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Photocatalytic destruction of potassium hydrogen phthalate using TiO_2 and sunlight: application for the treatment of industrial wastewater

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Abstract

The applicability of the photocatalytic detoxification for the treatment of Ras Lanuf Oil Co. (RASCO) wastewater was studied using potassium hydrogen phthalate (KHP) as a model compound. The conditions of the photocatalytic degradation process of KHP were optimised. Its disappearance in a titanium dioxide suspension, irradiated by sunlight, was followed by chemical oxygen demand (COD). The optimum catalyst concentration was found at 3 g/l of Degussa P25 and 10 g/l of Sachtleben Hombikat UV 100. The optimum degradation rate was obtained at pH 5.0 for both types of catalyst. The disappearance of KHP in the dark, using Sachtleben Hombikat UV 100, was due to the adsorption of the pollutant on the catalyst surface. The photonic efficiency was 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 $I^{-0.94}$. The complete degradation of organic pollutants in RASCO wastewater was achieved after 5 h of irradiation using the optimised reaction conditions obtained for KHP.

Keywords: Photocatalytic detoxification; Chemical oxygen demand; Poor man's model; Wastewater; Titanium dioxide

1. Introduction

It is well known that wastewater from refinery and petrochemical plants contains many different types of toxic organic substances such as phenolic compounds, aldehydes, polyaromatics and aliphatic compounds. These compounds are by-products of different industrial types of processes and must therefore be treated or removed before being discharged into the sea. The most widely used method for the treatment of industrial wastewater is biological treatment. Other treatment methods are known; among these is adsorption of organic pollutants on activated carbon [1]. In this process, the pollutants are transferred from the aqueous to the solid phase, and are desorbed by heat treatment that may lead to the formation of new toxic products.

Another method for the treatment of wastewater consists of the application of hydrogen peroxide/UV. This method is efficiently used to purify drinking water [2]. The hydroxyl radical produced from peroxide and UV-light is non-selective and can therefore oxidise all pollutants in the mixture [3]. The main disadvantage of this method is the high cost of hydrogen peroxide itself and the undesirable adsorption of UV-light by contaminants in the mixture that leads to the complete termination of the radical reaction. The combination of ozone/UV and hydrogen peroxide is another method for the detoxification of water which employs two oxidising agents, ozone and produced hydroxyl radicals [4,5].

The treatment of sewage with ozone and ozone/UV is also a well-established technical process [6]. It was found, however, that the treatment of water with ozone, in most cases, does not lead to complete mineralisation. Therefore, the ozone/UV system was developed [7]. In this system, the destruction of organic compounds becomes effective due to the reaction of ozone with water and subsequent formation of hydroxyl radicals. The use of γ-radiolysis in wastewater treatment is a more modern technique that does not require the addition of chemicals [8]. The high-energy light ionises water molecules and produces hydroxyl radicals for the destruction of organic pollutants.

A relatively new and promising method for wastewater treatment is photocatalytic detoxification (advanced

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oxidation). With this technique, the pollutants are degraded by irradiating suspensions of metal oxide semi-conductors, acting as photocatalysts, in the presence of UV-light and oxygen or air [9]. The most common metal oxide utilised in this process is titanium dioxide. Other works carried out in this field focus on the destruction of hydrocarbons, chlorinated compounds and organic compounds with heteroatoms, such as nitrogen and oxygen [10–15]. The separation of the titanium dioxide suspension after the clean-up of the wastewater poses a problem. An alternative method is the supporting of the photocatalyst on certain surfaces. Many researchers have attacked this problem and have faced several difficulties in the fixation and in the low degradation rate of the treated contaminant [16].

This work deals with the determination of the applicability of photocatalytic detoxification for the treatment of wastewater at the Ras Lanuf Oil Co. in Libya, under field conditions. KHP was used as a model compound for this study. The optimum conditions obtained for KHP (concentration of catalyst, pH, type of catalyst, and light intensity) were subsequently applied for the detoxification of the actual RASCO wastewater.

