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# Photocatalytic decomposition of textile dyes on $TiO_2$-Tytanpol A11 and $TiO_2$-Degussa P25

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## Abstract

The present studies report on the results from the photocatalytic decomposition of organic dyes (Reactive Red 198 (RR198), Acid Black 1 (AB1) and Acid Blue 7 (AB7)), using two photocatalysts: $TiO_2$-Tytanpol A11 and $TiO_2$-Degussa P25 under UV/Vis illumination. All experiments were conducted with a constant amount of photocatalyst (0.2 g per 0.5 $dm^3$ of dye solution), dye concentration (30 $mg/dm^3$) and at constant pH (pH = 2). The degree of dye decomposition in solution form the following order: RR198 > AB1 > AB7. The photodecomposition of the dyes on the photocatalyst surface was monitored by FTIR spectroscopy. Photocatalytic decomposition of the dyes takes place on the photocatalyst surface via intermediate by-products that are adsorbed on the surface with a higher intensity for A11 which exhibits lower activity. The results suggest that a surface reaction, where the dyes are adsorbed, is the controlling step of the process.

*Keywords:* Organic dye degradation; Titanium dioxide; FTIR spectroscopy

## 1. Introduction

Organic dyes are one of the largest groups of pollutants in wastewaters produced from textile and other industrial processes. The conventional methods used for textile wastewater purification are biological oxidation and physical–chemical treatment (e.g., coagulation-flocculation, activated carbon adsorption). These processes are not sufficiently efficient since dyes are hardly removable due to their low molecular weight and high water solubility. Moreover, chemical treatment results only in the separation of dyes and produces large amounts of sludge. In recent years, there have been many publications connected with organic dye photocatalytic degradation in water [1–5].

The most investigated photocatalyst is titanium dioxide. Application of $TiO_2$ in photocatalytic processes is based on its remarkable activity, chemical stability and also on its non-toxic properties. However, only light of wavelengths below 400 nm can be adsorbed by $TiO_2$ particles to generated $e^-/h^+$ pairs. It is known that less than about 5% of the solar energy reaching the surface of the earth is ultraviolet light. These features limit the applications of $TiO_2$ photocatalysis in the purification of polluted water by sunlight, the cheapest light resource.

The photodegradation of the coloured wastewater may occur through the excitation of the colour organic material onto a semiconductor surface under visible light and followed by the injection of charge from the excited organic into the semiconductor particle. The oxidized form of the organic compound can then undergo further reactions. This process is commonly referred to as photosensitization. The photosensitized oxidation of many coloured compound has been carried out on semiconductor surfaces [6].

The present study reports on the results from the photocatalytic decomposition of organic dyes (Reactive Red 198 (RR198), Acid Black 1 (AB1) and Acid Blue 7 (AB7)), using two photocatalysts: $TiO_2$-Tytanpol A11 and $TiO_2$-Degussa P25 under UV/Vis illumination. The studies were performed at pH = 2 because in our earlier works [7,8] we concluded that photocatalytic decomposition of the dyes are most efficient in acidic solution.

## 2. Experimental

### 2.1. Materials

Three dyes: RR198, AB1 and AB7 were used in the experiments. All dyes are supplied by the “Boruta Colour” company (Poland). Their molecular structure is shown in Fig. 1. RR198 and AB1 belong to the group of azodyes

