

PHOTOCATALYTICAL TREATMENT OF CAR-WASH WASTEWATER

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ABSTRACT

Photocatalytic oxidation is a promising technology for purification of biological pretreated wastewater or destruction of non-biodegradable compounds. For this reason photocatalytic process has been investigated to purification of biologically pretreated car-wash wastewater. The influence of the parameters UV-radiation, different types of TiO₂, TiO₂-concentration, pH, catalyst reuse, TiO₂-modification and improvement of biodegradability has been investigated. The biologically pretreated wastewater was treated with an Aerated Photoreactor (AP) which was modified for batch experiments. The total organic carbon (TOC) in the wastewater is able to remove with different photocatalysts, but at different reaction rates. The degradation rate of the TOC in the wastewater was found to be pseudo first order. Degradation with P25 was more active than UV-100 and PC 50 photocatalysts and also than the modified catalysts and TOC degradation reached 93 %. The degradation rate of TOC was increased with increasing TiO₂ concentration up to 5 g/L with P25 and 7 g/L with both UV-100 and PC 50. The adsorption rate with UV-100 was more than the other catalysts at all TiO₂ concentration and pH values. The maximum degradation rate of TOC was achieved at a pH of 5 with P25. UV light combined with a catalyst was the best available technique for degrading the TOC. P25 proved to be quite efficient in the enhancement of TOC biodegradability.

Keywords

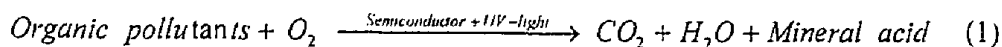
Car-wash wastewater; photocatalysts; titanium dioxide; wastewater treatment and reuse; improved biodegradability

INTRODUCTION

Car washing produces large volumes of wastewater which is polluting the environment. The average volume of wastewater discharged in one wash cycle is approximately 250 L for a car and 1200 L for buses/trucks. The main pollutants of car-wash wastewater are oils, greases, particles (such as dust, carbon, asphalt and salt) and detergents or solvents used in the washing operation [1]. The wastewater may also contain hydraulic fluids and motor oil as a result of leakage of the braking system and the engine. Like most industrial effluents, car-wash wastewater varies significantly in quantity as well as in composition [2-4]. Because of the large variety of chemicals applied in car washing, the organic content of wastewater is normally measured using integral parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) or hydrocarbon content.

The car-wash wastewater is treated by mechanical treatment steps such as filtration and oil-separation followed by a biological process [3]. However, these techniques do not completely remove the contaminants from water. In particular 10 - 30 % of the initial COD remains in the so treated wastewater in form of refractory contaminants like toxic and non-biodegradable substances and which have to be removed by specific methods such as advanced oxidation processes [5].

Water treatment by photocatalysts has been intensively investigated in recent years. A growing interest in the treatment of water by photocatalysts, especially for the removal of refractory organic pollutants, is evidenced by the ever-increasing number of studies in this field [6, 7]. Heterogeneous photocatalytic oxidation processes involve the use of a photoactive n-type semiconductor illuminated with near-UV light. In an oxygenated aqueous suspension a redox environment is produced which can oxidise organic compounds. The overall process can be summarised by the following reaction equation [8, 9]:



The most suitable semiconductor photocatalyst for sensitizing above reaction is TiO₂. There are many different source of TiO₂. The adopted wavelength of UV light for TiO₂ is about 365 nm in order to avoid the direct photolysis of organic compounds. The main objective of this study was the elimination of the refractory contaminants in biologically pre-treated car-wash wastewater by applied photocatalysts using three commercial types of TiO₂ (Degussa P25, Hombikat UV-100 and Millennium PC 50) changing the following parameters: UV-radiation, TiO₂ concentration, dark adsorption and pH. Additional parameters were studied with the P25 photocatalyst such as the effect of a catalyst reuse, biodegradability enhancement and the impact of a surface modification by aluminium dioxide, platinum oxide and iron oxide on the photocatalytic activity.

EXPERIMENTAL

Wastewater characteristics and collection

Different samples of biologically pre-treated wastewater were collected at the Aral/BP gas-station in Germany. The samples were stored at room temperature (20 ± 1 °C). The main properties of the investigated wastewater are listed in Table 1.

Table 1: Main characteristics of biologically pre-treated car-wash wastewater

<i>Parameter</i>	<i>Unit</i>	<i>Value</i>
pH	-	6.8 - 7.7
TOC	mg/L	25 - 51
COD	mg/L	57 - 118
BOD ₅	mg/L	< 3* - 24
Conductivity	mS/cm	0.54 - 2.58
T-P	mg/L	0.2 - 0.3
T-N	mg/L	1.6 - 6
O ₂ -content	mg/L	2.4 - 6.8
Chloride	g/L	0.12
Color	-	Light yellow

*below the detection limit of the standard BOD₅ test

Materials:

Three different commercially available titanium dioxide catalysts were used without further pretreatment. Degussa P25, Hombikat UV-100 and Millennium PC 50 photocatalysts are abbreviated as P25, UV-100 and PC 50, respectively. Their characteristics are given in Table 2. The surface areas of the P25 photocatalyst modified with aluminum dioxide (with two different Al₂O₃ concentrations), platinum oxide and iron oxide are listed in Table 3.