2. Materials and methods

2.1. Materials

Potassium dichromate, mercuric sulphate, potassium hydrogen phthalate (KHP), nitric acid, sulphuric acid, sodium hydroxide (convol), chloroform, methylene chloride, 1,10-phenanthroline, and hydrogen peroxide were all obtained from BDH and purified before use. Silver sulphate and ferrous sulphate were obtained from Merck and used without further purification. Ferrous ammonium sulphate heptahydrate was obtained from Riedel de Hain and used directly. Degussa P25 (primary particle size 20–30 nm, BET surface area $50 \pm 15\,m^2/g$, 70% anatase and 30% rutile) was obtained from Degussa GmbH and Sachtleben Hombikate UV 100 (primary particle size <10 nm, BET surface area $>250\,m^2/g$, >99% anatase) was purchased from Sachtleben Chemie GmbH. The high purity oxygen 99.99% was obtained from B.O.C., Ltd. and the nitrogen gas was obtained from the nitrogen plant in the RASCO company.

2.2. Instruments

- Seta—IEC oil test centrifuge from Stan-hop-seta.
- pH meter Beckman “select Ion 2000” ion analyser.
- GC, Carlo Erba 4100, equipped with FID and column SS, 3 m × 3/4 mm, porapak R, mesh 80/100. Including methaniser at 400 °C. Detector temperature = 200 °C. Carrier gas was N_2.
- Balance from Mettler PM 34 Delta range.
- UVA-meter from Dr. Hoenle GmbH.

3. Experiments

3.1. Preparation of potassium hydrogen phthalate (KHP) stock solution

About 10.0 g of potassium hydrogen phthalate was dissolved in 1 l distilled and demineralised water to prepare a stock solution to 11,670 mg O_2/l. To prepare the KHP solution with 200 mg O_2/l for the degradation experiments, 34 ml were taken from the stock solution and diluted with water to a final volume of 2 l.

3.2. Degradation experiments of the model compound KHP

3.2.1. Variation of the photocatalyst concentration, initial pH and light intensity

The photoreactor used for the degradation process was a 3 l beaker made of Pyrex glass, equipped with a magnetic stirrer and an oxygen-purging device, consisting of two gas washing bottles. One bottle was filled with pure water in order to humidify the oxygen and to minimise evaporation of water in the beaker. For the experiments with the model compound KHP, a 2 l KHP solution (concentration of 200 ppm) and the required amount of the photocatalyst were introduced into the reactor (1–5 g/l of Degussa P25 and 1, 5, 7, 10 and 15 g/l of Sachtleben Hombikat UV 100). The pH of the suspension was adjusted to 5.0 before starting the irradiation process. The suspensions were stirred while continuously bubbling oxygen for at least 1 h inside the laboratory in order to reach a state of system equilibrium. The reactor was then exposed to sunlight for 5 h. Two samples (75 ml each) were taken before the addition of the photocatalyst and directly before exposing the system to sunlight. In order to follow the degradation process, 75 ml of sample were taken at regular intervals (every 60 min) during irradiation. The pH was measured using a pH electrode every 60 min. The chemical oxygen demand (COD) was determined after separation of the TiO_2 by centrifuging the suspension for 15 min at 1500 rpm, according to the standard method ASTM D 1252 (ASTM book, 1993). The UV-intensity was determined at regular intervals at the top of the reactor using a UV-meter (Dr. Hoenle UV-A meter). For the pH variation, 3 g/l Degussa P25 and 10 g/l Sachtleben Hombikat UV 100 were taken. The degradation of KHP was carried out at pH levels of 3, 5, 7 and 11. In order to investigate the degradation rate at different light intensities, Degussa P25 at $pH = 5$ was considered. To obtain different light intensities, the experiments were carried out at different times during the day.

3.2.2. Conducting the experiments for the photodegradation of RASCO wastewater

The wastewater sample was collected in a 25 l plastic drum from the inlet of the effluent treatment plant (ETP). The location of sample collection was at the overflow of the oil separator to the equalisation basin. The sample was homogenised and 2 l of the solution were added to 3 g/l Degussa P25 or 10 g/l Sachtleben Hombikat UV 100. The suspension in the reactor was stirred under a continuous flow of oxygen. The pH of the solution was adjusted to 5.0. The collection, treatment, and the COD determination of the samples, were performed in a similar manner to the procedure described above.

