $C_{18}H_{11}CuN_6NaO_8S$) and Direct Blue One (DB1, $C_{34}H_{24}N_6Na_4O_{16}S_4$), were purchased from Dyetex (Ecuador). For the heterogeneous photocatalysis, a batch lab scale system (see the scheme in Figure 2) was built using two Sylvania UV lamps (8W, 254 nm) and a Petri dish with a magnetic stirrer (Thermo Scientific SP131015).

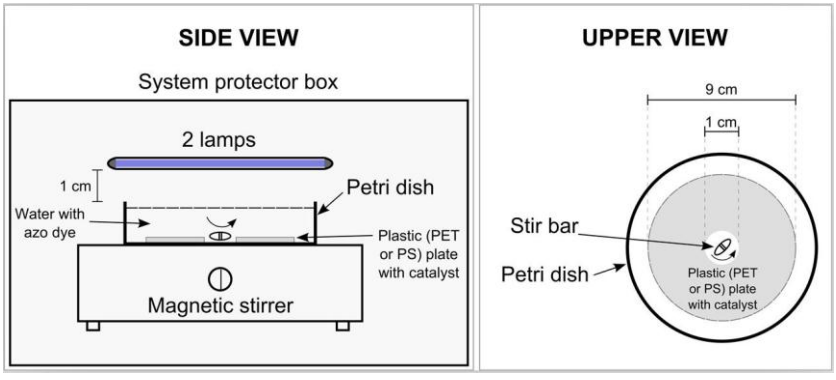

Figure 2: Batch lab scale system to test the performance (azo dye removal) of the treatment using different immobilized catalysts and applying different pH values

2.2 Immobilization of TiO_2 and ZnO on PET and PS substrates

PET and PS plates (diameter = 9 cm) were pretreated according to the method reported by Meichtry et al. [27]. The PET

and PS plates were washed with distilled water in an ultrasonic bath (Branson 1510) for 1 h and then dried for 24 h at room temperature.

TiO_2 and ZnO were immobilized employing a "dip-coating" technique with suspensions (2 g/L) of each catalyst (28). The pH values of these suspensions were fixed at 2.5 for TiO_2 and at 11.0 for ZnO and homogenized by agitation and ultrasound for 15 min and 25 min, respectively (28). Afterwards, the plates were submerged into the suspension for 15 s and dried in a vertical position for 2 h at room temperature. For purposes of this work, one immobilization should be understood as the process in which a plate is submerged in the suspension (of TiO_2 or ZnO) and then dried. Several immobilizations were necessary in order to retain an appropriate amount of the catalysts on the plates (see below).

Since it was necessary to evaluate the efficiency of the catalyst immobilization, the plates were subjected to gravimetric analysis using an analytical balance (Kern ABJ 220 – 4M).

2.3 Effect of the number of immobilizations and the used support

The effect of the number of immobilizations (5, 10 and 15) and the support used (PET and PS) on the AB83 and DB1 photocatalytic degradation constant was studied using a factorial 3x2 experimental design for each catalyst and dye.

AB83 and DB1 solutions (50 ppm) were prepared and the initial pH was adjusted to the same values as the catalyst suspensions. The dye solution samples (20 mL) were treated in the batch lab scale system (see the scheme in Figure 2) using the impregnated plates. The dye concentration was measured at different times using a spectrophotometer UV/Vis (Hitachi U-1900) at 415 nm for AB83 and at 565 nm for DB1. The selection of these wavelengths is consistent with the recorded UV-Vis absorption spectra of the solutions of dyes (see Figures 1a and 1b).

In order to verify whether the used support has influence on the reaction (rate constant) or not, the tests were carried out in triplicate and the data processed using the Statgraphics Centurion software (version 16.1.03).

2.4 Effect of pH value of aqueous dye solutions

The effect of the pH value on the photocatalytic degradation constant was studied by the treatment of AB83 and DB1 solutions (50 ppm) in the batch lab scale system using the supported catalysts. The considered pH values were 2.5 and 6.0 for TiO_2 and 7.0, 9.0 and 11.0 for ZnO. The pH values of the solutions were adjusted at the desired level using solutions 1 N of H_2SO_4 and NaOH. The pH values were measured with a Jenway 3510 pHmeter. A completely randomized experimental design was applied for this part of the work. The tests were carried out in triplicate and the data processed using the Statgraphics Centurion software (version 16.1.03).

2.5 Adsorption tests

The AB83 and DB1 adsorption on the plates with the immobilized catalysts (TiO_2 and ZnO) were studied at the same pH values mentioned before. The plates were submerged into solutions containing 10, 20, 30, 40 and 50 ppm of AB83 and DB1, with agitation for 50 minutes and without UV radiation exposure. In order to build the adsorption isotherms, the final concentrations of dyes were measured by UV/Vis spectrophotometry taking into account the appropriate wavelengths for each dye.

2.6 Microscopy

In order to characterize the materials (before and after the photocatalytic treatment), PET and PS plates were impregnated with TiO_2 and ZnO and then used in the treatment of the dyes at pH 2.5 for TiO_2 and 9.0 for ZnO. Photographs of the plates were taken using a regular camera (see Figures S1 and S2, Supplementary Material), while microphotographs were acquired using an Olympus SZX16 stereo microscope equipped with a 17.3 megapixel Olympus DP73

camera, and a Olympus SDF PLAPO 1XPF objective with a 0.15 numerical aperture. An amplification of 11.5x was applied. In addition, the microphotographs were processed using the software Olympus Stream Basic 1.9.2.

3 Results and Discussion

3.1 Immobilization of TiO_2 and ZnO on PET and PS substrates

The catalyst mass on the substrates increased with the number of immobilizations as shown in Table 1. Furthermore, the mass values of the immobilized catalysts were not affected by the use of PET or PS. In this work, the amounts of immobilized catalyst obtained were higher than those reported in literature. In particular, Lopes de Barros et al. [28] achieved 0.168 mg/cm^2 of TiO_2 after 15 immobilizations on PET. This difference in the immobilization of the catalysts may be attributable to material characteristics such as the particle size. In this work, the particle size of TiO_2 was smaller compared to the TiO_2 used by Lopes de Barros et al [28]. Furthermore, the standard deviation values for ZnO were higher than those for TiO_2. Also, microphotographs of the plates (see Figures S3 and S4, Supplementary Material) revealed that ZnO tends to form lumps. This means that there is a certain degree of aggregation of the catalysts. From the microphotographs, it can be noticed that the degree of aggregation of catalysts is higher for ZnO than for TiO_2, being this a possible explanation for the observed standard deviation values.

Table 1: TiO_2 and ZnO immobilized mass (mg/cm^2) on PET and PS substrates

Number of Immobilizations	Catalyst	Immobilized mass (mg/cm^2)	
		PET	PS
5	TiO_2	0.159 ± 0.027	0.155 ± 0.039
	ZnO	0.104 ± 0.033	0.140 ± 0.026
10	TiO_2	0.258 ± 0.039	0.273 ± 0.031
	ZnO	0.338 ± 0.150	0.398 ± 0.075
15	TiO_2	0.399 ± 0.035	0.418 ± 0.060
	ZnO	0.689 ± 0.197	0.709 ± 0.162

It is easy to observe the difference between the substrate without the catalyst and with the catalyst after the immobilizations. Photographs of polystyrene (PS) plates before and after the immobilization of TiO_2 (15 immobilizations) are depicted in Figure 3.