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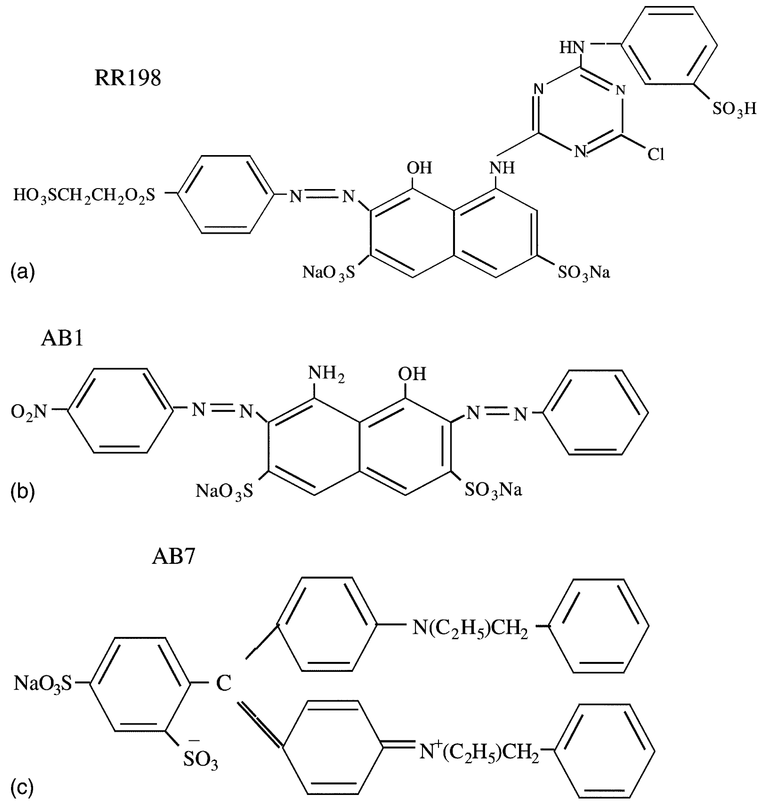

Fig. 1. The molecular structure of: (a) RR198, (b) AB1 and (c) AB7.

and AB7 is an arylmethane dye. All these compounds exhibit a maximum absorption in the range of visible light and give dyeing with different fastness properties to light (4–5 for RR198, 5–6 for AB1 and 2 for AB7—ISO BlueWool Scale). This parameter (photostability) was estimated by the "Boruta Colour" company, and it is defined in eight-gradual scale and refers to the dyes present in the final product. According to the manufacturer, all dyes are in the *cis* form.

Two types of photocatalyst were used in the reaction of photocatalytic decomposition of organic dyes in water: Tytanpol A11 supplied by the Chemical Factory "Police" (Poland) and P25 produced by Degussa (Germany). The photocatalysts are marked as A11 in case of $TiO_2$-Tytanpol A11 and P25 for $TiO_2$-Degussa P25.

According to the manufacturers data, A11 has a specific surface area of 11.4 $m^2/g$ and a mean pore diameter of about 7.7 nm, while the P25 has a specific surface area of 52 $m^2/g$ and a mean pore diameter of about 6.9 nm. These data were confirmed by our own analysis—nitrogen gas adsorption method using Micrometrics ASAP 2010 apparatus. The phase composition and crystallite size of the catalysts were identified by X-ray diffraction analysis (Germany HZG-4 diffractometer) using graphite monochromatized Co Kα radiation.

The band gap energies of titanium oxides were determined using a DR UV-Vis method. Specord M40 spectrometer was equipped with an integrating sphere for diffuse reflectance. $BaSO_4$ was used as a reference. The characteristic parameters of the photocatalysts are listed in Table 1. The experimental details were given earlier [7,8].

### 2.2. Procedure

The elimination of the dyes was studied under different conditions: (i) under UV/Vis illumination and in UV/Vis/$O_2$ system without the photocatalyst and (ii) under UV/Vis illumination in presence of the photocatalyst and oxygen. All the reactions were carried out at pH = 2. The pH of the solution was adjusted using HCl.