3.3. Determination of COD

About 50 ml of the sample were placed in a 500 ml refluxing flask with 1 g of mercuric sulphate. Slowly, 5 ml 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 h, the solution was cooled to room temperature. The condenser was washed with distilled water to about twice the volume of the sample. Five drops of ferroin indicator were added and 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 1 l 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 the addition of 10 ml of standard potassium dichromate to 100 ml distilled water, and 30 ml concentrated sulphuric acid. The distilled water, as a blank solution, was also titrated daily against the standard solution following the same procedure. The COD values can be calculated in terms of mg O_2/l by the following equation (ASTM 1252, ASTM 1993):

$$\mathrm{COD}\ (\mathrm{mg\,O_2/l}) = \frac{(B-A)N8000}{S} \tag{1}$$

where B is the millilitres of ferrous ammonium sulphate hexahydrate consumed by blank, A the millilitres of ferrous ammonium sulphate hexahydrate consumed by sample, N the normality of ferrous ammonium sulphate hexahydrate, and S the sample volume.

3.4. Experimental determination of CO_2 released from the photodegradation process of KHP

About 6 g of the catalyst, Degussa P25, were weighed out into a 5 l Erlenmeyer flask containing 1966 ml of distilled water as the first step towards the preparation of the final catalyst concentration (3 g/l). The flask was connected to a dropping funnel for KHP injection into the suspension. The flask was also equipped with an oxygen-purging system, consisting of two wash flasks and stoppers. The system was purged with oxygen under vigorous stirring for about 3 h. The CO_2 concentration was measured during this period. About 34 ml of KHP were then added to the mixture and a sample of gas from the outlet was collected with a gas-bag after 1 h stirring in the laboratory. The content of the bag (CO_2 concentration) was determined by GC-FID. The experimental setup was transferred outside the laboratory and exposed to direct sunlight. At intervals of 15 min for 160 min, the CO_2 concentration at the outlet gas stream was monitored using gas chromatography.

4. Results and discussion

4.1. Calculation methods and evaluation of poor man's model

This model allows for the prediction of non-linear dependence of the reaction rate on the light intensity or catalyst load without the consideration of any adsorption parameters [17,18].

The reaction rate in the poor man's model can be derived from the following equation:

$$h^+ + \text{Substrate} \rightarrow \text{Product} \tag{2}$$

and can therefore be written as follows:

$$\text{Rate} = \frac{\mathrm{d}[\text{product}]}{\mathrm{d}t} = k_1[\text{substance}][h^+] \tag{3}$$

and the photonic efficiency can be written as follows:

$$\text{Photonic efficiency} = \frac{\mathrm{d}[\text{product}]/\mathrm{d}t}{\mathrm{d}[h\nu]/\mathrm{d}t} = \frac{\text{rate}}{\text{light intensity}} \tag{4}$$

4.2. Degradation of 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 indicated that no degradation of KHP occurred due to direct photolysis. In the second blank experiment, a mixture of 226.3 mg O_2/l (COD) of KHP and 3 g/l Degussa P25 was stirred and bubbled with oxygen for 20 h inside the laboratory. The COD was measured every 60 min. 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 experimental time, the COD values remained constant (Fig. 2). The same adsorption test was also carried out for 10 g/l Sachtleben Hombikat UV 100. A strong adsorption (ca 75%) was observed in the first 60 min (Fig. 2). No significant change was observed over a period of 20 h following. From these experiments, one could conclude that no degradation occurred in the dark or by direct photolysis. Of course it cannot be dismissed that KHP was converted to other pollutants by direct sunlight, which would not lead to a change in the COD of the samples.

