Solar Detoxification of A Petroleum Wastewater in Aqueous Suspensions of Titanium Dioxide Photocatalyst

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مفتاح الغزالي و جميل الحكيمي

تمدراسة إمكانية استخدام مادة ثاني أكسيد التيتانيوم كمحفز ضوئي في تنقية المياه الملوثة بمواد عضوية والناتجة من مجمع رأس لانوف البتروكيماوي وذلك في وجود ضوء الشمس كمصدر للأشعة فوق البنفسجية. ظروف التفاعل تم تغييرها للحصول على أفضل النتائج حيث استخدمت مادة فثالات هيدروجين البوتاسيوم لهذا الغرض وذلك كمادة نموذجية. إختفاء مادة فثالات هيدروجين البوتاسيوم تم متابعتها بواسطة فحص كمية الاستهلاك الكيميائي للأكسجين (COD) للمحلول المعرض للشمس.

وجد أن معدل تفاعل المحفز الضوئي ثاني أكسيد التيتانيوم يكون في ذروته عند التركيز 3 جم/لتر للمحفز الضوئي ديجوسا و10جم/لتر للمحفز الضوئي هومبيكات (UV100) أما بالنسبة لوسط التفاعل فقد وجد أن أفضل وسط يكون عند الرقم الهيدروجيني 5 لكل من المحفزين الضوئيين. الاختفاء المباشر لمادة فثالات هيدروجين البوتاسيوم عند خلطها بالمحفز الضوئي هومبيكات UV100 ناتج عن عملية إمتزاز الملوث عند سطح الحفاز.

التحطيم الكلي للمواد العضوية الموجودة بمياه الصرف بمجمع رأس لانوف (Wastewater) لوحظ أنه يستغرق مدة من التفاعل قدرها 6 ساعات بنفس الظروف المختارة لمدة فثالات هيدروجين البوتاسيوم. كفاءة الفوتونات الناتجة من ضوء الشمس تمحسابها ووجد أنها تنخفض عند كثافة الضوء المنخفض (¹⁻ا.¹⁻ا.¹⁻¹. بقيمة 3-0.24) تنخفض بقيمة قدرها 1-0.94.

Abstract: The applicability of the photocatalytic detoxification, using titanium dioxide, for the treatment of wastewater from Ras Lanuf Petrochemical Complex was studied. The conditions of the photocatalytic degradation were optimised using the model compound potassium hydrogen phthalate (KHP). The disappearance of KHP was followed by chemical oxygen demand (COD) determination of irradiated solutions by sunlight. The optimal catalyst concentration was found at 3g/l of Degussa P25 and 10g/l of Sachtleben Hombikat UV 100. The best de-

gradation rate was obtained at pH 5.0 for the two catalysts types. The disappearance of KHP in the dark, using Sachtleben Hombikat UV100 was due to the adsorption of the pollutant on the catalyst surface. The complete degradation of organic pollutant in Ras Lanuf Oil and Gas Processing Co. (RASCO) wastewater was reached after 6 hours irradiation using the optimal reaction conditions. The photonic efficiency decreased at low light intensities (0.311–2.29 µmol photon s⁻¹ l⁻¹) with I-0.243 and at higher light intensities (2.29–2.919 µmol photon s⁻¹ l⁻¹) with I^{-0.94}.

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INTRODUCTION

It is well known that wastewater from refinery and petrochemical plants contain many types of toxic organic substances such as phenol compounds, aldehydes, polyaromatic compounds, etc. These compounds are produced from different types of processes and must therefore be purified or treated before being discharged into the sea. The most applicable method for the waste treatment of such industry complexes is the biological treatment. There are also several treatment processes used for the cleaning up of pollutant wastewater. One of them is the adsorption of organic pollutants on the activated carbon[1]. In this process the pollutants are transferred from the aqueous to the solid phase and must be again desorbed by heat treatment that may cause the formation of new toxic products.

Another method for the clean up of wastewater is the application of hydrogen peroxide/UV. This method is used efficiently to purify drinking water^[2]. The hydroxyl radical produced from peroxide and UV-light is non-selective and can oxidize all pollutants in the mixture^[3]. The main disadvantage of this method is the high cost of hydrogen peroxide and the adsorption of the UV-light by contaminants that lead to the complete termination of the reaction.

