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Removal of Refractory Contaminants Wastewater Using Biological Treatment Followed by Photocatalytic

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ABSTRACT

Biological treatment is considered environment-friendly and relatively cheap, but the complete removal of different contaminants is questionable. Photocatalytic process is widely used for the removal of refractory non-biodegradable compounds from industrial and municipal wastewater. Photocatalytic process has been investigated to purification of the refractory contaminants real wastewater after two steps of an aerobic biological treatment. The activities of three commercial types of titanium dioxide (TiO_2) photocatalysts (Degussa P25, Hombikat UV-100 and Millennium PC 50) were studied. In addition, TiO_2-concentration was investigated using an aerated photoreactor which was modified for batch experiments. After biological treatment the total organic carbon (TOC) degraded from 28 to 11 mg/L. The remaining of the hydrocarbon content was found 4.6 mg/L. Additionally, the biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio less than 0.02, the biological treatment was assumed to be complete. The results of photocatalytic treatment showed that, the TOC in the wastewater is able to remove with different photocatalysts, but at different reaction rates. Degussa P25 was more active than UV-100 and PC 50 photocatalysts with TOC degradation reached 83%. The degradation rate of TOC was increased with increasing P25 photocatalyst concentration up to 5 g/L. The degradation rate of the TOC in the wastewater was found to be pseudo first order and the maximum rate was achieved with P25. Reduction of 88 % of hydrocarbon content was achieved by P25.

Keywords: aerobic biological, photocatalytic degradation, titanium dioxide, gas-station wastewater, hydrocarbon content

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INTRODUCTION

Gas-stations generally produce a large volume of wastewater containing various pollutants. The average volume of wastewater discharged in one wash cycle is approximately 250 L for a car and 1200 L for buses/trucks [1]. This harmful wastewater and its enormous volume is one major

environmental concern. Gas-station wastewater is generated from many activities such as car washing, floor cleaning, toilet and cafeteria usage, etc. The main pollutants of gas-station wastewater are oils, greases, particles (such as dust, carbon, asphalt and salt) and detergents or solvents used in the washing operation [2]. The wastewater may also contain hydraulic fluids and motor oil as a result of leakage of the braking system and the engine [3]. Like most industrial effluents, gas-station wastewater varies significantly in quantity as well as in composition [2-5]. Because of the large variety of chemicals applied in gas-station, 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 treated of gas-station wastewater can probably be accomplished by the conventional treatment processes such as filtration and oil-separation followed by a biological process [2]. Biological treatment methods are favored as they are considered environment-friendly and relatively cheap. However, there are some limitations: it is not certain that all detergents and dissolved solids or heavy metals can be degraded, and the complete removal of other types of contaminants is questionable. 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 [1].

Due to these limitations, more and more research is focusing on combining different techniques for treatment of different types of wastewaters, such as photocatlytic degradation with coagulation-flocculation [6], biological treatment combined with ozonation and heterogeneous catalysts [7], fenton oxidation with coagulation pretreatment [8], and flocculation-column flotation (FCF), sand filtration and final chlorination [9].

The application of advanced oxidation processes (AOPs) to the treatment of wastewater is also used, where these technologies utilize the very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to harmless end products (carbon dioxide and water) [10-12]. Among the AOPs, heterogeneous photocatalysis has been the subject of several studies on the degradation of toxic effluents [13-15] and has shown good results in the removal of several contaminants from wastewater, especially for the removal of refractory organic pollutants [16, 17]. 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 [18]:

$$Organic\ pollutants + O_2 \xrightarrow{Semiconductor+UV-light} CO_2 + H_2O + Mineral\ acid$$

The most suitable semiconductor photocatalyst for sensitizing above reaction is TiO_2. There are many different source of TiO_2. The adopted wavelength of UV light for TiO_2 is about 365 nm in order to avoid the direct photolysis of organic compounds. The aim of this study was the elimination of the refractory contaminants in gas-station wastewater by two steps of biological treatment followed by photocatalytic degradation using three commercial types of TiO_2 (Degussa P25, Hombikat UV-100 and Millennium PC 50). Moreover, the effect of the P25 photocatalyst concentration was studied.

MATERIALS AND METHODS

Reagent grade chemicals were used as received. Three commercially available titanium dioxide catalysts were used without further pre-treatment. 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 1.