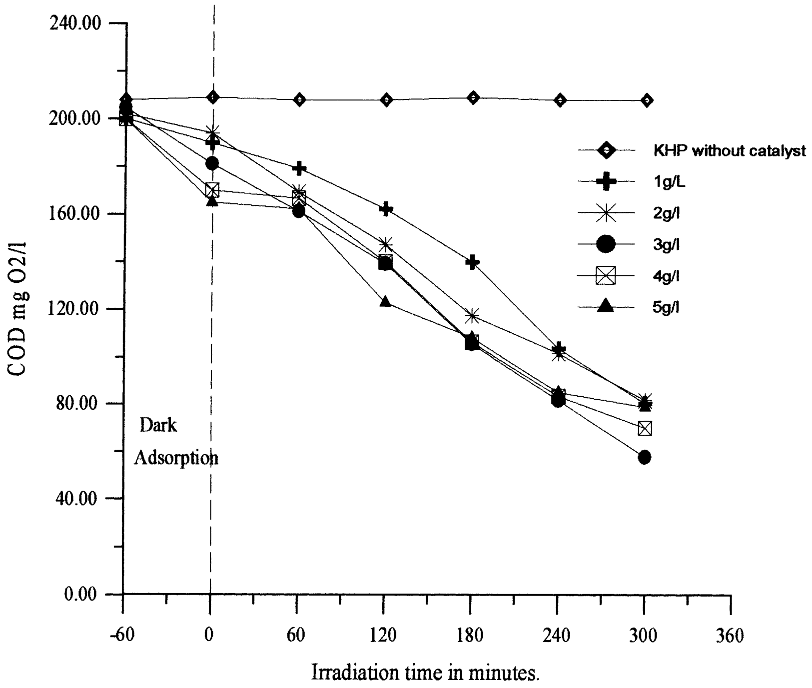


Fig. 1. The COD against the irradiation time for a KHP solution without catalyst and at different catalyst concentrations, pH 5.

During the optimisation process, the catalyst concentration was first varied. The disappearance of the model compound (KHP) was monitored every 60 min by measuring the COD. From the COD values obtained, 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 min) at five different catalyst concentrations are shown in Fig. 1. The COD

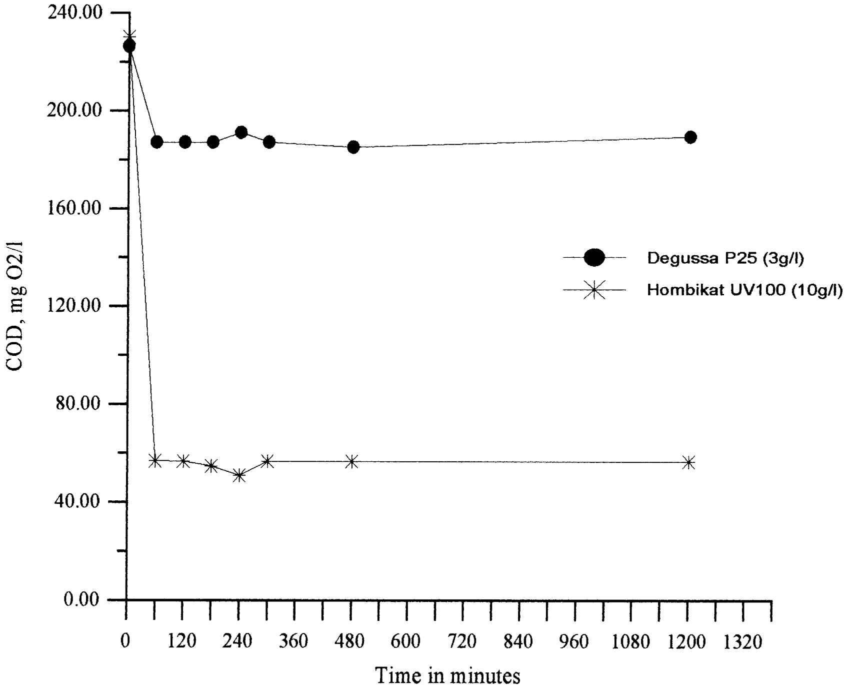


Fig. 2. COD values measured at different times for a KHP solution with 10 g/l Hombikat UV 100 and 3 g/l Degussa P25 without sunlight, irradiation at pH 5.

showed a non-significant adsorption of KHP at low catalyst load. After 60 min of stirring in the dark, 5 and 10 mg O_2/l COD could be measured for 1 and 2 g/l, respectively. In contrast, a relatively high adsorption of 30 and 43 mg O_2/l was detected at 4 and 5 g/l catalyst concentrations, respectively. This effect is due to a high concentration of the active sites that allow for adsorption onto KHP molecules. The degradation rate of the model compound, KHP, was determined at different catalyst loads. The kinetics were calculated using a semi-logarithmic plot, thus, the reaction can be interpreted as following pseudo-first-order kinetics.