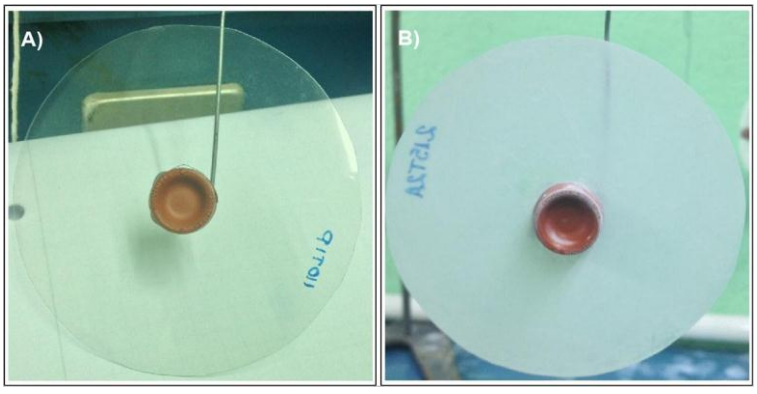

Figure 3: Polystyrene (PS) plate before (A) and after (B) immobilization of TiO_2. Photo B shows the plate after 15 immobilizations

3.2 Effect of the number of immobilizations and the support used on the rate constants

Plates with different numbers of immobilization were tested in order to determine the effect of this variable on the rate constants of the photocatalytic degradation reactions of AB83 and DB1 on both PET and PS substrates. Table 2 presents the average rate constants for both azo dyes on PET and PS substrates. The photocatalytic degradation followed a pseudo-first order kinetics.

Table 2: Rate constants (k) of the photocatalytic degradation reactions of AB83 and DB1 using TiO_2 and ZnO supported on PET and PS substrates as a function of the number of immobilizations

Number of immobilizations	AB83 k (min^{-1})			
	TiO_2		ZnO	
	PET	PS	PET	PS
5	0.0520 ± 0.0087	0.0744 ± 0.0099	0.0169 ± 0.0009	0.0283 ± 0.0016
10	0.0719 ± 0.0079	0.0619 ± 0.0084	0.0347 ± 0.0100	0.0479 ± 0.0092
15	0.0785 ± 0.0092	0.0922 ± 0.0195	0.0556 ± 0.0053	0.0508 ± 0.0310
Number of immobilizations	**DB1 k (min^{-1})**			
	TiO_2		ZnO	
	PET	PS	PET	PS
5	0.0499 ± 0.0035	0.0491 ± 0.011	0.0223 ± 0.0024	0.0239 ± 0.0036
10	0.0747 ± 0.0093	0.0608 ± 0.0103	0.0302 ± 0.0069	0.0412 ± 0.0075
15	0.0838 ± 0.0215	0.0845 ± 0.0177	0.0623 ± 0.0105	0.0529 ± 0.0025

The analysis of the data showed that the use of PET or PS did not influence the rate constant values of both dyes using TiO_2 (see Figures S5 and S6, Supplementary Material) and ZnO (see Figures S7 and S8, Supplementary Material). For AB83 there was no significant differences between 5 and 10 immobilizations, but there was a significant increase with 15 immobilizations using TiO_2 (Figure S9, Supplementary Material). For the case of DB1, the rate constants showed no significant difference when 5 and 10 immobilizations and 10 and 15 immobilizations were compared. However, the rate constant increased between 5 and 15 immobilizations using TiO_2 (see Figure S10, Supplementary Material). In addition, there was a significant improvement of the rate constants between 5, 10 and 15 immobilizations for both dyes using supported ZnO (Figures S11 and S12, Supplementary Material).

Lopes de Barros et al. [28] demonstrated that although the catalyst mass increases with the number of immobilizations, the degradation rate constant value depends on the percentage of surface coverage. However, the heterogeneity (i.e., formation of lumps) of the immobilized catalyst onto the plate should also be considered. The aggregation of the catalyst could result in a higher weight of the catalyst on the plate, a minor change in the surface area of the catalyst and, therefore, just a slight increase of the rate constant value may be observed. As mentioned before the microphotographs of the plates revealed that the degree of aggregation of catalysts is higher for ZnO than for TiO_2. Considering both the rate constants and the surface characteristics of the plates, it seems that after more than 10 immobilizations TiO_2 fully covers the plates or, at least, its coverage is close to complete. This fact could explain why in the case of DB1 the rate constants did not showed a significant difference between 10 and 15 immobilizations. On the other hand, with 15 immobilizations of ZnO, there is still not a complete coverage, so it could explain why the rate constants for both dyes increased with 15 immobilizations.

Other azo dye degradation studies with suspended TiO_2 and ZnO achieved similar values to those obtained in this study with supported catalysts. For example, Byberg et al. (32) studied the degradation of Direct Yellow, Direct Red and Direct Violet 51 using TiO_2 and found rate constants of 0.0543 min^{-1}, 0.0453 min^{-1} and 0.0306 min^{-1}, respectively. Abo-Farha [33] achieved degradation rate constants of 0.0429 min^{-1} and 0.0352 min^{-1} for Acid Orange 10 and Acid Red

114, respectively. Daneshvar et al. [34] evaluated the degradation of Acid Red 14 using suspended ZnO and found a rate constant of 0.0548 min^{-1}.

3.3 Effect of pH value of aqueous dye solution

The pH value influences the azo dye adsorption over the surface of catalysts because the charge of TiO_2 or ZnO surface depends on it [33, 35]. For pH values below the zero point charge (ZPC), the catalysts are positively charged, while above this value the catalysts are negatively charged. The equations 2 and 3 provide an explanation on this aspect [36].

$$\text{pH} < \text{ZPC: M-OH} + H^+ \rightleftharpoons MOH_2 \quad (2)$$

$$\text{pH} > \text{ZPC: M-OH} + OH^- \rightleftharpoons MO^- + H^+ \quad (3)$$

The ZPC of TiO_2 is approximately 6.8, and the ZPC of ZnO is 9.4 [37, 38].

The photocatalytic degradation rates of AB83 and DB1 using TiO_2 and ZnO supported on PS at different pH values are shown in Figure 4, where C is the concentration of the dye at time zero and C_0 is the concentration of the dye at time t. The concentrations were measured in parts per million (ppm).

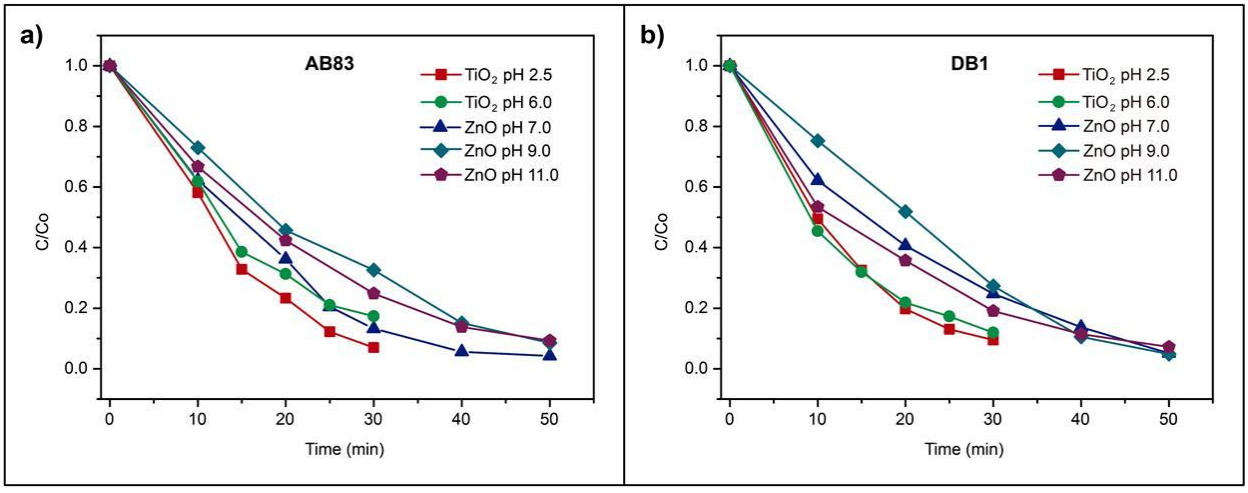

Figure 4: Photocatalytic degradation rate of Acid Brown 83, AB83 (a) and Direct Blue 1, DB1 (b) using TiO2 and ZnO supported on polystyrene, PS (15 immobilizations) at different initial pH values

AB83 and DB1 are acid azo dyes, therefore they are negatively charged. When TiO_2 was used, the rate constants revealed no significant statistical difference between pH 2.5 and 6.0 (see Figures S13 and S14, Supplementary Material). This can be explained by the fact that below pH 6.8 the attraction between the surface of the catalyst and the dye favors the adsorption and consequently the photocatalysis. Other degradation studies of acid azo dyes such as Reactive Orange 107, Reactive Black 5, Acid Orange 10 and Acid Red 14 demonstrated that the photocatalysis using TiO_2 is higher at acidic conditions [33, 39]. Additionally, Daneshvar et al. [40] proved that the rate constant for the degradation of Acid Red 14 did not decrease significantly between pH 2.0 and 7.0. Therefore, the results presented in this work are in good agreement with earlier observations.