The combination of ozone/UV and hydrogen peroxide is also a method for the detoxification of water which used two oxidizing agents ozone and produced hydroxyl radicals ^[4,5].

The treatment of sewage with ozone and ozone/ UV is also a well established technical process¹⁶¹. It was found that the treatment of water with ozone in the most cases does not lead to the complete mineralization. Therefore ozone/UV system was developed¹⁷¹. In this system the destruction of organic compounds becomes effective, that is due to the reaction of ozone with water and formation of hydroxyl radicals. The use of g-radiolysis in wastewater treatment is a modern technique that does not need the addition of chemicals¹⁸¹. The high energetic light ionized water molecules and produces hydroxyl radicals for the destruction of organic pollutants.

A new promising method for the wastewater

treatment is the photocatalytic detoxification. With this technique the pollutants are degraded by irradiating suspensions of metal oxide semiconductors, acting as photocatalyst in the presence of light and oxygen or air[9]. The most applied metal oxide in this process is titanium dioxide. Many works are carried out in this field for distraction of hydrocarbon, chlorinated compounds and organic compounds with heteroatoms[10,11,12]. To reach the complete mineralization an additional method is required, for example biological treatment. An unsolved problem in this technique is the separation of titanium dioxide suspension after clean up the wastewater. On the other hand the fixation of photocatalyst on surfaces lead to the decreasing of the degradation rate[13].

This work is dealing with determination of the applicability of photocatalytic detoxification for the treatment of wastewater of Ras Lanuf Petrochemical Complex in Libya under the field conditions. This was carried out using the model compound potassium hydrogen phthalate (KHP). The concentration of the catalyst, the pH, the type of the catalyst and light intensity were varied and optimized. The obtained optimal conditions were used for the detoxification of the RASCO actual wastewater.

EXPERIMENTAL

Equipment and Chemicals:

Equipment

- Seta-IEC oil test centrifuge from Stan-hop-seta
- pH meter Beckman "select Ion 2000" ion analyzer.
- GC, Carlo Erba 4100, equipped with FID and column SS, 3m × ³/₄ mm, porapak R, mesh 80/ 100. Including methanizer at 400 °C. Detector temp. =
- 200 °C. Carrier gas was N₂.
- Balance from Mettler PM 34 Delta range.
- UVA-meter from Dr Hoenle GmbH.

Chemicals:

Potassium dichromat, mercuric sulphate, potassium hydrogen phthalate, nitric acid, sulfiric acid, sodium hydroxide (convol), chloroform,

methylene chloride and 1,10-phenanthroline and hydrogen peroxide are of BDH product and purified before use. Silver sulphate and ferrous sulphate are from Merk and used without any purification. Ferrous ammonium sulphate hepta hydrate are obtained from Riedel de Hain and directly used. Degussa P25 (primary particle size 20-30 nm, BET surface area $50 \pm 15 \text{ m}^2/\text{g}$, 70% anatase and 30% rutile) is obtained from Degussa GmbH and Sachtleben Hombikate UV 100 (primary particle size <10 nm BET surface area >250 m²/g, > 99% anatase) is from Sachtleben Chemie GmbH. The high purity oxygen 99.99% is obtained form B.O.C, Ltd. and the nitrogen gas from nitrogen plant in RASCO Company.

Preparation of Potassium Hydrogen Phthalate (KHP) Stock Solution

10.0 g of potassium hydrogen phthalate were dissolved in 1 litre water (distilled and demineralized) to prepare a stock solution, which is equal to 11670 mg O₂/l. To prepare KHP solution with 200 mg O₂/l for the degradation experiments, 34 mls were taken from the stock solution and diluted with water to a final volume of 2 litres.