Table 1: Physical characteristics of the TiO_2 photocatalysts

Photocatalyst	*Company*	*Specific surface area, m^2/g*	*Particle size, nm*	*Crystal structure*
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

Wastewater characteristics and collection

The wastewater from the gas-station is collected and transferred to the multi-stage treatment system as shown in the Figure 1.

- First stage: Treatment is achieved by a primary trap to separate oil and grease from the water. The collected material is removed regularly from the traps and placed into temporary seepage bins to remove excess water.
- Second stage: The water is pumped to a secondary settlement tank in form of a sand filter for further removal of solids, oil and greases.
- The third stage of treatment is the aerated bio-reactor where specific microorganisms degrade the organic compounds. Under optimal conditions the microorganisms will convert the organic contaminants into harmless end products like carbon dioxide, water and salts.
- The final stage takes place in the settling tank. This settling tank is used for separating remaining particles and the sludge which is returned to the bio-reactor.

Different samples of this biologically pre-treated wastewater were collected from a gas-station. The samples were stored in the laboratory at room temperature (20 ± 1 ^oC). The main properties of the investigated wastewater are listed in Table 2.

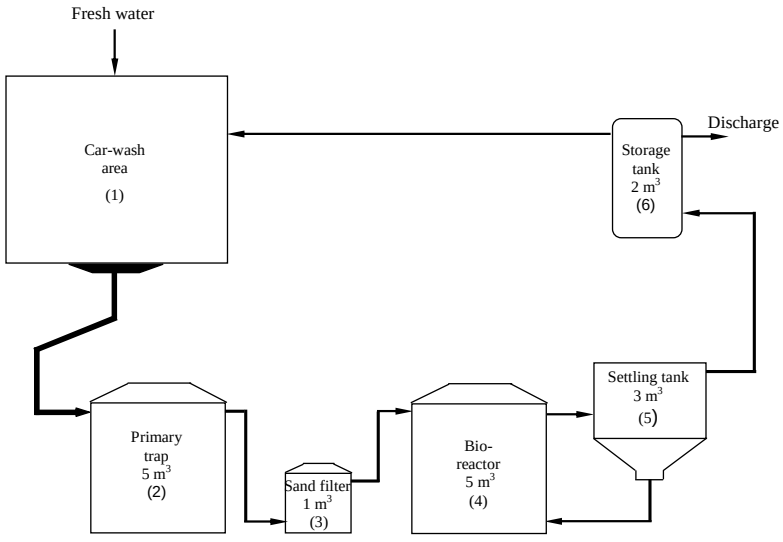

Figure 1: Treatment system of wastewater at gas-station

Analyses

The catalyst was separated by sedimentation before analysing the samples. TOC was detected by a Shimadzu Analyzer TOC 5000. COD and BOD_5 were analyzed according to the German standards of DIN 38 409-H41 and DIN 38 409-H51. The hydrocarbon content was measured according to DIN 38 409-H18. The anionic and cationic surfactants were reacted with methylene blue (MBAS) and bromophenol blue (CTAB), respectively, to form a coloured complex which were extracted with an organic phase measured according to DIN 38 409-H23 and DIN 38 409-H20, respectively. The measurement of surface tension was carried out according to DIN 53914.

RESULTS AND DISCUSSIONS

Wastewater was collected from gas-station after multi-stage treatment system as shown in the Figure 1 and stored in the laboratory at room temperature. It was observed that the characteristics of some samples taken from the gas-station changed during their storage in the laboratory. For example, the surface tension of one sample changed within 24 hr after sampling from 42 to 71 dyn/cm and the BOD_5 of the different samples were in the range of < 3 to 24 mg/L indicating that some samples were still biologically active. Therefore, the different samples of biologically pre-treated wastewater were collected from the gas-station on seven consecutive days, mixed in an aerated holding tank of the laboratory and treated biologically until the BOD_5 remained constant. This wastewater was subsequently treated by the photocatalytic process

Biological treatment

The TOC of the seven samples is shown in Figure 2 with the main properties of the second sample (2^{nd}) are given in Table 2. The BOD_5 of the second sample (2^{nd}) was 87 mg/L indicating an uncompleted biological treatment at the gas-station. The biological treatment in the laboratory was carried out at 20 ± 2 ^{o}C adding air with a medium-bubble size sparger and controlling pH, total phosphorous and total nitrogen. During 20 days the TOC changed from 28 to 11 mg/L and the COD from 72 to 43 mg/L as shown in Figure 3. As the BOD_5 was less than 3 mg/L after 20 days and the BOD_5/COD ratio less than 0.02, the biological treatment was assumed to be complete.