When ZnO is employed, although the attraction below pH 9.4 improves the photocatalytic process, acidic conditions do not favor the photocatalysis due to catalyst corrosion. As a result, dye adsorption and •OH radicals production are reduced [31, 34]. For AB83, the higher degradation rate constants using supported ZnO were achieved at pH 7.0 (0.0694 min^{-1}). Also, no significant differences in the rate constants were observed between pH values of 9.0 and 11.0

(see Figure S15, Supplementary Material). On the other hand, the rate constants of DB1 showed no significant differences between pH 7.0 and 9.0, but there was a significant decrease at pH 11.0 (see Figure S16, Supplementary Material). The difference between the results for both dyes could be attributed to differences in the adsorption onto the surface of the catalysts (see below in subsection 3.4). Similar findings were reported in the past for Acid Red 14, Reactive Blue 160 and Methyl Orange [34, 41, 42].

In order to find the best conditions for the degradation reactions, both pH value and catalyst were evaluated respect to their effect on the degradation rate constant. This statistical analysis was carried out for both dyes considered in this study and the results are depicted in Figure 5a and 5b for AB83 and DB1, respectively. The best (highest) rate constant for AB83 (0.0922 min^{-1}) was obtained at pH 2.5 for supported TiO_2, while in the case of DB1 there were significant differences only between the treatment using TiO_2 at pH 2.5 and the treatment using ZnO at pH 11.0.

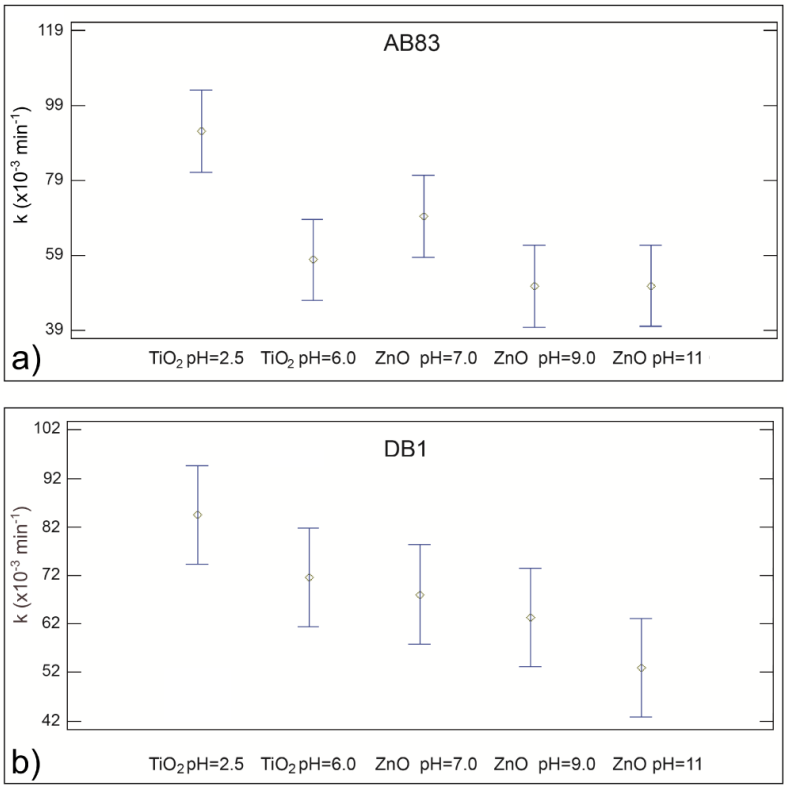

Figure 5: Effect of the catalyst and the pH value on the degradation rate constant (k) of a) Acid Brown 83, AB83, and b) Direct Blue 1, DB1

3.4 Adsorption tests

During the photocatalytic experiments for the azo dyes degradation, gradual coloration of the plates was observed for both dyes (see Figures S1 and S2, Supplementary Material). It is well known that the adsorption of dye molecules onto the catalyst surface is an important step for the photocatalytic reaction [43]. Therefore, it is necessary to estimate the influence of the adsorption process in the treatment. Taking into account this aspect, the adsorption of both azo dyes onto the plates at different pH values and for both catalysts was studied and the data evaluated by mean of the Freundlich model. The linear form of the Freundlich adsorption model is presented in equation (4).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

In equation (4), C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed (mg/g), while K_f and n are

Freundlich constants related to adsorption capacity and adsorption intensity, respectively. For interpretation purposes, it is known that a high value of K_f implies a high adsorption capacity. It is accepted that values of n>1 represent favorable adsorption conditions [44].

The calculated Freundlich constants for AB83 and DB1 adsorption on supported TiO_2 and ZnO (PS, 15 immobilizations) are summarized in Table 3. The adsorption was studied using only PS plates because the material of the polymeric support did not influence the degradation rate constant values of both dyes. In addition, Figure 6 shows two of the linearized adsorption isotherms for illustrative purposes.

Table 3: Freundlich constants of AB83 and DB1 adsorption on supported TiO_2 and ZnO (PS, 15 immobilizations)

pH	AB83			DB1		
	K_f (mg AB83/g cat)	n	R^2	K_f (mg DB1/g cat)	n	R^2
2.5 (TiO_2)	33.14	4.48	0.9979	17.08	0.77	0.8970
6.0 (TiO_2)	9.87	1.81	0.6609	20.63	3.25	0.8905
7.0 (ZnO)	5.86	3.71	0.9037	9.60	1.72	0.4108
9.0 (ZnO)	2.02	1.79	0.8103	24.35	4.21	0.877
2.5 (TiO_2)	33.14	4.48	0.9979	17.08	0.77	0.8970

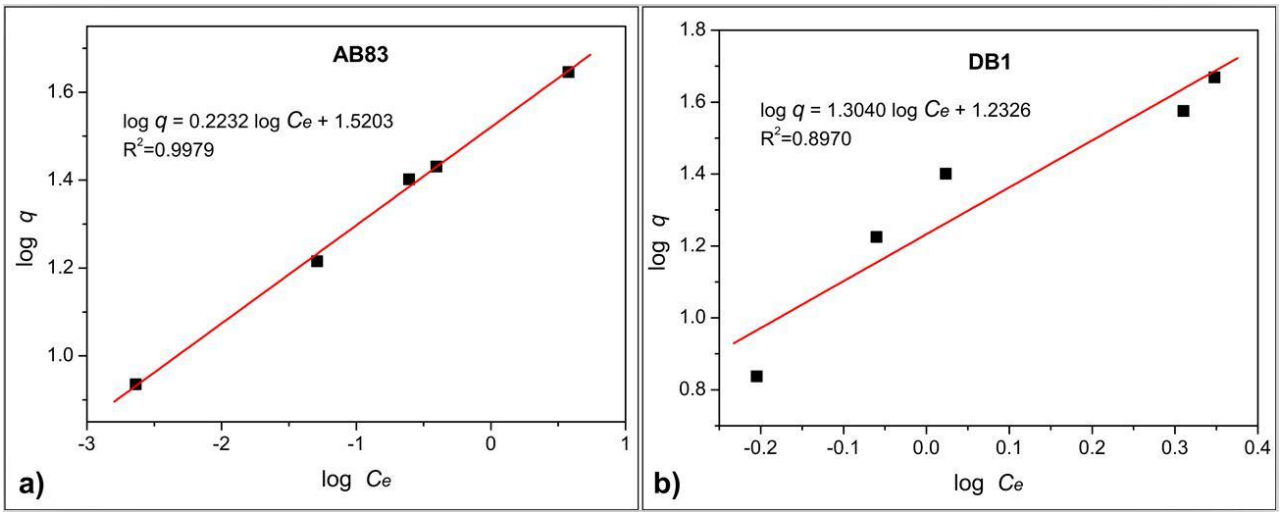

Figure 6: Linearized Freundlich adsorption isotherms of the dyes onto PS plates: a) AB83 on TiO_2 at pH=2.5 and b) DB1 on TiO_2 at pH=2.5