Degradation Experiments with the Model Compound KHP

Variation of the photocatalyst concentration:

The photoreactor was a 3 litres beaker made of Pyrex-glass, equipped with a magnetic stirring and an oxygen purging devices, consisting of two gas washing bottles and two sintered glasses. One bottle was filled with pure water to humidify the oxygen and to minimise evaporation of water in the beaker. For the experiments with the model compound potassium hydrogen phthalate (KHP), a 2 litre KHP solution of a concentration of 200 ppm and the required amount of the photocatalyst were introduced into the reactor, (1 g/l, 2 g/l, 3 g/ 1, 4 g/l, and 5 g/l of Degussa P25 and 1 g/l, 5 g/l, 7 g/l, 10 g/l and 15 g/l of Sachtleben Hombikat UV100 respectively). The pH of the suspension was adjusted to 5.0. The suspensions were stirred, under continuous bubbling of oxygen, for at least one hour inside the laboratory to reach a state of system equilibrium. Then the reactor was exposed to sun light and the suspensions were irradiated

for 5 hours. 75 mls sample was taken before the addition of photocatalyst and directly before exposing the system to the sun and in regular intervals (every 60 minutes) during irradiation. The pH was measured by a pH meter. The COD was determined after centrifuging the suspension for 15 minutes at 1500 rpm according to a standard method ASTM D 1252 (ASTM, 1993). The UV-intensity was determined in regular intervals at the top of the reactor by a UV-meter (Dr Hoenle UV-A meter)

Variation of the initial pH:

The degradation experiments were carried out following the procedure described above. The photocatalyst concentration were chosen as 3 g/l of Degussa P25 and 10 g/l of Sachtleben Hombikat UV 100, respectively, which were found to be the optimum concentration for the degradation of the model compound KHP. The degradation of KHP was carried out at different pH (3.0, 5.0, 7.0 and 11.0). The COD determination of the irradiated solution was performed every 60 minutes for every pH value.

Variation of the light intensity:

Degradation experiments were performed by the same procedure as described. Degussa P25 was chosen as the photocatalyst with concentration of 3 g/l and initial pH 5.0. The photodegradation reactions were carried out at different sun light intensities. The COD's of the solutions were carried out as mentioned above.

Running the experiments for the photodegradation of RASCO wastewater:

The wastewater sample was collected in 25 litres plastic drum from the inlet of the effluent treatment plant (ETP). The collection place of the sample was the overflow of the oil separator to the equalization basin. The sample was then shaked well and 2 litres of the solution were added to 3 g/l Degussa P25 or 10 g/l Sachtleben Hombikat UV 100, respectively. During stirring and continuously bubbling of oxygen. The pH of the solution was adjusted to 5.0. The treatment, collection of the samples and the COD determination were performed similar as described before.

Determination of Chemical Oxygen Demand (COD)

50 ml sample were placed in a 500 ml refluxing flask with 1 g of mercuric sulphate. Slowly, 5 mls of silver sulphate reagent (prepared from 5.5 g silver sulphate per kilogram concentrated sulphuric acid) were added to the solution. In order to avoid possible loss of volatile materials cooling of the mixture was necessary. While stirring, 10 ml of 0.25 N potassium dichromate, solution was added to the mixture. The flask was attached to the condenser and 70 ml silver sulphate reagent was added. After refluxing for 2 hours the solution was cooled down to room temperature. The condenser was washed with distilled water to about twice of the volume of the sample. Five drops of ferroin indicator were added and then titrated against a standard solution of ferrous ammonium sulphate (prepared from 98 g ferrous ammonium sulphate hexahydrate dissolved in 20 ml concentrated sulphuric acid and diluted to one litre with distilled water) until the appearance of the first sharp colour change from bluish-green to reddish brown. The concentration of the titrant was determined daily by adding 10 ml standard potassium dichromate to 100 ml distilled water, and 30 ml concentrated sulphuric acid. The distilled water, as a blank solution, was also daily titrated against the standard solution following the same procedure. The COD values can be calculated in terms of mg O₂/l by the following equation (ASTM 1252, ASTM 1993)

$$COD (mgO2/I) = \frac{(B - A) \times N \times 8000}{S}$$

where,

B = mls of ferrous ammonium sulphate hexahydrate consumed by blank

A = mls of ferrous ammonium sulphate hexahydrate consumed by sample

N = Normality of ferrous ammonium sulphate hexahydrate

S = Sample volume

Experimental Determination of CO₂ Released from the Photodegradation Process

Six g of catalyst Degussa P25 was taken into 5 litres Erlenmeyer flask containing 1966 mls of