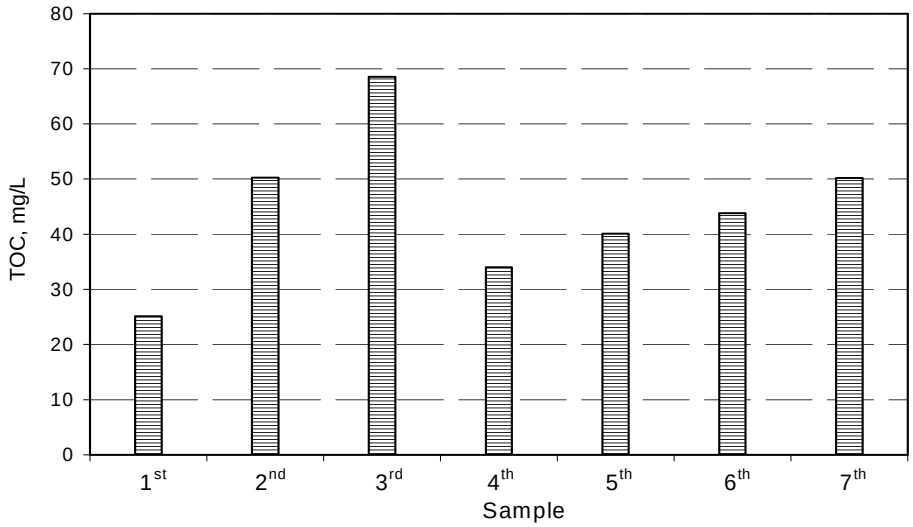

Figure 2: TOC of the different car-wash wastewater samples

The main properties of the mixture after 20 days of biological treatment are given in Table 2. As may be noted, the concentration of anionic and cationic surfactants was reduced from 0.55 and 1.12 mg/L to less than 0.02 and 0.05 mg/L, respectively, and the surface tension increased from 58.2 to 71.9 dyn/cm. The high concentration of hydrocarbon of 4.6 mg/L after the treatment indicates that these can not be reduced to zero by biodegradation [19] and the objective of this study to remove these refractory contaminants by photocatalytic using TiO_2 as far as possible.

Table 2: The most important parameters of the biologically pre-treated wastewater from the gas-station and an additional 20 days of biological treatment

Parameter	*Unit*	*2nd sample*	*Mixture after 20 days*
pH	-	7.2	7.7
Surface tension	dyn/cm	58.2	71.9
Cationic surfactants (CTAB)	mg/L	1.12	< 0.05*
Anionic surfactants (MBAS)	mg/L	0.55	< 0.02*
TC	mg/L	85	42
IC	mg/L	34	31
TOC	mg/L	50	11
COD	mg/L	192	43
BOD_5	mg/L	87	< 3*
Conductivity	mS/cm	0.53	0.54
Total phosphorous	mg/L	0.31	0.14
Total nitrogen	mg/L	2.9	2.8
O_2 concentration	mg/L	5.64	5.56
Hydrocarbon concentration	mg/L	-	4.55
Colour	-	Light brown	Colourless

* The value is below the detection limit of the measurement method.