DB1 and specially AB83 show a high adsorption on TiO_2 at pH 2.5. This behavior was also reported in the past for other azo dyes like Acid Orange 10 and Acid Red 14 at pH values below 6.8 (33). From the values in Table 3 can be inferred that the adsorption tends to be higher on TiO_2 than on ZnO. Since non-adsorption was observed for ZnO at pH 11.0, no data was presented for this pH value in Table 3. It can also be observed that some values of R^2 are low. Perhaps the explanation for the observed low correlation factor may be found analyzing the characteristics of the adsorption tests and the immobilized catalysts. The adsorption tests were performed using the catalysts immobilized on the plates, and it is possible that this experimental setup could affect the mixing and the contact of the solution with the adsorbent during the agitation. Moreover, as it was explained in subsection 3.1 the degree of aggregation of catalysts is higher for ZnO than for TiO_2 (see Figures S3 and S4, Supplementary Material). This could explain why lowest values of R^2 were observed for ZnO. In general, the results show that the adsorption on the plates is important and it seems that has a positive effect in the treatment.

4 Conclusions

As expected, the catalyst mass on the substrates (PET and PS) increased with the number of immobilizations. The catalyst mass reached values of 0.399 mg/cm^2 for TiO_2 and 0.689 mg/cm^2 for ZnO on PET, and 0.418 mg/cm^2 and 0.709 mg/cm^2 on PS, respectively. For the specific case of TiO_2 on PET, the mass of immobilized catalyst was higher than previously reported by other authors, probably due to the characteristics of the TiO_2 used in this work. The AB83 and DB1 photocatalytic degradation rates followed pseudo-first order kinetics and were not influenced by the substrate material (PET or PS). The rate constant depended on the catalyst surface coverage percentage of the plates. It increased with the number of immobilizations using supported ZnO and TiO_2.

The highest rate constant of the photocatalytic degradation reaction of AB83 (0.0922 min^{-1}) was obtained at pH 2.5 with supported TiO_2. On the other hand, the rate constant for DB1 showed a significant difference between the treatment at pH 2.5 using TiO_2 (0.0529 min^{-1}) and the treatment at pH 11.0 using ZnO (0.0845 min^{-1}). The adsorption of both dyes is higher on TiO_2 than on ZnO. No adsorption was found on ZnO at pH 11.0.

Considering that both PET and PS are materials usually discarded after their primary use, the recovery of these materials for water treatment purposes is an attractive alternative. This may help developing countries not only to deal with a common fraction of solid waste (plastics), but also to implement treatment systems for industrial wastewater, thus protecting the environmental quality of water bodies.

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Supplementary Material

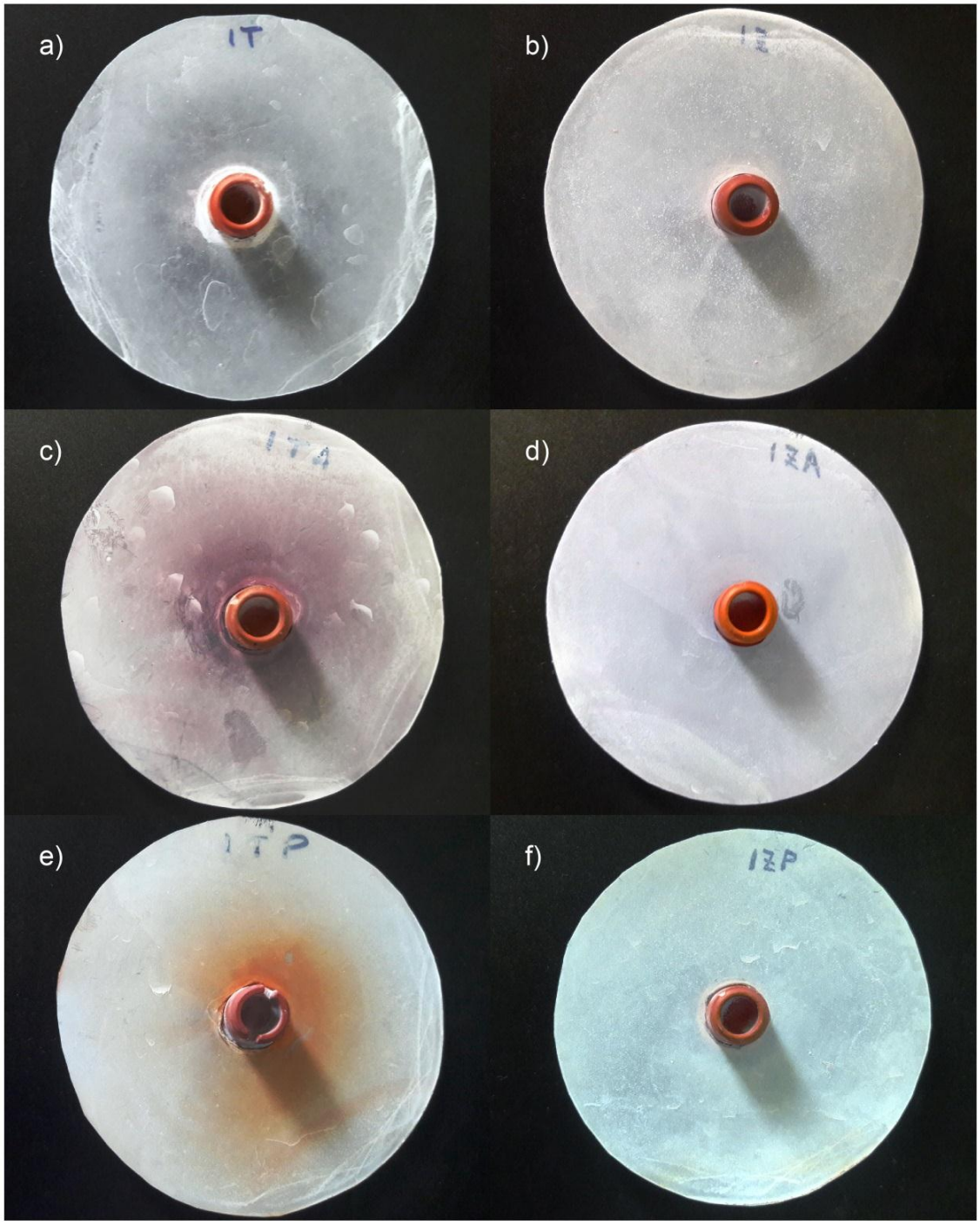

Figure S1: Photographs of polyethylene terephthalate (PET) plates impregnated with TiO_2 (left) and ZnO (right). Photographs a) and b) shows the plates impregnated with TiO_2 and ZnO, respectively, after 15 immobilizations. Photographs c) and d) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of DB1. Photographs e) and f) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of AB83. The treatments of the solutions of dyes were performed at pH values of 2.5 and 9.0 for the plates impregnated with TiO_2 and ZnO, respectively (due to considerations of stability)