distilled water as a first step towards the preparation of final catalyst concentration (3 g/l). The flask was connected to a dropper funnel for KHP injection into the suspension. The flask was also equipped with oxygen purging system, which consists of two wash flasks and stoppers. The system was purged with oxygen under vigorous stirring for about 3 hours. During this period the CO₂ concentration was registered. After that, 34 mls KHP was added and after one hour stirring in the laboratory a sample of gas from the outlet was collected with gas bag. The content of the bag was determined of CO₂ concentration by GC-FID. The experimental set-up was transferred outside laboratory and exposed to direct sun light. At intervals of 15 min for 160 minutes, the CO₂ concentration at the outlet stream of gases was measured using Gas Chromatography.

RESULTS AND DISCUSSION

Calculation Methods and Evaluation of Poor Man's Model:

This model allows the prediction of non-linear dependence of the reaction rate on the light intensity or catalyst load without the consideration of any adsorption parameters^[14,15]

The reaction rate in the Poor Man's Model can be derived from equation:

It can therefore be written as follows:

Rate =
$$\frac{d[product]}{dt}$$
 = $K_1[substance][h]$ (2)

The photonic efficiency can be written as follow:

Photonic efficiency =
$$\frac{d[product]/dt}{d[hn]/dt} = \frac{rate}{light intensity}$$
(3)

Degradation of the KHP and RASCO Wastewater:

To ensure that no degradation occurred in the dark or due to oxidation by oxygen, three blank

experiments were carried out. Firstly KHP was dissolved in water and exposed to direct sunlight in the absence of catalyst and excess oxygen (Fig. 1). The COD remained constant for the duration of the experiment (300 min.). This indicates that no degradation of KHP is occurred due to direct photolysis. In the second blank a mixture of 226.3 mg O₂/l (COD) of KHP and 3 g/l Degussa P25 was stirred and bubbled with oxygen for 20 hours inside the laboratory. The COD was measured every 60 minutes. In the first hour the COD decreased by 17%. This change in COD was due to the adsorption of KHP on the catalyst surface. In the remaining time of the experiment the COD's remained constant (Fig. 2). In the third experiment, 10 g/l Sachtleben Hombikat UV 100 was used, under the same conditions as the 2nd experiment,

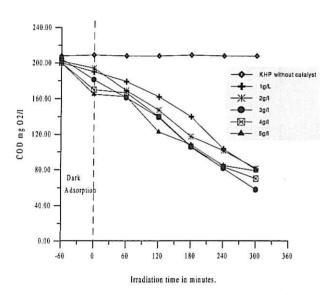


Fig. 1. COD reduction of KHP versus time at different catalyst concentration of Degussa P25, pH 5.0.

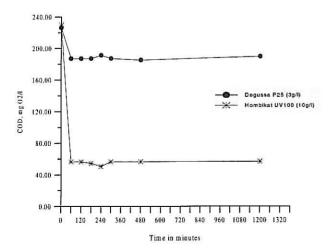


Fig. 2. Influence of catalyst on the COD reduction of KHP without irradiation, at pH 5.0.

and a strong adsorption (ca 75%) was observed in the first 60 minutes (Fig. 2). Therefore no significant change was observed over a period of 20 hours. From these experiments it was concluded that no degradation occurred in the dark or by direct photolysis regarding the COD. It can not be excluded that KHP was converted to other pollutants by direct sunlight which would not lead to a change in the COD of the sample.