Table 2: Physical characteristics of the TiO₂ photocatalysts

<i>Photocatalyst</i>	<i>Company</i>	<i>Specific surface area, m²/g</i>	<i>Particle size, nm</i>	<i>Crystal structure</i>
P25	Degussa	50 ± 15	20 - 30	70 % Anatase, 30 % Rutile
Hombikat UV-100	Sachtleben Chemie GmbH	> 250	< 10	> 99 % Anatase
Millennium PC 50	Millennium Inorganic Chemicals	50	20 - 30	100 % Anatase

Table 3: Physical characteristics of the modified P25 photocatalyst

<i>Photocatalyst</i>	<i>Company</i>	<i>Specific surface area, m²/g</i>
Al ₂ O ₃ /TiO ₂	Degussa	85
Al ₂ O ₃ /TiO ₂	Degussa	55
Fe ₂ O ₃ /TiO ₂	Degussa	77
PtO ₂ /TiO ₂	Degussa	73

Photocatalytic reactor

The experimental set-up of the aerated photoreactor (AP) system employed for the photocatalytic treatment is presented in Fig. 1. The photoreactor (1) consists of a double-skin sheet with five channels where each channel with one liter acts as a small stirred tank reactor. It is made of UV-transparent acrylic glass (Plexiglas) (SDP 16/600-32) manufactured by Röhm GmbH, Darmstadt, Germany [10]. Air was supplied and distributed to the channels by an ethylpropylene-membrane (Gummi Jäger, Hannover, Germany) installed at the bottom of the reactor (2). The reactor system is open at the top for adding the catalyst and wastewater, taking samples and for venting the exhaust air. The reactor was illuminated with 10 UV-A lamps (Ergoline R 100 W/1760 from Philips) forming a constant UV-A light field with a specific intensity of approximately 100 - 110 W/m². The illuminated reactor surface area for each channel was 0.077 m². The UV-A lamps were cooled with a fan incorporated into the lamp housing. The pH was continuously monitored by electrodes installed in the reactor (4).

Experimental procedure

The inclination angle of the AP reactor was adjusted at 60°. Prior to and during the experiments the pH of the solution was adjusted to the desired value employing dilute H₂SO₄ and NaOH solutions for pH control. For the photocatalytic experiments the wastewater was mixed with the catalyst and aerated at a constant superficial gas velocity of 2 mm/s in the reactor. Prior to radiation the suspension (catalyst and wastewater) was maintained in the dark for 30 min to reach adsorption equilibrium of the pollutant. Time zero corresponded to the beginning of UV-radiation. Samples were periodically withdrawn after 0, 15, 30, 60, 90, 120 and 180 min. The photocatalytic operating conditions are summarised in Table 4.

Analyses

The catalyst was separated by sedimentation before analysing the samples. TOC was detected by a Shimadzu Analyzer TOC 5000. COD and BOD₅ were analyzed according to the German standards of DIN 38 409 - H 41 and DIN 38 409 - H 51.

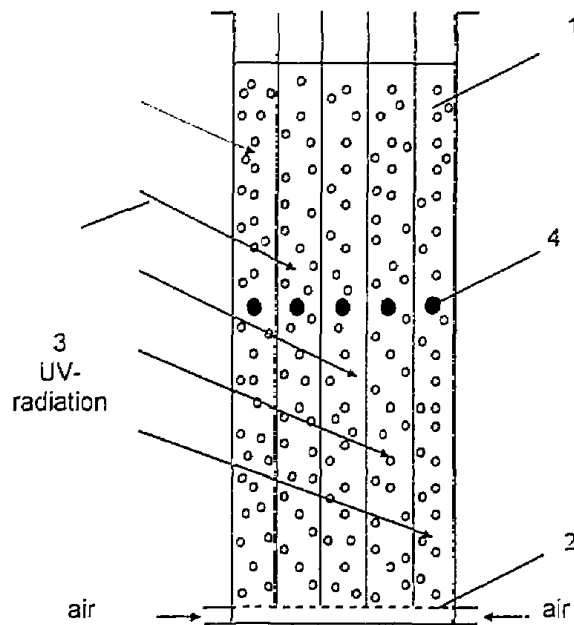


Fig. 1: Set-up of the Aerated Photoreactor (AP)

Table 4: Conditions of the photocatalytic experiments

<i>Parameter</i>	<i>Unit</i>	<i>Value</i>
TiO ₂ concentration	g/L	0.5 - 10
Superficial gas velocity	mm/s	2
Reaction volume	L	1
Initial TOC concentration	mg/L	29 - 45
pH	-	3 - 9
Temperature	°C	20 ± 1

RESULTS AND DISCUSSION

The evaluation of the treatment process is based on measuring the changes of TOC, COD and BOD₅ under variation of the more important parameters.

1. Effect of UV-radiation

The performance of photocatalysts with and without an artificial radiation source was studied with a catalyst concentration of 5 g/L at a pH of 5. The photocatalytic data have been corrected by discounting the adsorption during the first 30 min in dark. The extent of photocatalytic degradation of the total organic carbon (TOC) with P25 is shown in Fig. 2.

The TOC was reduced from 40 to 30 mg/L during 30 min of dark adsorption. As can be seen in Fig. 2 the TOC concentration drops from 30 to 2 mg/L during 3 hr treatment by P25/UV-A. Only a very small decrease in the concentration of TOC was observed when irradiated by UV-A only whereas P25 removes more than 30 % of the TOC by adsorption during 3 hr. A comparison of these experiments indicates the improvement of purification by using photocatalytic oxidation.