The degradation rate increased linearly by increasing the photocatalyst load up to a certain limit. At 3 g/l of Degussa P25, a maximum degradation rate was reached. The degradation rate at this concentration reached more than double its value in comparison to the 1 g/l concentration. Further increase of the TiO_2 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 [18].

For each of the five catalyst loads, the photonic efficiencies were calculated from the ratio of the 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 concentrations could be explained by the limited amount of TiO_2 particles that absorb the solar photons. The optimum catalyst dose was reached at 3 g/l Degussa P25. At higher photocatalyst loads, no further change of the photonic efficiency was observed.

It is known from the literature that the particle size and the type of photocatalyst play a significant role in the degradation rate of organic pollutants. Therefore, the photodegradation of KHP by direct sunlight was investigated using another photocatalyst (Sachtleben Hombikat UV 100) with a different particle size. Fig. 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%). A stronger adsorption of KHP was observed at higher catalyst loadings. The maximum KHP adsorption was reached at 10 g and levelled off for higher concentrations, suggesting 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 CO_2 development during the experiment (Fig. 6). It was found that no CO_2 occurs in the dark (for Degussa P25 and Hombikat UV 100) despite the low COD values found in the solution.

Further experimentation revealed that the adsorption of KHP on the catalyst surface is pH dependent. 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

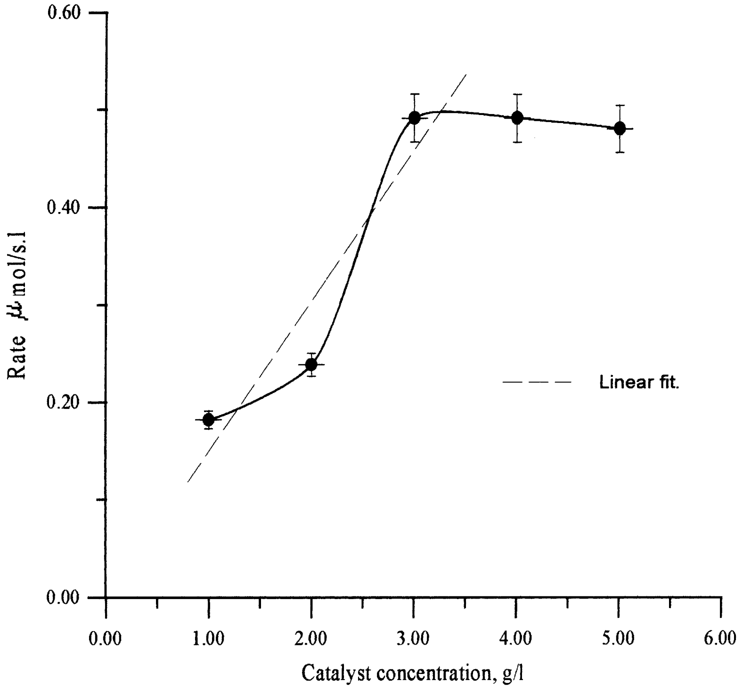


Fig. 3. Degradation rate of KHP at different catalyst concentrations (Degussa P25), pH 5.