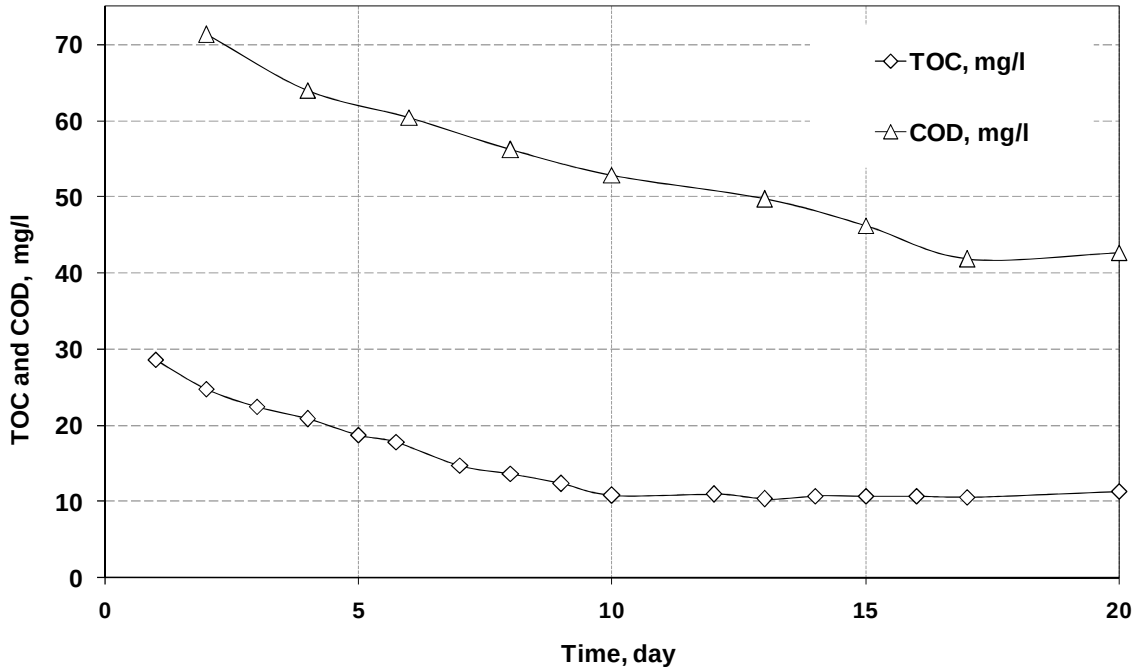

Figure 3: Degradation of TOC and COD of the mixture of gas-station wastewater

Photocatalytic with titanium dioxide

In order to minimise the TOC and hydrocarbon content, three TiO_2 photocatalysts (P25, UV-100 and PC 50) and the effect of different concentrations of P25 were investigated. The experiments were carried out in the aerated photoreactor (Figure 4) as discuss in the following sections.

Photoreactor

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 [20]. 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/m^2. 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).

Photcatalytic procedure

The inclination angle of the photoreactor reactor was adjusted at 60°. Prior to and during the experiments the pH of the solution was adjusted to the desired value employing dilute H_2SO_4 and NaOH solutions for pH control. 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 3.

Effect of different types of TiO_2 photocatalysts

The photocatalytic activities of P25, UV-100 and PC 50 photocatalysts were compared at a photocatalyst concentration of 5 g/L and a pH = 5. The degradation of TOC and hydrocarbon content as a function of radiation time are illustrated in Figures 5 and 6.

The effect of adsorption during the first 30 min in the absence of light and the effect of UV radiation were investigated. By dark adsorption the TOC was reduced from 11 to 8.6, 7.8 and 9.4 mg/L with P25, UV-100 and PC 50, respectively. The adsorption of UV-100 was the highest compared to the other TiO_2 catalysts. This is possibly due to the difference in the specific interfacial area of the three catalysts. The specific surface area of the catalysts is 250, 50 and 50 m^2/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.

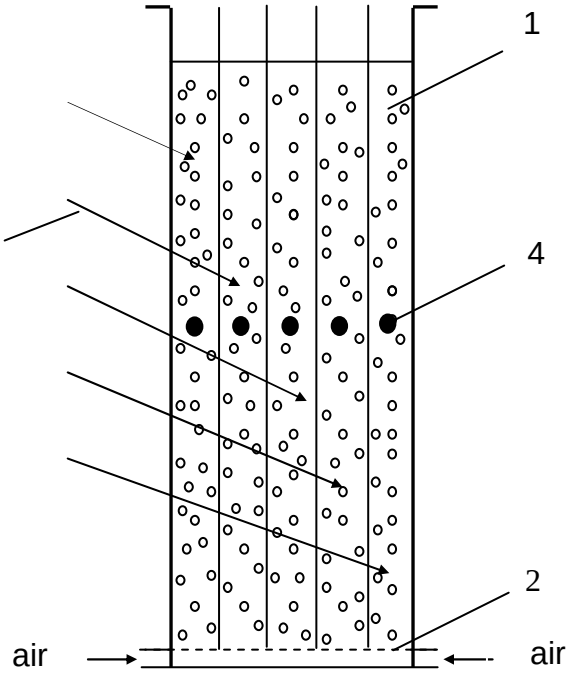

Figure 4: Set-up of the aerated photoreactor

Table 3: Conditions of the photocatalytic experiments

Parameter	*Unit*	*Value*
TiO_2 concentration	g/L	5
Superficial gas velocity	mm/s	2
Reaction volume	L	1
Initial TOC concentration	mg/L	11
pH	-	5
Temperature	^oC	20 ± 1