The same effect of UV-radiation on TOC degradation rate was observed with UV-100 and PC 50 photocatalysts but at different TOC degradation rates. It can be concluded that UV light combined with the TiO₂ photocatalyst is the best available technique for degrading TOC.

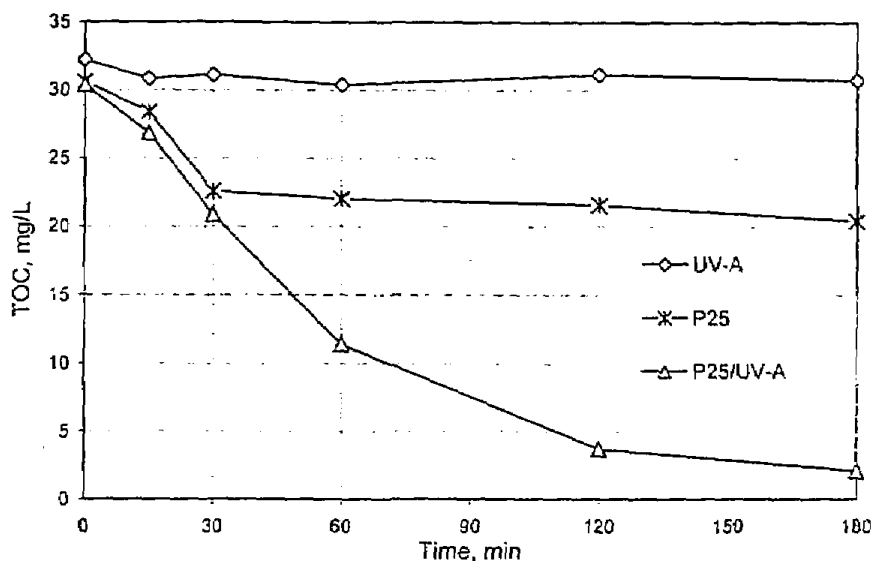


Fig. 2: Effect of P25 on the TOC degradation at a TiO_2 concentration = 5 g/L and pH = 5

2. Effect of different types of TiO_2 photocatalysts

The photocatalytic activities of P25, UV-100 and PC 50 were compared under identical conditions. All data were corrected by discounting the adsorption during the first 30 min in dark. The degradation of TOC as a function of radiation time for a TiO_2 concentration of 5 g/L and pH = 5 is illustrated in Fig. 3.

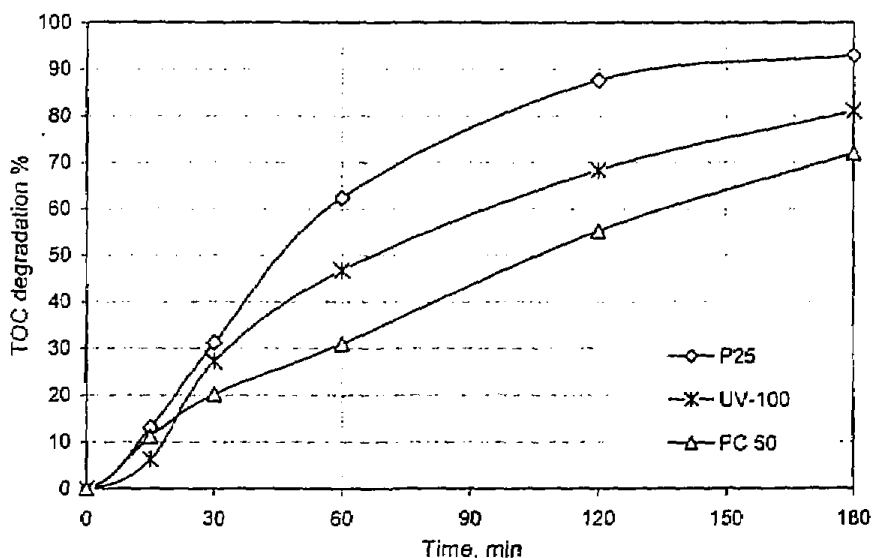


Fig. 3: The effect of three TiO_2 photocatalysts on the TOC degradation at a TiO_2 concentration = 5 g/L and pH = 5

Obviously P25 is more active than UV-100 and PC 50 in the photodegradation of TOC. TOC degradation increased with increasing radiation time for all catalysts. P25 degraded more than 93 % of the TOC after 3 hr of photocatalytic treatment resulting in a residual TOC of 2.5 and 9 mg/L with P25, UV-100 and PC 50, respectively.

A kinetic expression for the degradation is very useful for the design of large scale photoreactors. The TOC photodegradation of all photocatalysts could be modeled assuming pseudo-first-order

kinetics. Table 5 shows the calculated rate constant K and the half-life ($t_{1/2}$) for each catalyst after three hours of radiation.

Table 5: Pseudo first order rate constant and half-life time of different photocatalysts

<i>Photocatalyst</i>	<i>K, 1/min</i>	<i>R²</i>	<i>t_{1/2}, min</i>
P25	0.016	0.9854	44
UV-100	0.009	0.9939	74
PC 50	0.007	0.9970	99

In order to understand the different photocatalytic activities of P25, UV-100 and PC 50, a basic knowledge of the three photocatalysts as listed in Table 2 is essential. Undoubtedly, the photocatalytic activity of the photocatalyst will be influenced by the particle size of the catalyst. It is well known that the TOC degradation by photocatalysts is limited by the undesired recombination of photogenerated charge carriers which are of two kinds: volume recombination and surface recombination. Each recombination relates directly to the particle size and active surface sites. A decrease in particle size leads to the reduction of volume recombination. Also the active surface sites increase with decreasing particle size.