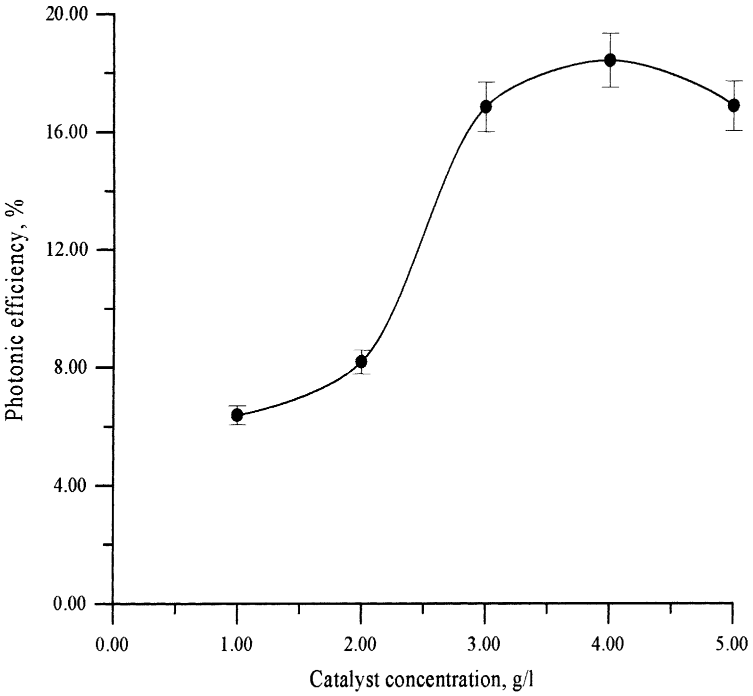


Fig. 4. The photonic efficiency in percent against different catalyst concentrations (Degussa P25) at pH 5.

results showed that the degradation rate is 3.5 times higher in acidic media (pH 3.0 and 5.0) compared to basic (pH 7–11) media. The lowering of the degradation rate at high pH levels can be explained by the adsorption–desorption effect.

At low pH values (<6), the TiO_2 surface is positively charged and the KHP is present at this pH as hydrogen phthalate, capable of adsorbing onto the catalyst surface.

At higher pH values (>6), the TiO_2 surface is negatively charged (Eq. (6)) and the KHP lies in di-ionic negative form

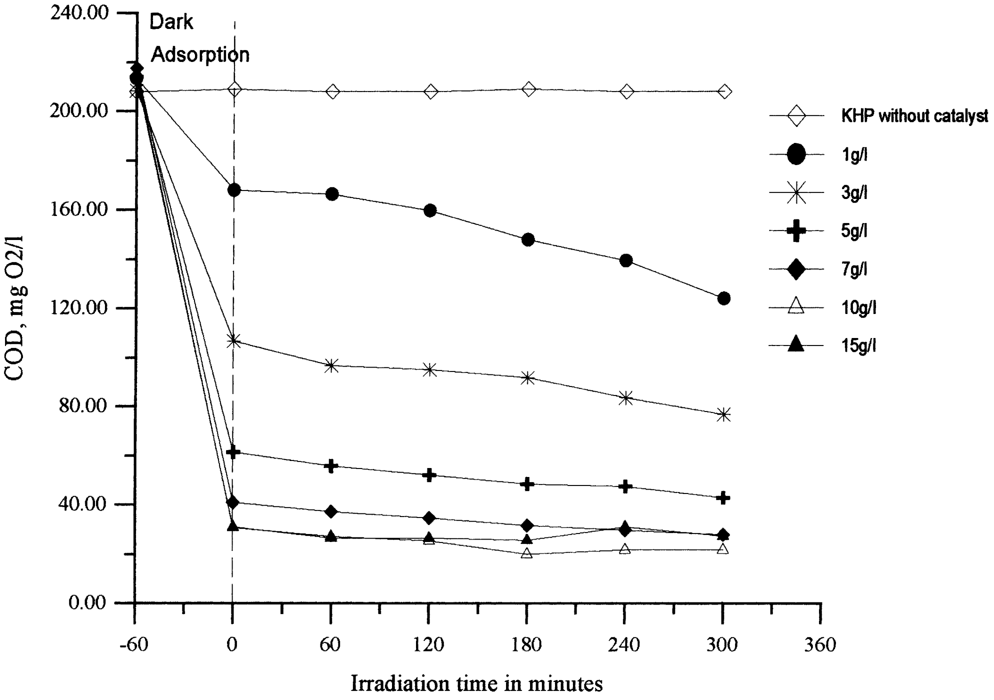


Fig. 5. The COD values at different irradiation times for the KHP solution at different Hombikat UV 100 concentrations, pH 5.