As shown in Fig. 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 83 % of the TOC after 3 hr of photocatalytic treatment. Fig. 6 shows the hydrocarbon content before and after 3 hr of photocatalytic treatment. The maximum reduction of hydrocarbon was obtained with P25 (from 4.6 to 0.55 mg/L) followed by UV-100 and PC 50.

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 4 shows the calculated rate constant K and the half-life time ($t_{1/2}$) for each catalyst after three hours of radiation. The photocatalyst P25 gave the maximum pseudo-first order kinetic constant rates and the calculated half-life time.

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 1 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 five times that of PC 50 and four 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 Bacsa and Kiwi who found that titania containing both anatase and rutile shows a significantly higher photocatalytic activity compared to pure anatase or rutile [21]. P25 is also reported to have a higher hydroxyl radical generation than anatase TiO_2 particles [22].

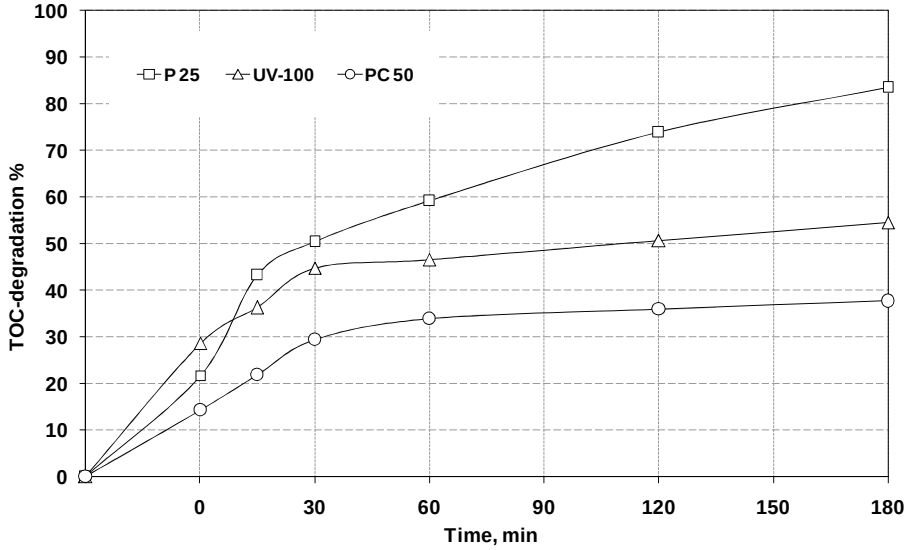

Figure 5: Effect of TiO_2 photocatalysts on the TOC degradation

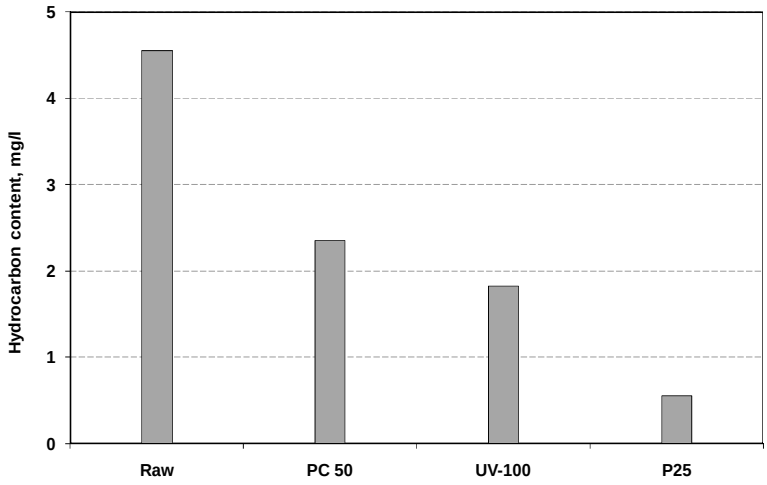

Figure 6: Effect of TiO_2 photocatalysts on the hydrocarbon degradation

Table 4: Reaction rate constants and half-life times for TiO_2 photocatalysts

Photocatalyst	*K, 1/min*	R^2	$t_{1/2}$
P25	0.008	0.9806	87
UV-100	0.002	0.8255	315
PC 50	0.0015	0.7334	462

Effect of P25 concentration

The effect of a P25 concentration from 0 to 10 g/L on the degradation of TOC and the variation in rate constant at a pH = 5 vs. radiation time is shown in Figure 7. In the absence of TiO_2 (UV-A radiation only) no degradation of TOC was observed.