The particle size of P25 and PC 50 is the same and approx. three times the particle size of UV-100. The rate constant of P25 was more than two times that of PC 50 and 1.5 times that of UV-100 indicating that the photocatalytic activity is not determined alone by the particle size but also influenced by other factors such as the microstructure, composition and surface characteristics, etc. The high photoactivity of P25 may be accounted for by the anatase-rutile ratio of the catalyst. Whereas UV-100 and PC 50 consist of pure anatase, P25 is made up of 70 % anatase and 30 % rutile. This agrees with results from Bacsá and Kiwi [11] who found that titania containing both anatase and rutile shows a significantly higher photocatalytic activity compared to pure anatase or rutile. P25 is also reported to have a higher hydroxyl radical generation than anatase TiO₂ particles [12].

3. Effect of TiO₂ concentration

The catalyst concentration is one of the main parameters and its optimal value is closely connected with light intensity, optical properties of the catalyst, reactor configuration and absorption spectra of the wastewater. TiO₂ concentration in photocatalytic slurries strongly affects the degradation of TOC as found in experiments where the concentration of the photocatalysts was changed from 0.5 to 10 g/L at a pH of 5 during 3 hr of radiation. The effect of adsorption during the first 30 min in the absence of light and the effect of UV radiation were investigated as follows:

Effect of dark adsorption

The dark adsorption of TOC during the first 30 min with P25, UV-100 and PC 50 catalysts is shown in Fig. 4. The adsorption of UV-100 was higher compared to the other catalysts for all TiO₂ concentrations. The adsorption order of the three catalysts was: UV-100 > P25 > PC 50 which is possibly due to the different specific surface area of the catalysts. The specific surface area of the catalysts is 250, 50 and 50 m²/g for UV-100, P25 and PC 50, respectively. This result was to be expected as adsorption depends on the surface area of the catalyst.

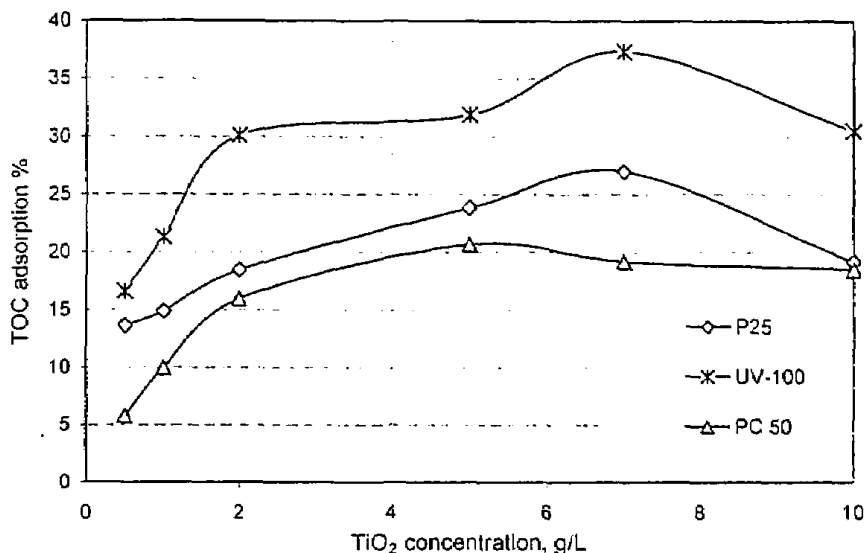


Fig. 4: Effect of TiO₂ photocatalyst concentration on the dark adsorption of TOC at a pH = 5 and 30 min of dark adsorption

As to be expected, the adsorption increased with the catalyst concentration (see Fig. 4). The maximum TOC adsorption was achieved with 7 g/L of TiO₂ and decreased if the catalyst concentration was further increased (10 g/L). The explanation of this result may be related to the suspendibility of the catalyst particles. At high catalyst concentrations (> 7 g/L) it becomes difficult to get a uniform suspension throughout the solution as the catalyst tends to accumulate on the surface of the reactor. All experiments were conducted at a constant superficial gas velocity of 2 mm/s.

Effect of UV-radiation time

Fig. 5 shows the TOC degradation as a function of the radiation time for P25. The TOC degradation was more rapid at higher catalyst concentrations and increased with increasing radiation time. This was to be expected as more catalyst particles will provide for more sites for photocatalytic oxidation and thus for a faster TOC degradation.