Photoreaction of the dye decomposition was carried out in the quartz bath photoreactor with the outer light source (VT-400 mercury lamp with power of 180 W). The scheme

Table 1
The characteristic parameters of photocatalysts A11 and P25

| Photocatalyst | Crystalline phase | Crystallite size (nm) | Specific surface area ($m^2/g$) | Average pore diameter (nm) | Band gap energy (eV) |
|---|---|---|---|---|---|
| A11 | Anatase | 37.3 | 11.4 | 7.7 | 3.31 |
| P25 | Anatase + rutile | 25.5 | 52 | 6.9 | 3.14 |

of the apparatus is presented elsewhere [9]. The reactions carried out in the presence of a photocatalyst were performed according to the following procedure: 0.5 $dm^3$ of a dye solution containing 15 mg of dye and 0.2 g of photocatalyst powder were placed in the photoreactor and was magnetically stirred before and during illumination. The suspension was mixed for 15 min in the dark (for adsorption of dye onto photocatalyst surface) and then the reaction mixture was exposed to the UV/Vis light. The suspension was oxidized. The samples of reaction mixture were taken from reactor, at appropriate time intervals, in order to determine the dye concentration. The photocatalyst was removed from the solution using the PVDF membrane with 0.45 μm pore diameter.

In the case of the elimination of the dyes studied without photocatalyst under UV/Vis illumination and in UV/Vis/$O_2$ system, the dye concentration was 30 $mg/dm^3$ (15 mg of a dye in 0.5 $dm^3$ of the solution). This solution was illuminated with UV/Vis light for 40 min.

The change in concentration of the dyes was measured using a UV/Vis spectrophotometer (Specord M40) at fixed wavelength of 638, 619 and 518 nm for AB7, AB1 and RR198, respectively.

Some experiments were performed in order to examine if the dye decomposition occurs on the photocatalyst surface. Dye solution of 0.5 $dm^3$ containing 15 mg of a dye and 0.2 g of a photocatalyst powder were magnetically stirred for 15 min in the dark. After this time the reaction mixture was illuminated for 100 min in the case of both A11 and P25 photocatalyst. The suspension was aerated. After 100 min of illumination the photocatalyst was separated from the solution and dried at a temperature of 50 °C. The obtained photocatalyst samples were analysed using a FTIR/DRS method (Jasco-Japan/Harrick-USA).

The adsorption of dyes on the $TiO_2$ surface (A11 and P25) was measured at $pH = 2$. For each dye, equal amounts of photocatalyst (0.2 g) and 200 ml of the dye solution (30 $mg/dm^3$) were placed in test tubes. The samples were magnetic stirred for 15 min in the dark, and then filtered. The photocatalyst samples were dried at a temperature of 50 °C and the obtained materials were analysed using the FTIR/DRS method.

## 3. Results and discussion

At the beginning, the blank experiments were carried out under the following conditions: without photocatalyst and under UV/Vis irradiation, and without the photocatalyst and under illumination and simultaneous aeration. The effect of UV/Vis illumination and simultaneous illumination and aeration on the bleaching of the dye solution is presented in Fig. 2. In the case of both experimental conditions the degree of bleaching of the dyes in decreasing order is as follows: RR198 > AB1 > AB7. The RR198, AB1, AB7 bleaching degrees were 10.4, 6.2, 3.6%, respectively. Simultaneous irradiation and aeration caused an increase of the degree of the dye decomposition indicating possible role of an active oxygen species. After 40 min of UV/Vis illumination and aeration, degrees were 24.2% for RR198, 13.7% for AB1 and 7.2% for AB7.

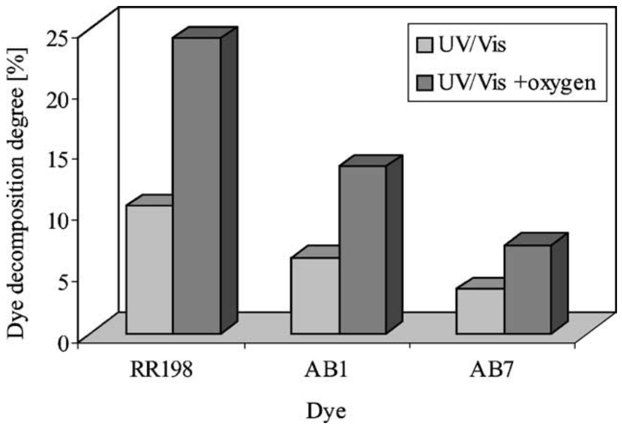

Fig. 2. Photocatalytic decomposition of RR198, AB1 and AB7 under UV/Vis illumination and under illumination and simultaneous aeration at $pH = 2$.