To carry out the experiments with best conditions of the photocatalytic degradation reaction of KHP, the catalyst concentration was first optimised. The disappearance of the model compound (KHP) was monitored every 60 minutes by measuring the COD. From the obtained CODvalues, the kinetics of the degradation were fitted. The results showed that the degradation rate of KHP followed first order kinetics. The degradation rates were calculated by multiplication of the first order rate constant by the initial COD concentration. The measured COD values (every 60 minutes) at five different catalyst concentrations, are shown in (Fig. 1). The COD showed a non significant adsorption of KHP at low catalyst load 1 and 2 g/l, the adsorption was 5 and 10 mg O_2/l , respectively after 60 minutes of stirring in the dark. In contrary, a relative high adsorption of 30 and 43 mg O₂/l was detected at 4 and 5 g/l catalyst concentration, respectively. This effect is due to a high concentration of the active sites which able to adsorb KHP molecules. The degradation rate of the model compound KHP was determined at different catalyst loads. The kinetics was calculated by a semi-logarithmic plot, thus, the reaction can be interpreted as pseudo first order kinetics.

The degradation rate increased linearly by increasing the photocatalyst load up to a certain limit. At 3 g/l Degussa P25 a maximum degradation rate was obtained. The degradation rate at this concentration reached more than double of its value in comparison to the 1 g/l concentration. Further increase the TiO₂ concentration produced no significant improvement in the degradation rate (Fig. 3). This can be explained by the fact that at 3 g/l catalyst concentration the maximum amount of incident light, which could be absorbed, was reached in the reactor used in this study^[15].

For each of the five catalyst loads the photonic efficiencies were calculated from the ratio of the

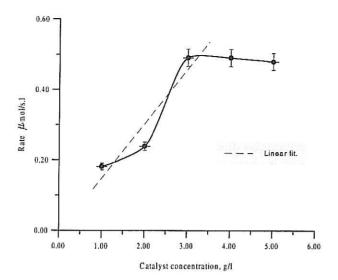


Fig. 3. Degradation rate of KHP at different catalyst concentrations. Degussa P25, pH 5.0).

photocatalytic degradation rates and the corresponding photon fluxes. The results are shown in (Fig. 4). The relatively low values of the photonic efficiency (6%) at low catalyst concentration could be explained by the limited amount of TiO_2 particles which absorbe the solar photons. The optimum catalyst dose was reached at 3 g/l Degussa P25. At higher photocatalyst load no further change of the photonic efficiency was achieved.

It is known from the literature that the particle size and the type of the photocatalyst play a significant role in the degradation rate of organic pollutants. Therefore, the photodegradation of

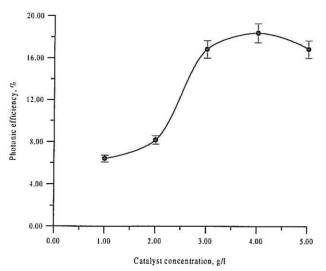


Fig. 4. Photonic efficiency versus catalyst concentration for Degussa P25, at pH 5.0. for KHP model.

KHP by direct sunlight was investigated using different concentrations of Sachtleben Hombikat UV 100 as an alternative photocatalyst. Figure 5 illustrates the behaviour of the COD reduction for different catalyst concentrations. At a catalyst concentration of 1 g/l the adsorption of KHP in the dark was low (21%). Adsorption of KHP was stronger at higher catalyst loadings. The maximum KHP adsorption is reached by 10 g and levelled off for higher concentrations which suggest saturation coverage of the surface active sites with KHP.

The reason for the rapid disappearance of the organic pollutant in the dark is due to strong adsorption of KHP and not to oxidation which was proven by the time controlling of the CO₂ development during the experiment.

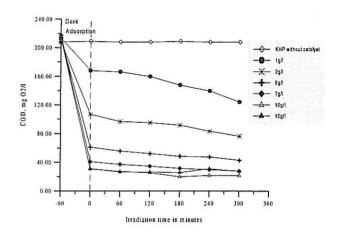


Fig. 5. COD reduction of KHP at different concentrations of Sachtleben Humbikat UV 100, at pH 5.0.

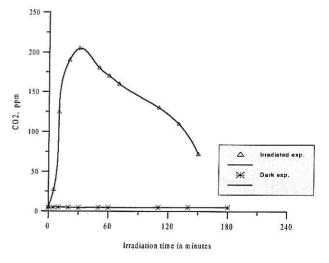


Fig. 6. CO₂ production as a function of time using Degussa P25, at pH 5.0 for KHP.