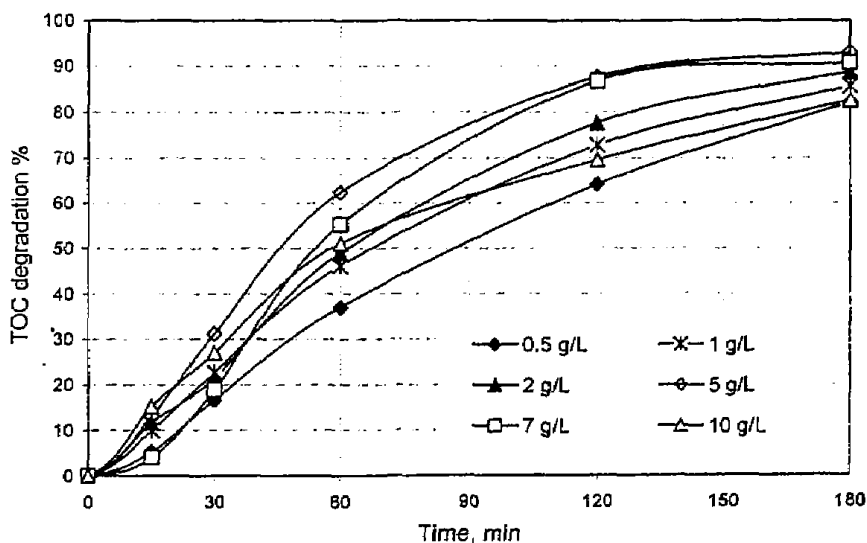


Fig. 5: Effect of P25 concentration on the TOC degradation at a pH = 5

The variation in degradation rate constant of TOC against the concentration of TiO₂ was determined (see Fig. 6) as a function of the type of catalyst for 3 hr radiation time and a pH = 5. The rate constant of P25 is higher for all catalyst concentrations compared to the other catalysts. The maximal K value was 0.016 1/min at a P25 catalyst concentration of 5 g/L and TOC degradation was more rapid with a half-life time of 44 min. The most efficient TiO₂ concentration was not the same for all catalysts and the maximum rate constant was found with UV-100 and PC 50 at a catalyst concentration of 7 g/L.

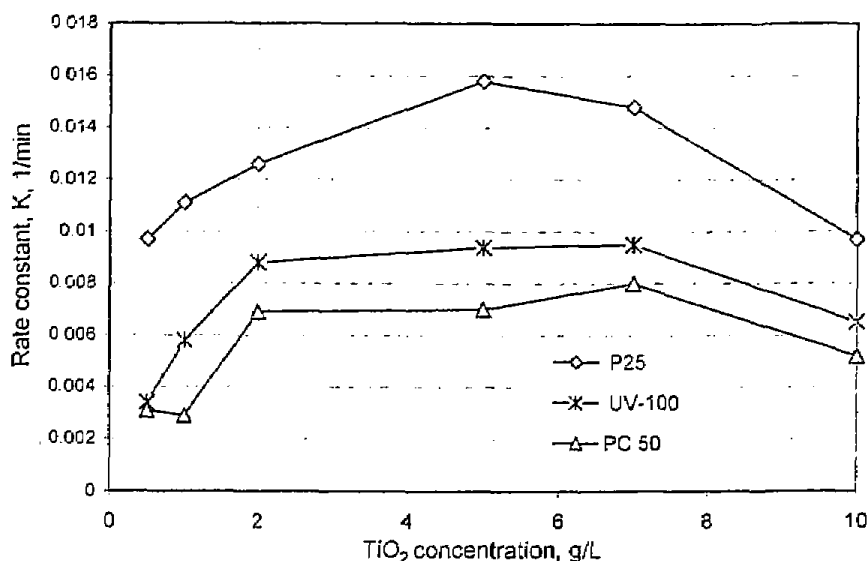
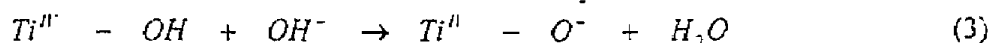


Fig. 6: Rate constants of TiO₂ photocatalysts for 3 hr radiation time and a pH = 5

This optimal catalyst concentration of 7 g/L can be explained as follows: (a) at high catalyst concentrations the TiO₂ particles aggregate resulting in a decrease of the number of surface active sites, (b) the increase in opacity and light scattering of TiO₂ particles at high concentrations leads to a decrease in the transmittance of radiation through the sample and thus reduces the photoactivity of TiO₂. Similar results have been reported in previous studies [6, 13] for several photosystems. The optimal catalyst concentration for P25 is reported to be in the range of 0.1 to 5 g/L depending on the nature of the compounds and the photoreactor geometry [14]. From Fig. 6 the optimal catalyst concentration is 5 g/L for P25 and 7 g/L for UV-100 and PC 50 at a pH of 5.

4. Effect of pH

The pH is an important parameter in photodegradation as it affects the surface chemistry of the photocatalyst. The point of zero charge (pzc) for TiO₂ is between a pH of 5.6 and 6.4 [6]. Hence at a more acidic pH the catalyst surface is positively charged whereas at pH above 5.6 it is negatively charged [15]. Depending on the charge of the organic components present in the solution, there may be an electrostatic attraction or repulsion between the organic components and the titanium dioxide surface at different pH values [7, 16]. This is an important consideration in water treatment when the organic matter present in the water will vary in speciation and concentration [17].



The effect of pH on the degradation of TOC for a pH between 3 - 9 at a P25 concentration of 5 g/L is shown in Fig. 7. The effect of pH in the same range on the degradation rate constant for the three photocatalysts at a catalyst concentration of 2 g/L and 3 hr radiation time is given in Fig. 8. Fig. 7 indicates an increasing TOC degradation with increasing radiation time at all pH values and thus confirms the importance of the pH. Maximum degradation rates for TOC are obtained at a pH of 5 with $K = 0.013$, 0.009 and 0.007 1/min for P25, UV-100 and PC 50, respectively (see Fig. 8). Similar results have been reported in a previous study with paper-mill wastewater [18].