The results of the photobleaching of RR198, AB1 and AB7 dye solutions (30 $mg/dm^3$) in the presence of titanium oxides A11 and P25 at $pH = 2$ are shown in Fig. 3. After 15 min of magnetic stirring without UV/Vis illumination, the

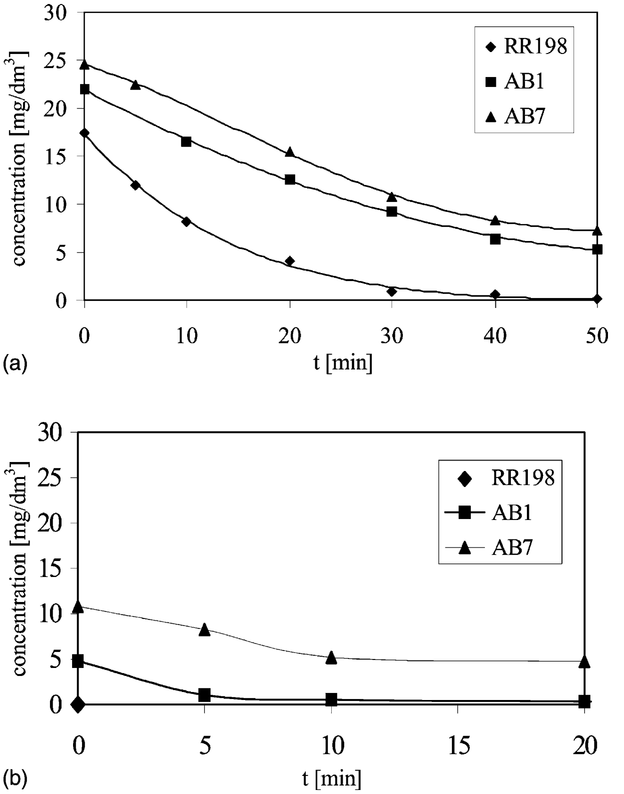

Fig. 3. Photocatalytic degradation of RR198, AB1 and AB7 at $pH = 2$; A11 (a) and P25 (b).

adsorption of RR198, AB1, AB7 on A11 surface was 12.6, 8, 5.4 mg, respectively. In the presence of $TiO_2$-A11 the dyes bleached in decreasing order as follows: RR198 > AB1 > AB7. It is clearly seen from Fig. 3a that RR198 solution has the highest bleaching rate and AB7 has the lowest one. After 50 min of UV-Vis irradiation, 100% of RR198 in the solution and 85% of AB1 in the solution bleached. In case of AB7, degree of bleaching was only 70%.