It was found that no CO₂ occurs in the dark (for Degussa and Humbikat) despite the disappearance of the KHP in solution (Fig. 6).

Further experiment showed that the adsorption of KHP on the catalyst surface is pH dependence. The dissociation of the organic pollutant and the surface properties of the photocatalyst in aqueous suspensions are highly influenced by the pH. For these reasons the effect of initial pH on the degradation rate of the model compound KHP by direct sunlight was studied. In all pH adjustment experiments the optimum catalyst concentration (3 g/l for Degussa P25) was used. The degradation rates at the different pH values were calculated from the measured COD. A plot of the degradation rate versus pH is illustrated in (Fig. 7). The results showed degradation rate 3.5 times higher in acidic medium (pH 3.0 and 5.0) compared to the basic (pH 7-11) media. The lowering of the degradation rate at high pH can be explained by adsorption desorption effect.

$$pK_2 = 5.51$$
 $pK_2 = 5.51$
 $pK_2 = 0.89$
 $pK_3 = 0.89$
 $pK_4 = 0.89$
 $pK_5 = 0.89$
 $pK_6 = 0.89$

At low pH values < 6 the TiO₂ surface is positively charged and the KHP is present at this pH as hydrogen phthalate, which is capable to adsorb on the catalyst surface.

At higher pH > 6 the TiO2 surface is negatively charged (eq. 5) and the KHP lies in di-ionic negative form (eq. 4), which would be repelled by the catalyst surface, resulting in negligible adsorption of KHP.

The photonic efficiencies for the pH variation experiments were calculated from the obtained rates and corresponding photon flux. It was obvious that the photonic efficiency reached its maximum at pH 3.0, and then decreased in neutral and basic medium (Fig. 8). Thus, high photonic

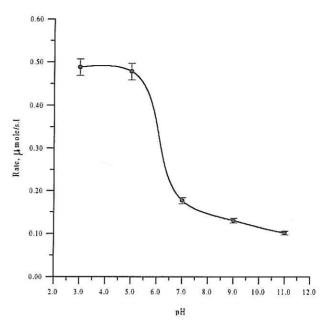


Fig. 7. Degradation rate of KHP at different pH values using 3 g/1 of Degussa P25.

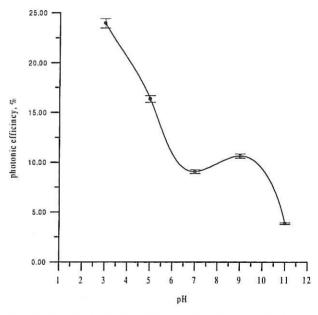


Fig. 8. The effect of pH variation on the photonic efficiency for Degussa P25 using KHP as a model compound.

efficiency was observed for pH values where a strong adsorption of the pollutant at the catalyst surface occurred, i.e., for pH values below 5.0.

The influence of light intensity on the degradation rate for many pollutants classes is reported in the literature^[13]. In the present work the effect of the sun light intensity during the day on KHP degradation using Degussa P25 as photocatalyst was examined. All experiments were

carried out at pH 5.0 and the catalyst concentration was 3 g/l under vigorous stirring and continuous supply of oxygen into the suspension. The COD data were collected at different days with different sun light intensities. From the obtained results the degradation rates were calculated. Figure 9 shows the variation in KHP degradation rate as a function of light intensity for the Degussa P25 catalyst. It was obvious that the degradation rate increased linearly at low light intensities (0.311–2.29 µmol photon/s.l). At higher light intensities (2.756 -2.919 µmol photon/s.l) a non-linear increase was observed. This effect occurred for high photon fluxes due to a predominance of recombination of photogenerated charges[16]. The effect of light intensity on the photonic efficiency of the photocatalytic degradation of KHP using Degussa P25 is illustrated in (Fig. 10). It was noticed that the efficiency considerably decreased as the light intensity increased. This is due to the high recombination rate at high light intensities which makes the photocatalytic oxidation reaction less effective. The maximum reached photonic efficiency value was 33.9 % which was a remarkably high in comparison to data found in literature for other model pollutants^[17].