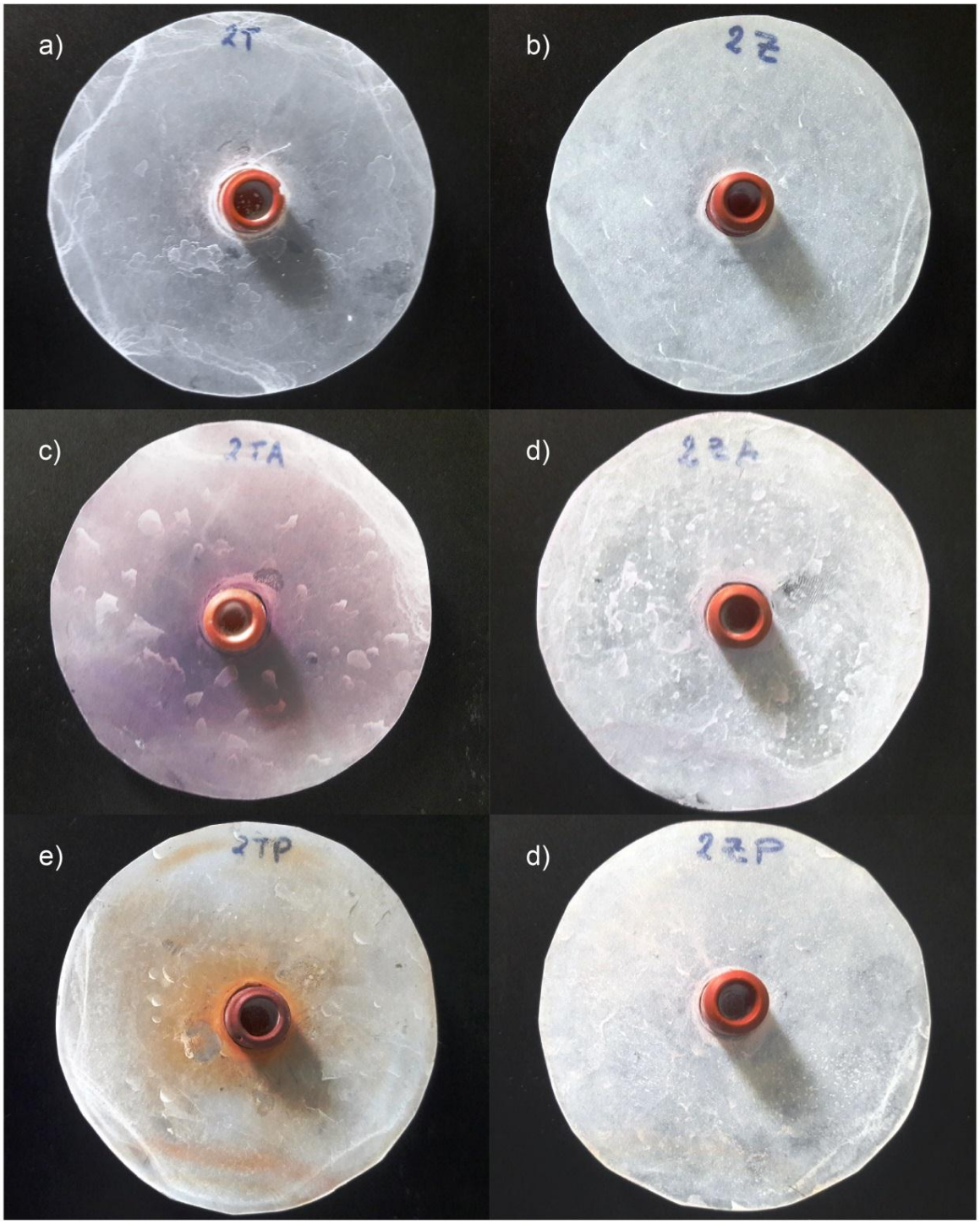

Figure S2: Photographs of polystyrene (PS) plates impregnated with TiO2 (left) and ZnO (right). Photographs a) and b) shows the plates impregnated with TiO_2 and ZnO, respectively, after 15 immobilizations. Photographs c) and d) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of DB1. Photographs e) and f) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of AB83. The treatments of the solutions of dyes were performed at pH values of 2.5 and 9.0 for the plates impregnated with TiO_2 and ZnO, respectively (due to considerations of stability).

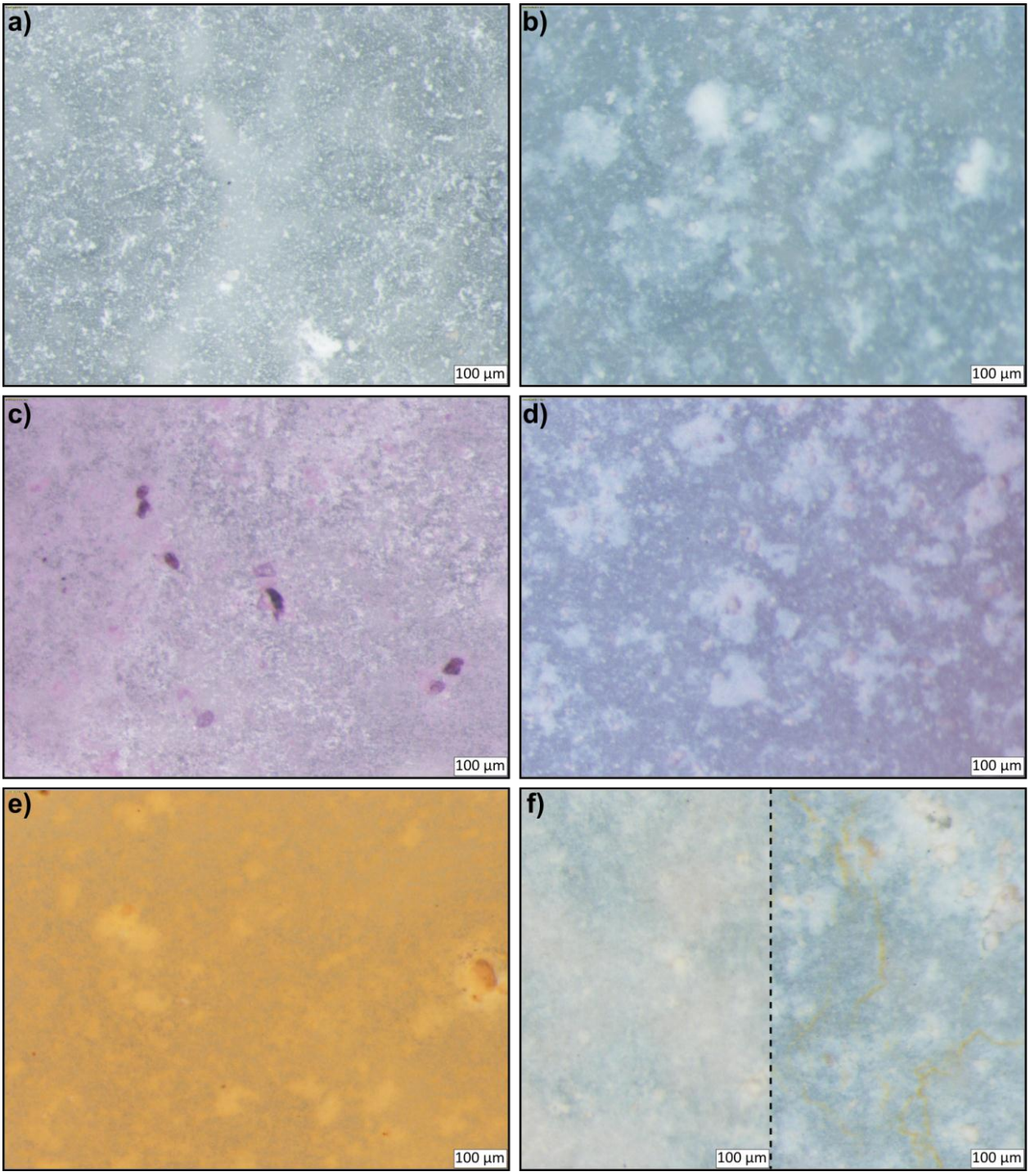

Figure S3: Photographs of polystyrene (PS) plates impregnated with TiO_2 (left) and ZnO (right). Photographs a) and b) shows the plates impregnated with TiO_2 and ZnO, respectively, after 15 immobilizations. Photographs c) and d) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of DB1. Photographs e) and f) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of AB83. The treatments of the solutions of dyes were performed at pH values of 2.5 and 9.0 for the plates impregnated with TiO_2 and ZnO, respectively (due to considerations of stability)