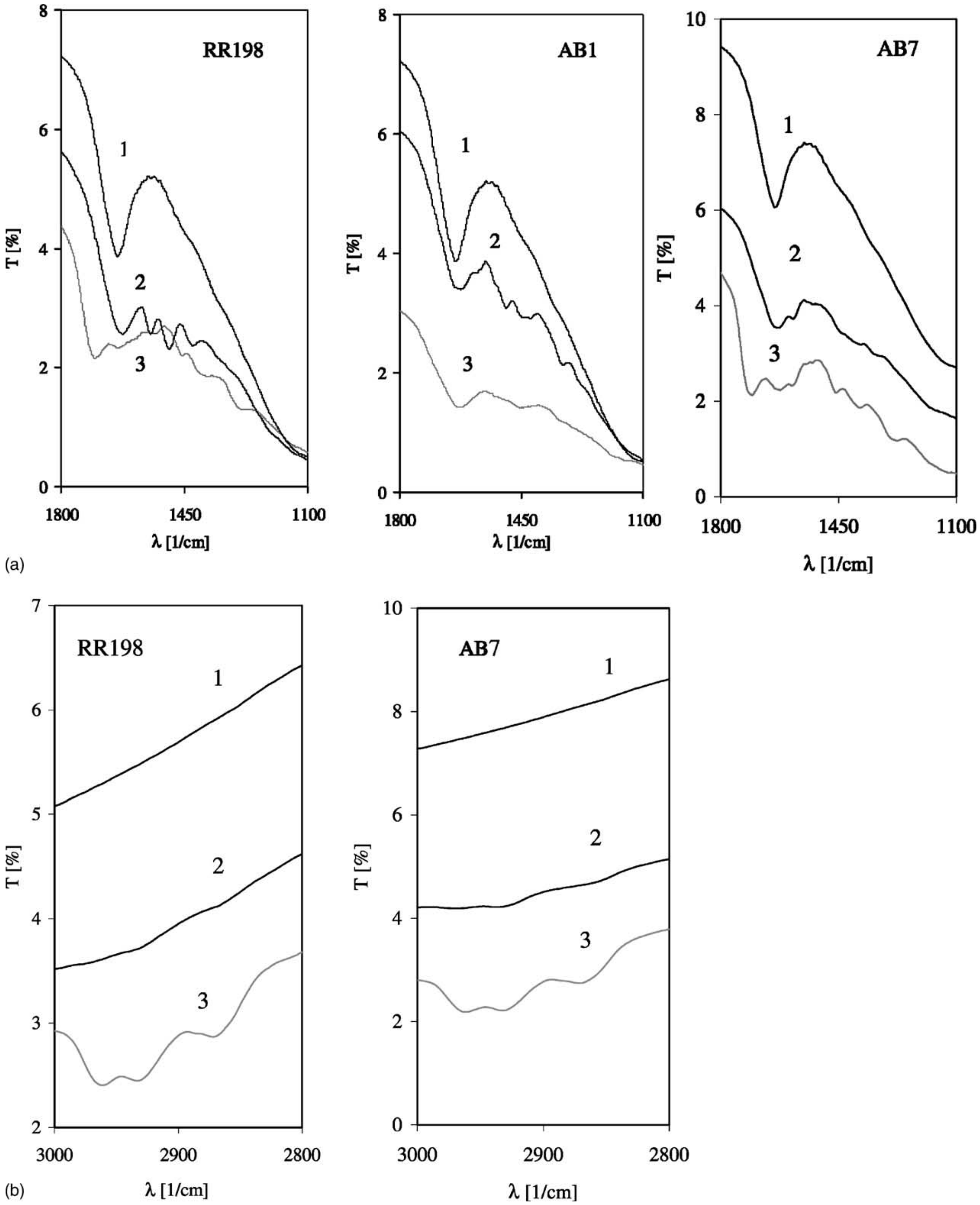

Fig. 4. FTIR/DRS spectra of RR198, AB1 and AB7 in range (a) 1100–1800 $cm^{-1}$ and of RR198, AB7 in range (b) 2800–3100 $cm^{-1}$ for photocatalyst A11. Pure photocatalyst (1), photocatalyst after adsorption (2) and photocatalyst after illumination (3).

For photocatalyst P25 (Fig. 3b) the solution of RR198 was decolourized after 15 min of magnetic stirring without UV/Vis illumination. This fact suggests that all RR198 was adsorbed on the P25 photocatalyst surface. After the same time period the adsorption for the other two dyes on the P25 surface was 25.2 mg for AB1 and 19.2 for AB7. After 20 min of UV-Vis irradiation 100% of AB1 and 90% of AB7 bleached. After 50 min of illumination for A11 and 20 min of illumination in case of P25, the photocatalysts were strongly coloured. On the basis of these observations we can state that the tested dyes did not undergo complete decomposition in the solution at $\mathrm{pH} = 2$, but they were strongly adsorbed on the photocatalyst surface. In the case of both photocatalysts, AB7 was the most difficult to decompose among the three dyes in this study.