The results showed that when illuminations were carried out with light intensities between 0.311–0.986 µmol photon s⁻¹ l⁻¹ the photonic efficiency of KHP degradation hardly depended upon the irradiation intensity (I^{-0.243}). In the higher ranges, between 2.29 and 2.919 µmol photon s⁻¹ l⁻¹ the influence of light intensity was more pronounced (I^{-0.94}).

The optimal conditions (catalyst type, catalyst concentration, initial pH and sunlight intensity)

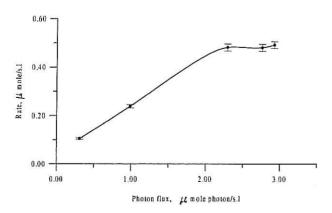


Fig. 9. Degradation rate of KHP against different photon flux for 3 g/1 Degussa P25, at pH 5.0.

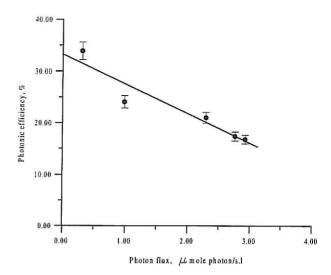


Fig. 10. Influence of the photon flux on the photonic efficiency, using 3 g/1 Degussa P25 and KHP as a pollutant.

found for KHP degradation were used for RASCO wastewater. The organic and inorganic pollutants present in RASCO wastewater are summarised in Table 1. Figure 11 illustrate the COD values of the degraded pollutants in the RASCO wastewater over a along period of irradiation time (900 minutes). This experiment was carried out with Degussa P25 and Sachtleben Hombikat UV 100. It is obvious that the degradation rate reached a minimum after 300 minutes of irradiation for both photocatalysts. Irradiation of the sample for further 600 minutes produced no detectable degradation. The COD values remain in the range

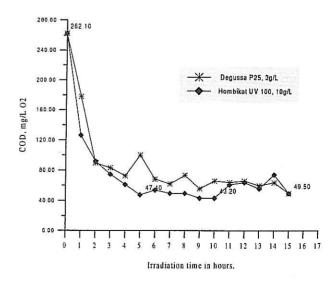


Fig.11. The degradation of organic pollutants in RASCO wastewater using 2 types of photocatalysts at pH 5.0.

of 47–49 mg O₂/l. These results indicate a possible existence of inorganic salts (chloride, ammonia etc.), which give a corresponding COD value. The experiments showed that the pollutants in the RASCO wastewater are completely degraded at the mentioned conditions within 300 minutes. Mechanistical study of individual compounds in RASCO wastewater like naphthalene and anthracene was already done^[19].

CONCLUSION

A complete degradation of the model compound KHP using titanium dioxide as photocatalyst and sun light was reached within 6h. The optimal catalyst concentration was found to be by

Table 1: Organic and inorganic pollutants in RASCO wastewater.

Pollutant	Quantity in mg/l
Total hardness	290
Silica	3.15
Chloride	1420
Nitrate	1.4
Sulfate	550
Phosphate	2.46
Sodium	724
Potassium	22.2
Calcium	99.75
Magnesium	59.25
Iron	0.24
Copper	0.011
Zinc	0.075
Chromium	0.00649
Nickel	0.090
Organic pollutants	Mixture of n-and iso-C8 to C30, cyclopentadiene, benzene, toluene, ethylbenzene, o,m,p xylene, styrene, trimethylbenzene, ethylmethylbenzene, dimethylethylbenzene, indene, 1,2,3,4-tetrahydronaphthalene, naphthalene, benzenecycloheptatriene, cyclopentanon, methylcyclpentanon, 2-hexanone, benzeneacetaldehyde, acetophenone, 1-indanone, 3,4-dihydronaphthalenone, phenol, o-, p-methylphenol.

3 g/l for Degussa and 10 g/l for Humbikat. The best media for the photodegradation rate of the pollutant was found at pH 5.0 in both photocatalyst Degussa and Humbikat. The high values of light intensity affects the degradation rate negatively due to the high recombination rate. The photonic efficiency decreased by increasing the light intensity. The complete destruction of the organic pollutants in the RASCO wastewater was reached in 6 h at the same conditions used for the KHP.

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