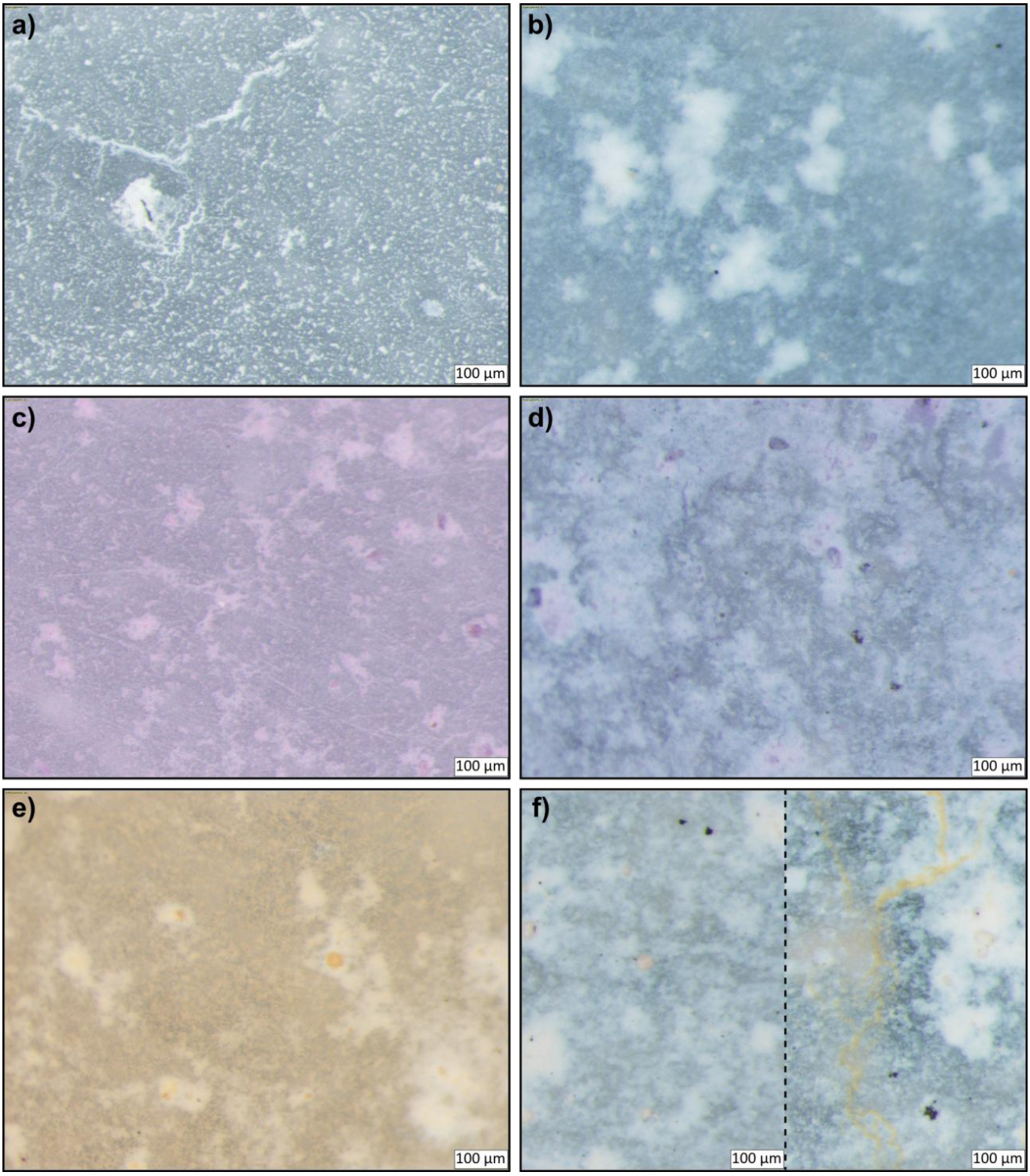

Figure S4: Microphotographs of the polystyrene (PS) plates impregnated with TiO_2 (left) and ZnO (right). Microphotographs a) and b) shows the plates impregnated with TiO_2 and ZnO, respectively, after 15 immobilizations. Microphotographs c) and d) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of DB1. Microphotographs e) and f) show the plates impregnated with TiO_2 and ZnO, respectively, after the treatment of a solution of AB83. In f), two sections of the plate are shown. The treatments of the solutions of dyes were performed at pH values of 2.5 and 9.0 for the plates impregnated with TiO_2 and ZnO, respectively (due to considerations of stability)

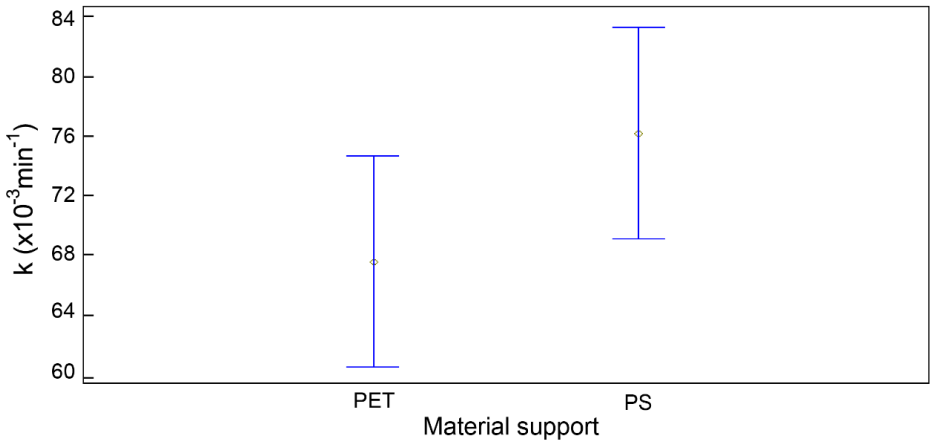

Figure S5: Effect of the material support on the degradation rate constant (k) of Acid Brown 83 (AB83) using TiO_2 at pH 2.5

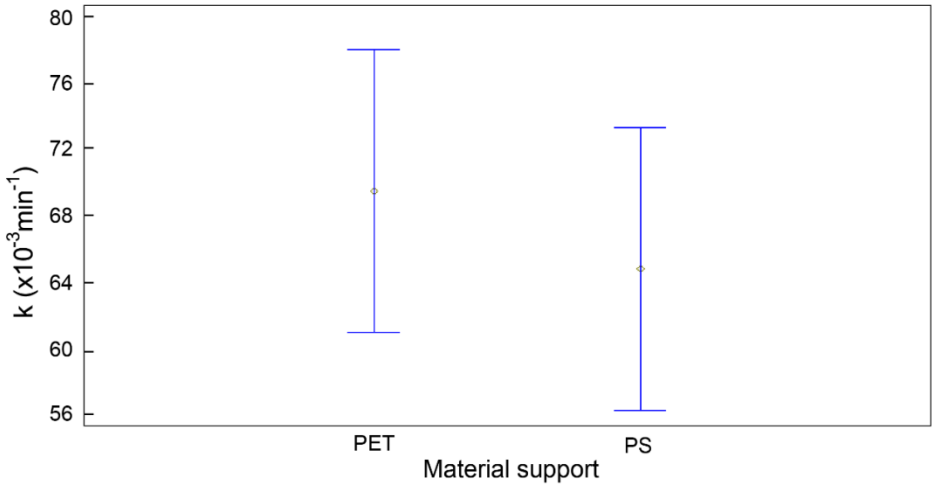

Figure S6: Effect of the material support on the degradation rate constant (k) of Direct Blue 1 (DB1) using TiO_2 at pH 2.5