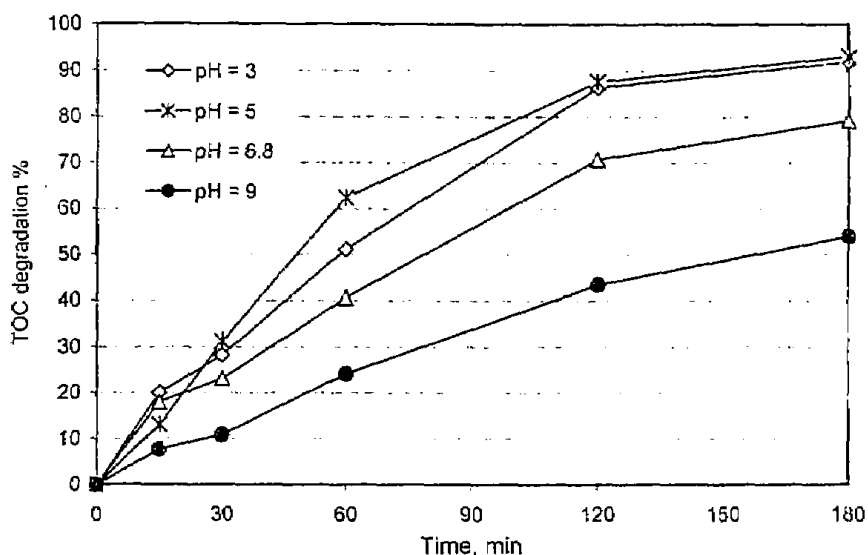


Fig. 7: Effect of pH on the TOC degradation for P25 at a catalyst concentration of 5 g/L

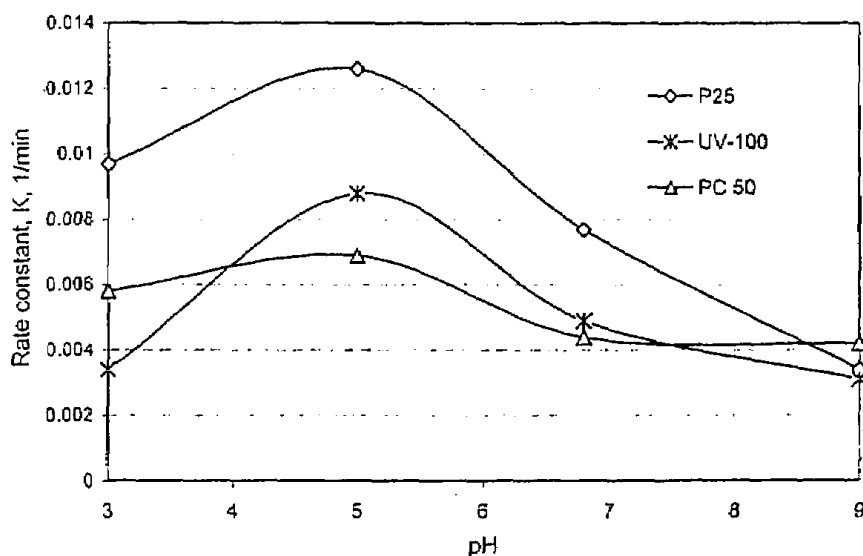


Fig. 8: Effect of pH on the TOC rate constant at a TiO_2 concentration of 2 g/L and 3 hr radiation time

As the optimum pH is near the point of zero charge of the catalyst, the explanation for the effect of pH on the degradation rate may be the charge separation on the particles as a high OH^- ion concentration enhances the electron-hole separation [19]. The photogenerated CO_2 , however, will be trapped in the solution. In alkaline systems bicarbonate and carbonate are formed which are efficient scavengers of hydroxyl radicals due to their rapid reaction with the hydroxyl radicals. On

the other hand, according to equation 4, low OH^- concentrations in an acidic system (at a pH = 3) hinder the formation of hydroxyl radicals and subsequently reduce the degradation rate.



Effect of pH on the adsorption

The effect of pH on a dark adsorption is shown in Fig. 9 at 2 g/L TiO_2 concentration and for 30 min. It was observed that the increase of the pH resulted in a significant decrease in the adsorption on TiO_2 .

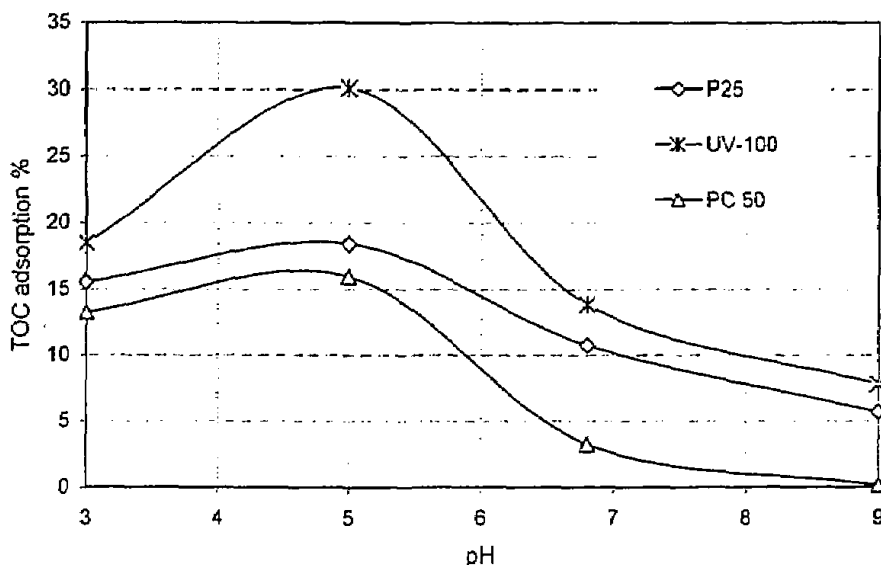


Fig. 9: Effect of pH on the dark adsorption of TOC for different TiO_2 catalysts at a TiO_2 concentration of 2 g/L and 30 min dark adsorption