The next series of experiments was conducted in order to decompose the dyes adsorbed on the photocatalyst A11 and P25 surfaces. The photocatalyst samples A11 and P25 both after adsorption of dyes in the dark and 100 min of illumination in the solution at $\mathrm{pH} = 2$ were than analysed by the FTIR method. The FTIR patterns of pure photocatalysts A11 and P25, photocatalysts after adsorption and after illumination are shown in Fig. 4 (for A11) and Fig. 5 (for P25). In both cases after adsorption of the dyes in the dark, new lines at region 1100–1800 $\mathrm{cm}^{-1}$ in the patterns appeared. In the cases of RR198 and AB1, characteristic vibrations with maxima at about 1620, 1550, 1500, 1420 $\mathrm{cm}^{-1}$ are observed for both photocatalysts. These bands are characteristic for the adsorbed dyes. These peaks can be attributed to aromatic skeletal vibrations. The bands at region 1625–1575 and 1525–1440 $\mathrm{cm}^{-1}$ are characteristic of C=C aromatic skeletal vibrations. Band at 1500 $\mathrm{cm}^{-1}$ can be assigned to an azo-bond vibration or aromatic ring vibration. For AB7 characteristic vibrations at 1623, 1580, 1400, 1345 $\mathrm{cm}^{-1}$ are observed in cases of both photocatalysts. AB7 does not have an azo-bond (N=N) in its structure, and there is no peak at 1500 $\mathrm{cm}^{-1}$ at FTIR pattern [6,10,11].

After 100 min of irradiation of the photocatalyst P25 with adsorbed dyes, peaks in a range 1100–1800 $\mathrm{cm}^{-1}$ diminished. This fact confirmed that at $\mathrm{pH} = 2$ the degradation of the tested dyes takes place on the photocatalyst surface. It was visible to the naked eye: the catalyst after illumination had less coloration than the catalyst after adsorption.

For A11 photocatalyst, absorption bands in the range 1100–1800 $\mathrm{cm}^{-1}$ also diminished for RR198 and AB1 but not as strongly as for P25 after 100 min of irradiation. In the case of AB7 bands in this range deepened. Additionally, in the case of RR198 and AB7, new adsorption bands appeared in the range 2800–3100 $\mathrm{cm}^{-1}$ (Fig. 4b). The peak positions are noticed at 2961, 2931, 2869 $\mathrm{cm}^{-1}$. Bands at about 2961 and 2869 $\mathrm{cm}^{-1}$ originate from the $\mathrm{CH_3}$ asymmetric and symmetric stretching vibrations while the band at 2931 $\mathrm{cm}^{-1}$ is the $\mathrm{CH_2}$ asymmetric stretching vibration [11,12]. The spectra in Fig. 4a also show a new band appearing at 1700 $\mathrm{cm}^{-1}$, which is characteristic of a carboxylic acid functional group [6]. This suggests that the molecules of dyes undergo chemical changes, and by-products are adsorbed on the photocatalyst surface. After 100 min of illumination