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. No significant observed of the degradation of TOC with increasing the concentration of the catalyst more than 5 g/L. This may be explained as follows: (a) at high catalyst concentrations the TiO_2 particles aggregate resulting in a decrease of the number of surface active sites, (b) the increase in opacity and light scattering of TiO_2 particles at high concentrations leads to a decrease in the transmittance of radiation through the sample and thus reduces the photoactivity of TiO_2. Similar results have been reported in previous studies for several photosystems [16, 23]. 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 [24, 25]. After 3 hr of photodegradation, the concentration of TOC was decreased to 17 % of the initial concentration. The reaction rate constant increases with the catalyst concentration up to the optimum concentration of 5 g/L

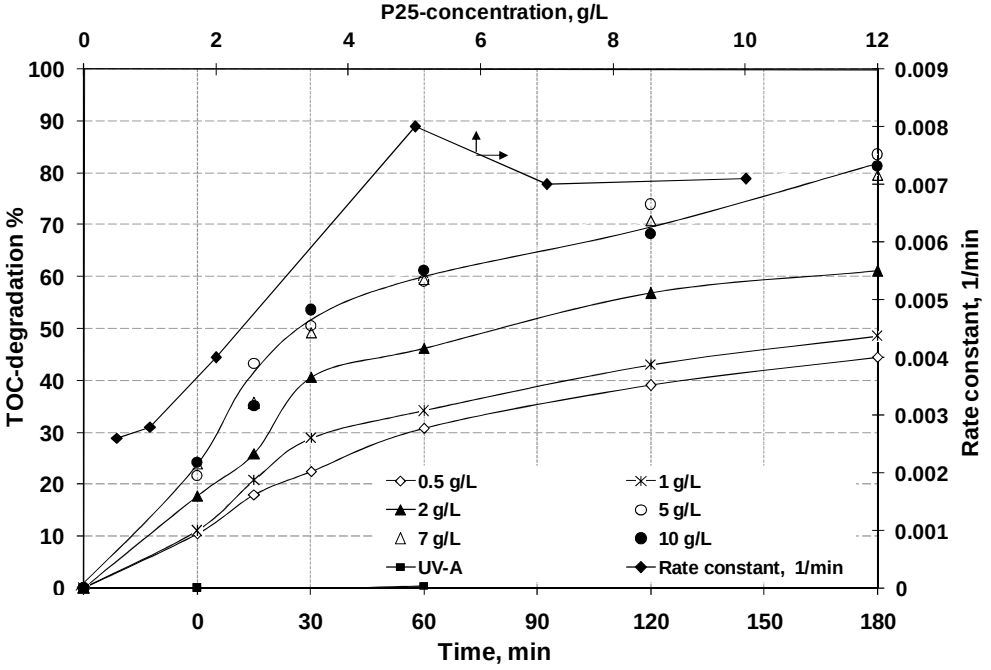

Figure 7: Effect of P25 concentration on the TOC degradation and rate constant

CONCLUSION

This study has presented the results of the degradation of contaminants in gas-station wastewater by the following processes: two steps of the biological treatment followed by photocatalytic process to remove the remaining refractory contaminants. Biological treatment reduced the TOC and COD from 28 and 72 mg/L to 11 and 43 mg/L, respectively and the surface tension increased from 58.2 to 71.9 dyn/cm. The photocatalytic process using different types of TiO_2 can efficiently catalyze the photodegradation of refractory contaminants. The photocatalyst Degussa P25 was the higher photocatalytic activity than Hombikat UV-100 and Millennium PC 50. In addition, P25 gave the maximum pseudo-first order kinetic constant rate and the calculated half-life time. The maximum degradation of TOC and hydrocarbon content was achieved with 5 g/L of P25.

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