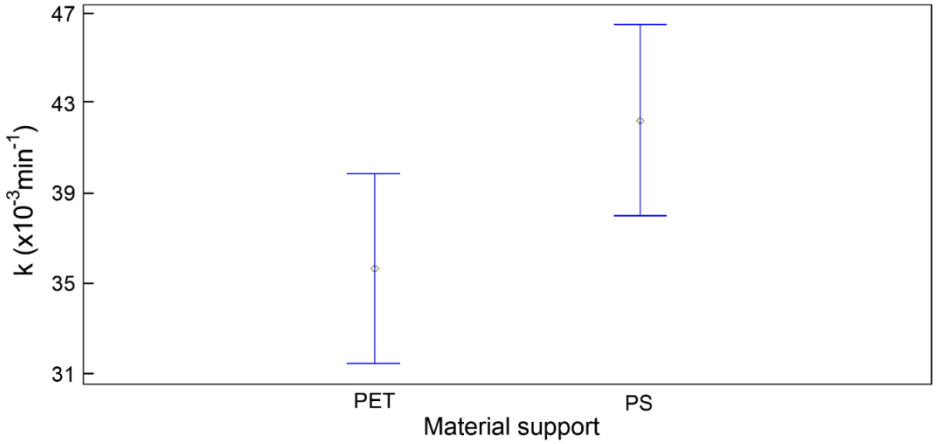

Figure S7: Effect of the material support on the degradation rate constant (k) of Acid Brown 83 (AB83) using ZnO at pH 11.0

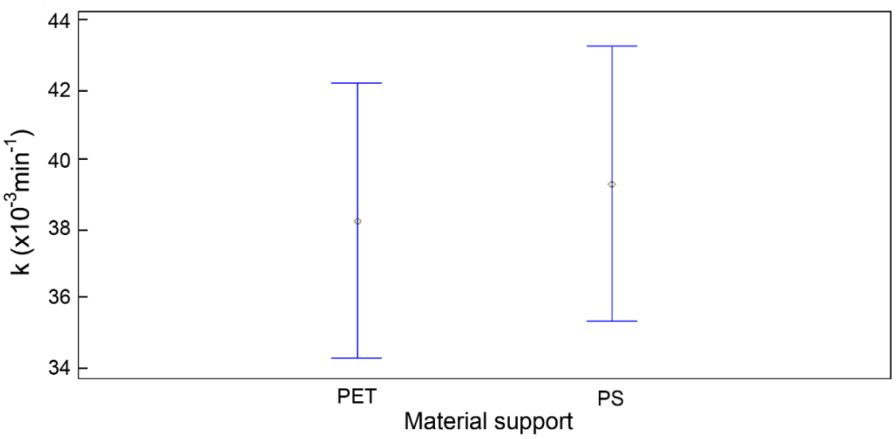

Figure S8: Effect of the material support on the degradation rate constant (k) of Acid Brown 83 (AB83) using ZnO at pH 11.0

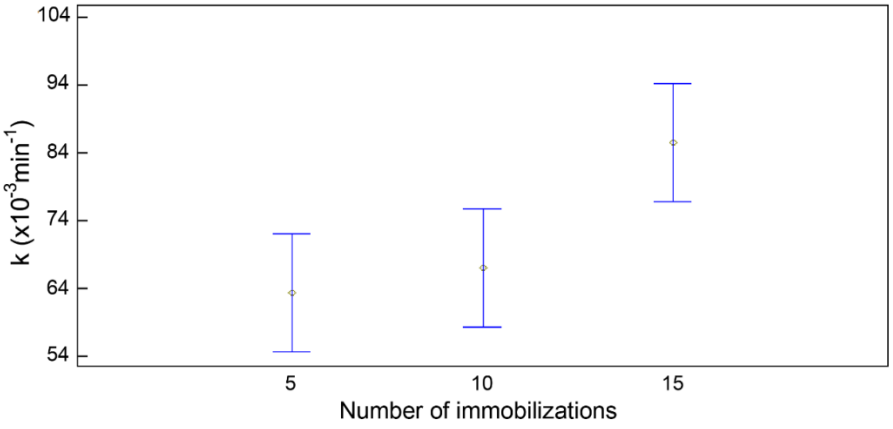

Figure S9: Effect of the number of immobilizations on the degradation rate constant (k) of Acid Brown 83 (AB83) using TiO_2 at pH 2.5

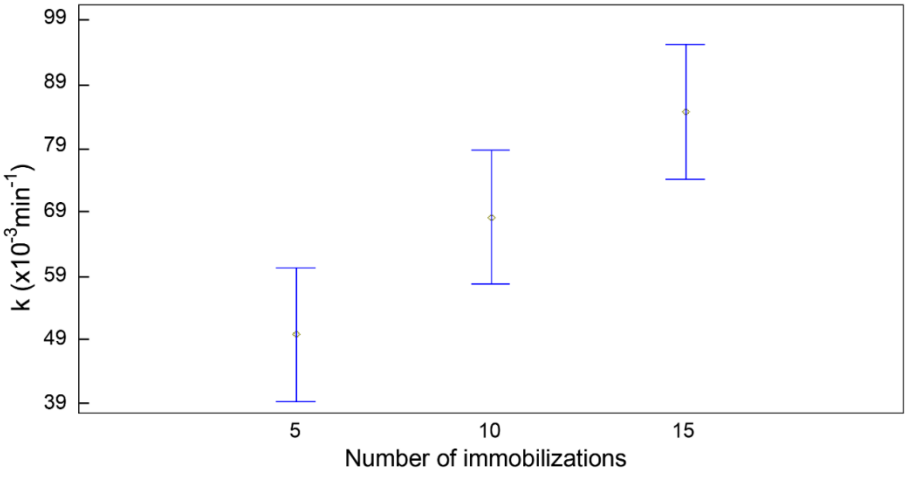

Figure S10: Effect of the number of immobilizations on the degradation rate constant (k) of Direct Blue 1 (DB1) using TiO_2 at pH 2.5

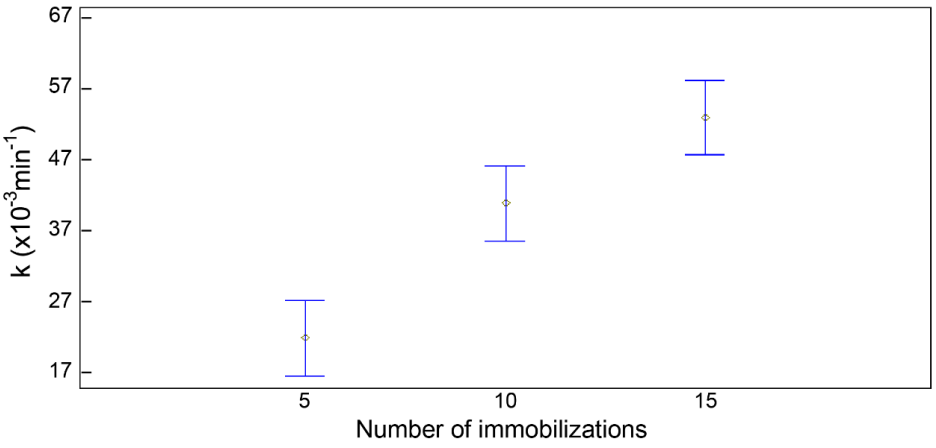

Figure S11 : Effect of the number of immobilizations on the degradation rate constant (k) of Direct Blue 1 (DB1) using TiO_2 at pH 2.5