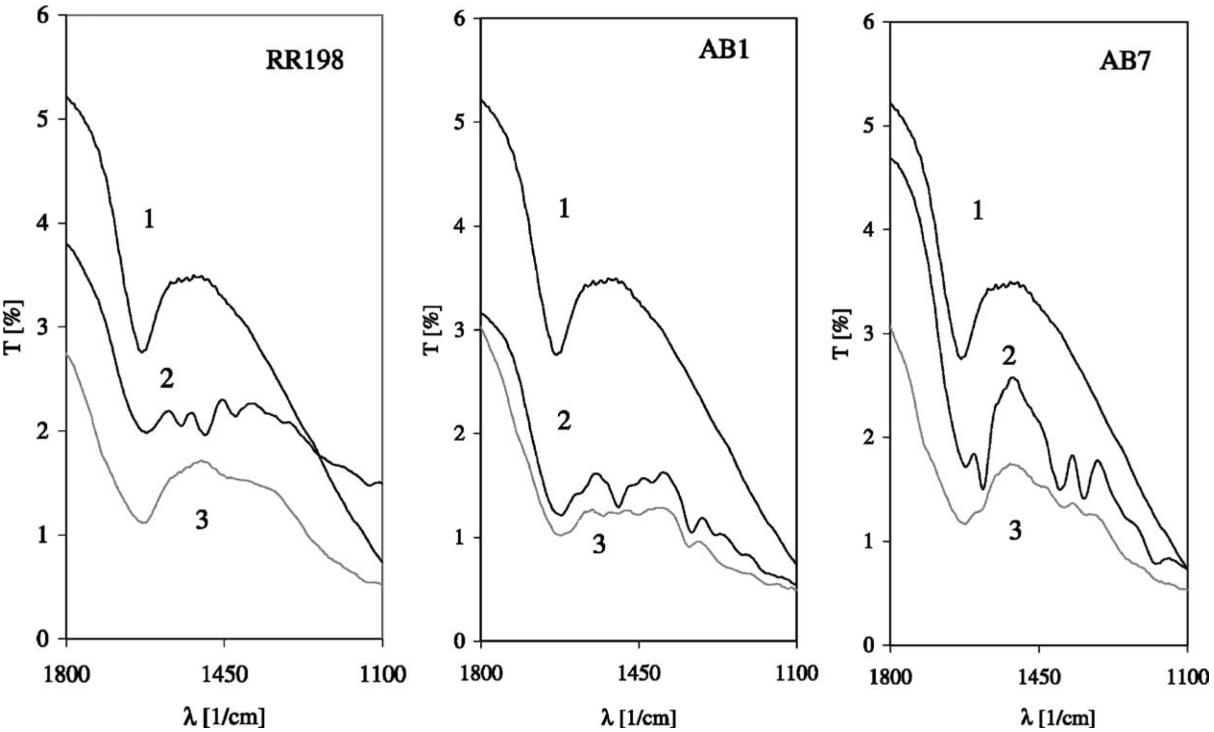

Fig. 5. FTIR/DRS spectra of RR198, AB1, AB7 for photocatalyst P25. Pure photocatalyst (1), photocatalyst after adsorption (2) and photocatalyst after illumination (3).

the photocatalysts A11 and P25 did not completely decolourize and P25 had less colouration than A11.

## 4. Conclusions

In this work the photocatalytic decomposition of three dyes (RR198, AB1, AB7) has been studied under UV/Vis irradiation at $\mathrm{pH} = 2$, in the presence of two catalysts: Tytanpol A11 and Degussa P25. The established order of decolouration was as follows: RR198 $>$ AB1 $>$ AB7. This order does not cover the light resistance of the dyes. On the basis of obtained FTIR results, we can state that, in the applied reaction conditions, decomposition of the tested dyes is controlled by the photocatalyst surface. In the case of both studied photocatalysts, after adsorption of the tested dyes on the catalyst surface in the dark, new lines in the FTIR patterns appeared in the range 1100–1800 $\mathrm{cm}^{-1}$, which belongs to the pure dyes. These absorption bands almost completely diminished after 100 min of UV/Vis illumination of the P25 sample. The P25 catalyst after 100 min of illumination had significantly less colouration than the catalyst after adsorption. In the case of photocatalyst A11, after 100 min of irradiation other new absorption bands in the region of 1700 and 2800–3100 $\mathrm{cm}^{-1}$ for RR198 and AB7 appeared that are characteristic for the intermediate by-products. This suggests that created by-products are adsorbed on the photocatalyst surface active sites and therefore photocatalyst A11 showed a lower activity than P25. Higher specific surface area and lower band gap energy of P25 prevents by-product formation on active sites and accelerates activity for photocatalysis.

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