The effect of the dark adsorption has a similar trend as the rate constants (see Fig. 8). UV-100 shows the highest activity of TOC adsorption at all pH values with the maximum adsorption at pH = 5. This result may be attributed to the surface area of UV-100 which is five times that of P25 and PC 50. The highest TOC elimination was achieved by UV-100 with a reduction from 37 to 26 mg/L.

5. Effect of reusing the catalyst

For using a catalyst in a technical application it must be known how the activity of the catalyst changes with time. Therefore, the performance of P25 was studied as a function of recycling the catalyst without regeneration. Sedimentation of P25 was fast and complete after turning off the aeration of the reactor and no TiO_2 could be detected in the clear water phase. Following sedimentation, the catalyst was washed with distilled water and reused several times. The experiments were irradiated for 2 hr at a pH of 5 and a P25 concentration of 5 g/L. In every run the photodegradation reaction was started after 30 min dark adsorption.

The results, as illustrated in Fig. 10, indicate a reduction of the TOC by 24 and 17 % from the initial TOC concentration during the dark period for the first and the last run, respectively.

The overall activity of P25 decreased slightly by 8 % for the second run and remained constant during the next four runs. The result agrees with findings of [20] showing that the photonic efficiency of a photocatalyst can be easily restored after washing the catalyst.

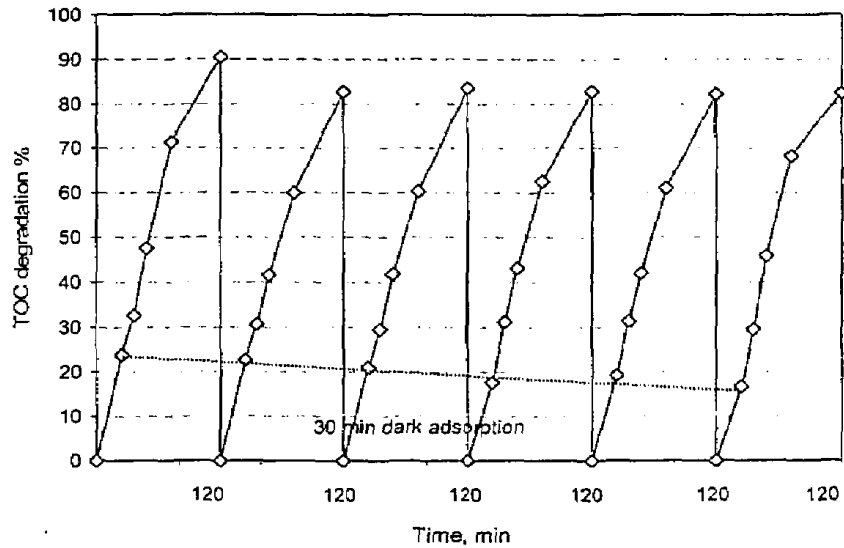


Fig. 10: Effect of reused P25 on the TOC degradation at a TiO_2 concentration = 5 g/L and pH = 5

6. Effect of photocatalyst modifications

A surface modification of TiO_2 changes the surface properties and may very effectively improve the photocatalytic activity of TiO_2 as demonstrated e.g. by impregnating the surface of titanium dioxide with platinum or silver [21–23]. Doping of titanium dioxide also leads to a better photodegradation of model compounds [24].

P25 from Degussa is widely used as a photocatalyst and prepared in a flame hydrolysis process, the so-called Aerosil[®] process. To improve the activity of P25 Degussa added different metals/oxides by flame hydrolysis and spray-doping during the titanium dioxide production by the Aerosil[®] process. P25 was, therefore, compared with four titanium dioxides doped with aluminium dioxide, platinum oxide or iron oxide (see Table 3). The photocatalysts were applied at a concentration of 5 g/L and a pH = 5 with the results shown in Fig. 11.

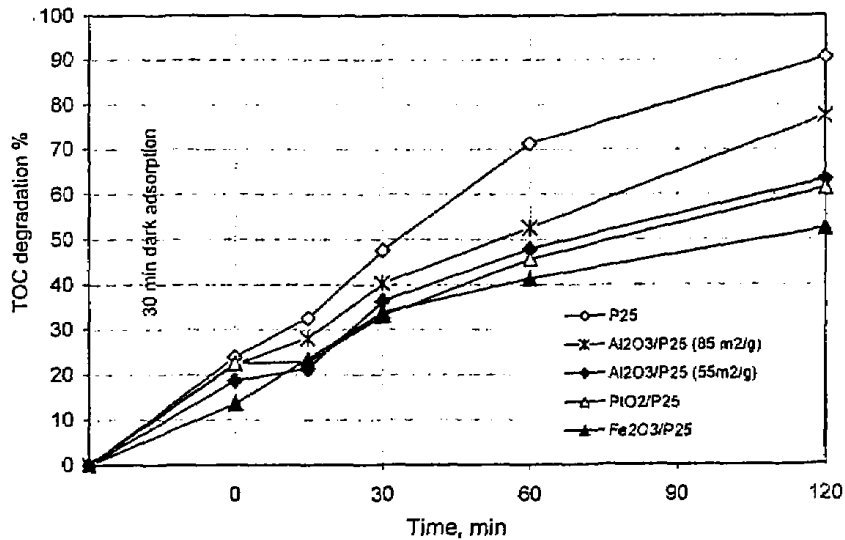


Fig. 11: Effect of modified P25 photocatalysts on the TOC degradation at a TiO_2 concentration = 5 g/L and pH = 5