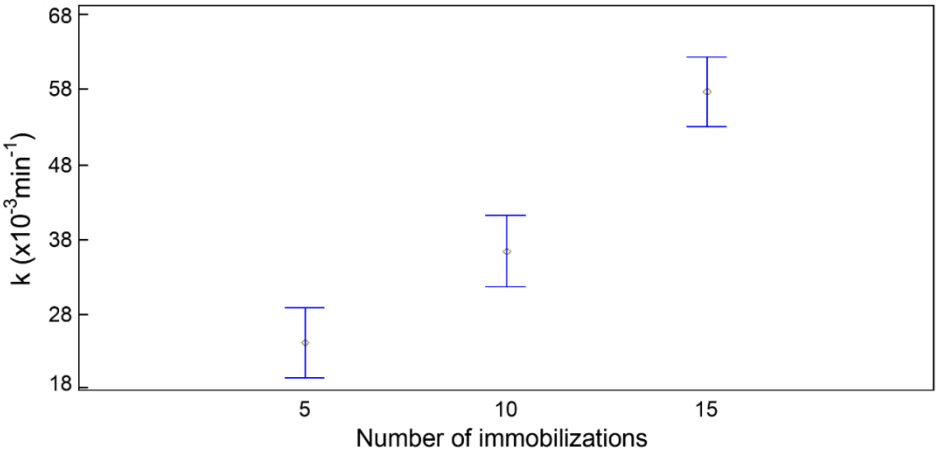

Figure S12: Effect of the number of immobilizations on the degradation rate constant (k) of Direct Blue 1 (DB1) using ZnO at 11.0

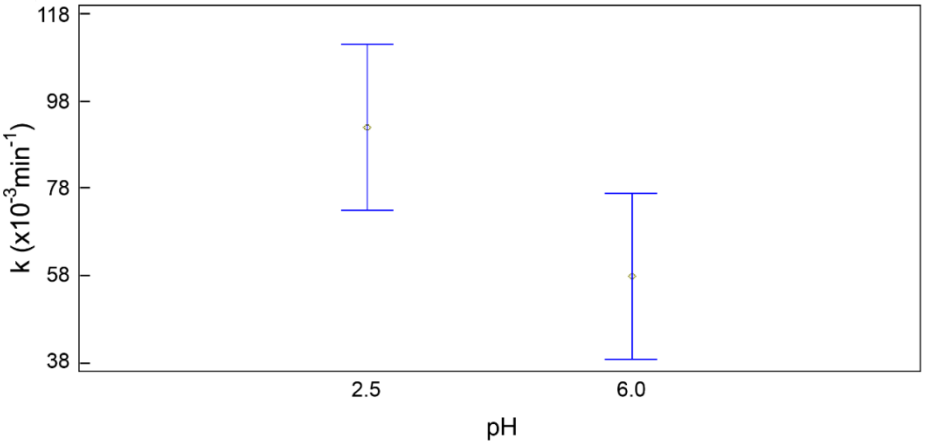

Figure S13: Effect of the pH value on the degradation rate constant (k) of Acid Brown 83 (AB83) using TiO_2 (15 immobilizations)

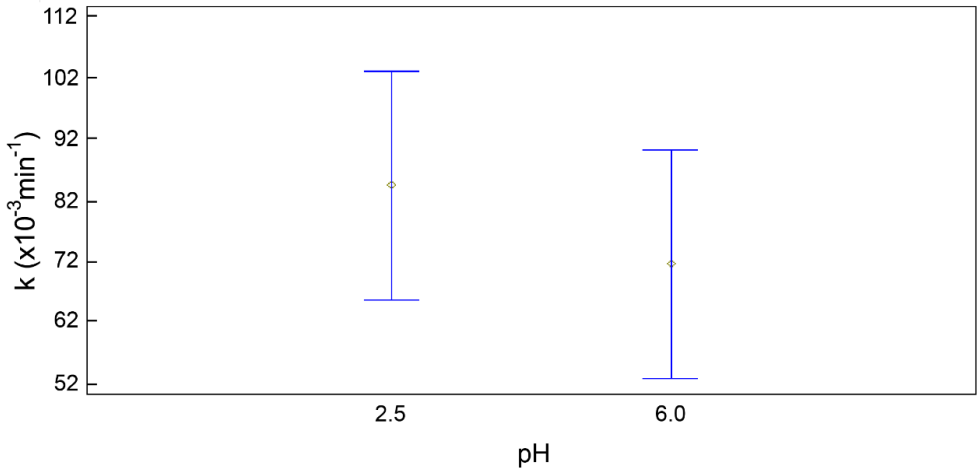

Figure S14: Effect of the pH value on the degradation rate constant (k) of Direct Blue 1 using TiO_2 (15 immobilizations)

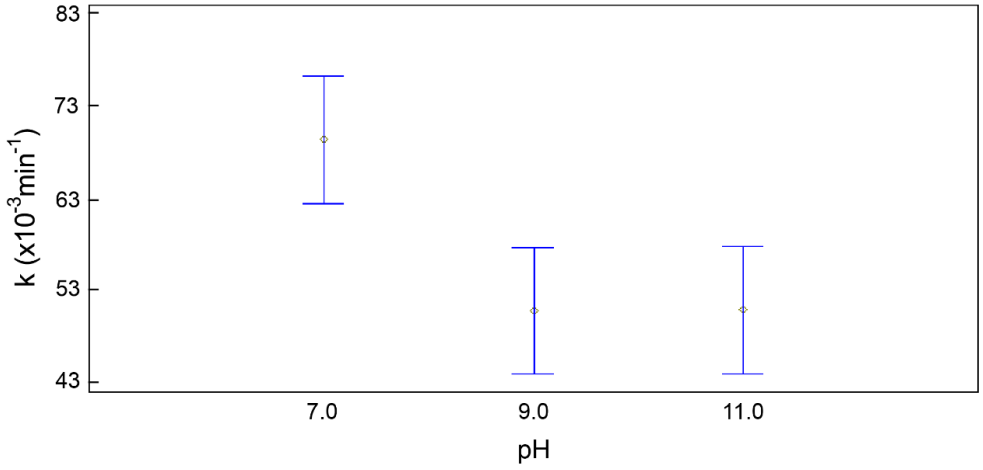

Figure S15: Effect of the pH value on the degradation rate constant (k) of Acid Brown 83 (AB83) using ZnO (15 Immobilizations)

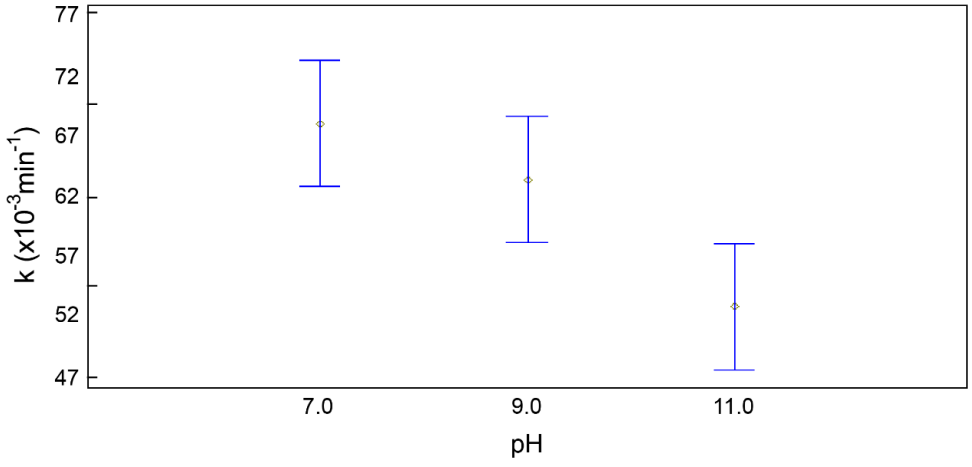

Figure S16: Effect of the pH value on the degradation rate constant (k) of Acid Brown 83 (AB83) using ZnO (15 Immobilizations)