Aluminised P25 gave better results than platinised P25 or P25 oxidised with iron but all modified catalysts show a lower activity than the unmodified P25. In contrast to the claims of Moiseev [18] who investigated the photodegradation of DCA in illuminated modified TiO₂ catalysts has reported that the photocatalytic activity was improved with the modified catalysts [Al₂O₃/P25 (85 m²/g), PtO₂/P25 and Fe₂O₃/P25] than the unmodified P25. Crittenden et al., [21] also found that the photocatalytic activity of P25 was reduced by platinizing the surface whereas spray-doping of P25 proved to enhance the photocatalytic activity [24].

Table 3 shows that the specific surface area of the modified catalysts is higher than that of P25 indicating that the surface area is not a deciding parameter. The reduction of the photocatalytic activity in Fig. 11 may be due to a reduction of the active sites resulting from a poor distribution of the metals/oxides on or in the TiO₂ particle.

7. Improvement of biodegradability

Degradation of contaminants by AOP's yields partially oxidised intermediates which may be more biodegradable than the original contaminants. In addition, the complete mineralisation of organic compounds is often neither necessary nor economical. It is often of advantage, therefore, to combine AOP's with other treatment processes. AOP's can be used e.g. as a pre-treatment process for the partial oxidation of organic compounds that are either too toxic or refractory for biological treatment followed by a biological oxidation [25-26].

A BOD₅/COD-ratio of 0.4 or higher is a useful indicator for assessing the biocompatibility of a wastewater as such wastewaters may easily be degraded biologically. Therefore, the biodegradability of the car-wash wastewater after photocatalytic treatment was determined at the following conditions: 30 min dark adsorption, 2 hr photocatalytic treatment, P25 concentration = 5 g/L and pH = 5.

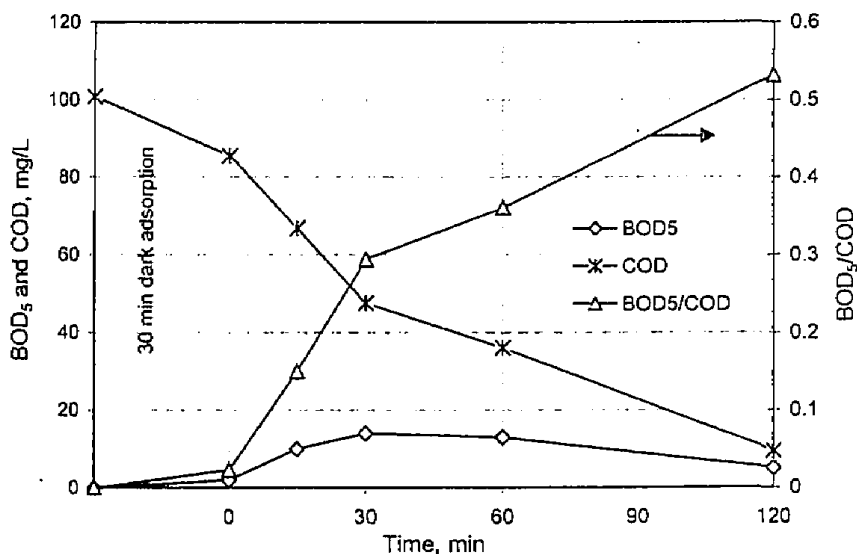


Fig. 12: P25 photocatalytic effect on biodegradability at a TiO₂ concentration = 5 g/L and pH = 5

The BOD₅ was less than 3 mg/L after the dark period indicating a poor biodegradability and increased to 14 mg/L during the first 30 min of radiation as shown in Fig. 12. This trend was to be expected since photocatalytic oxidation of organic matter results in a destruction of larger molecules into smaller more biodegradable compounds with about 90 % of the COD being degraded after 120 min. The biodegradability, defined by the BOD₅/COD-ratio, increased from zero to 0.54 indicating that the remaining pollutants may easily be removed by a conventional biological treatment.

CONCLUSION

To minimize the environmental impact of car washing, this study has presented the results of the degradation of refractory contaminants in biologically pre-treatment car-wash wastewater by photocatalytic with different TiO₂ and different parameters. P25 was the highest photocatalytic activity than UV-100 and PC 50. The adsorption rate with UV-100 was more than the other catalysts at all TiO₂ concentration and pH values. P25 gave the maximum pseudo-first order kinetic constants and the calculated half-life time was 44, 74 and 99 min with P25, UV-100 and PC 50 respectively. The maximum TOC degradation rate was achieved with 5 g/L of P25. The activity of the single P25 dose had a small influence during the second reuse and no catalyst deactivation was observed during the following four runs. The Degussa P25 was more active than the modified catalysts. In addition, photocatalytic by P25 has reduced chemical oxygen demand and enhanced the biodegradability of the wastewater by improving BOD₅/COD ratio from zero to 0.54.

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