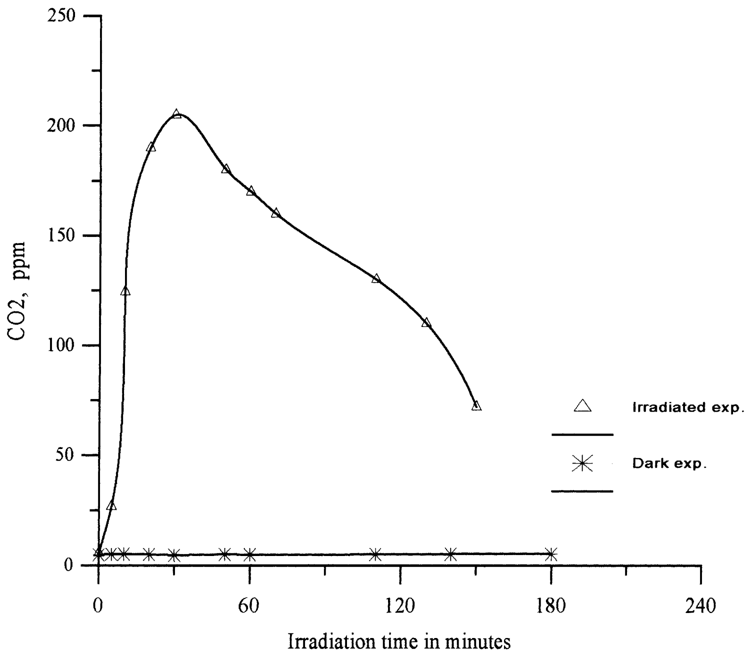
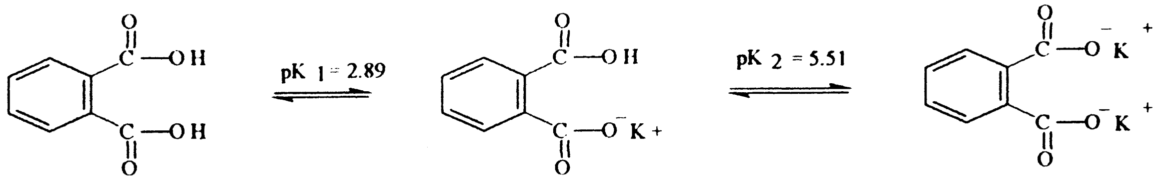


Fig. 6. The measured CO_2 concentrations at different irradiation times and in the dark for a KHP solution at 3 g/l Degussa P25, pH 5.

(Eq. (5)), which would lead to repulsion by the catalyst surface, resulting in negligible adsorption of KHP:



(5)

$$\mathrm{Ti{-}OH} + \mathrm{OH}^- \leftrightarrow \mathrm{Ti{-}O}^- + \mathrm{H_2O} \qquad (6)$$

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 media (Fig. 8). Thus, high photonic efficiency was observed for pH values where a strong adsorption of the pollutant at the catalyst surface occurred (pH values below 5.0).

The influence of light intensity on the degradation rate, for many different classes of pollutants, is reported in the literature [18]. In this work, we studied the effect of sunlight intensity in different weather conditions on KHP degradation, using Degussa P25 as a photocatalyst. All experiments were carried out at pH 5.0 with a catalyst concentration of 3 g/l, under vigorous stirring and with a continuous supply of oxygen into the suspension. The COD data was collected on different days at different sunlight intensities. From the results obtained, the degradation rates were calculated. Fig. 9 shows the variation in the 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 $s^{-1}\,l^{-1}$). At higher light intensities (2.756–2.919 μmol photon $s^{-1}\,l^{-1}$), a non-linear increase was observed. This effect occurred for high photon fluxes due to a predominance of recombination of photogenerated charges [19]. The effect of light intensity on the photonic efficiency of the photocatalytic degradation of KHP using Degussa P25 is illustrated in Fig. 10. The efficiency decreased considerably as the light intensity increased due to the high recombination rate at high light intensities. This makes the photocatalytic oxidation reaction less effective. The maximum photonic efficiency value reached was 33.9%, which was remarkably high in comparison to literature data for other model pollutants [20]. The results showed that when illuminations were carried out with light intensities between 0.311 and 0.986 μmol photon $s^{-1}\,l^{-1}$, the photonic efficiency of KHP degradation was hardly dependent 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 optimum conditions (catalyst type, catalyst concentration, initial pH and sunlight intensity) found for KHP degradation were used for the purification of RASCO wastewater. The organic and inorganic pollutants present in RASCO wastewater are summarised in Table 1. Fig. 11

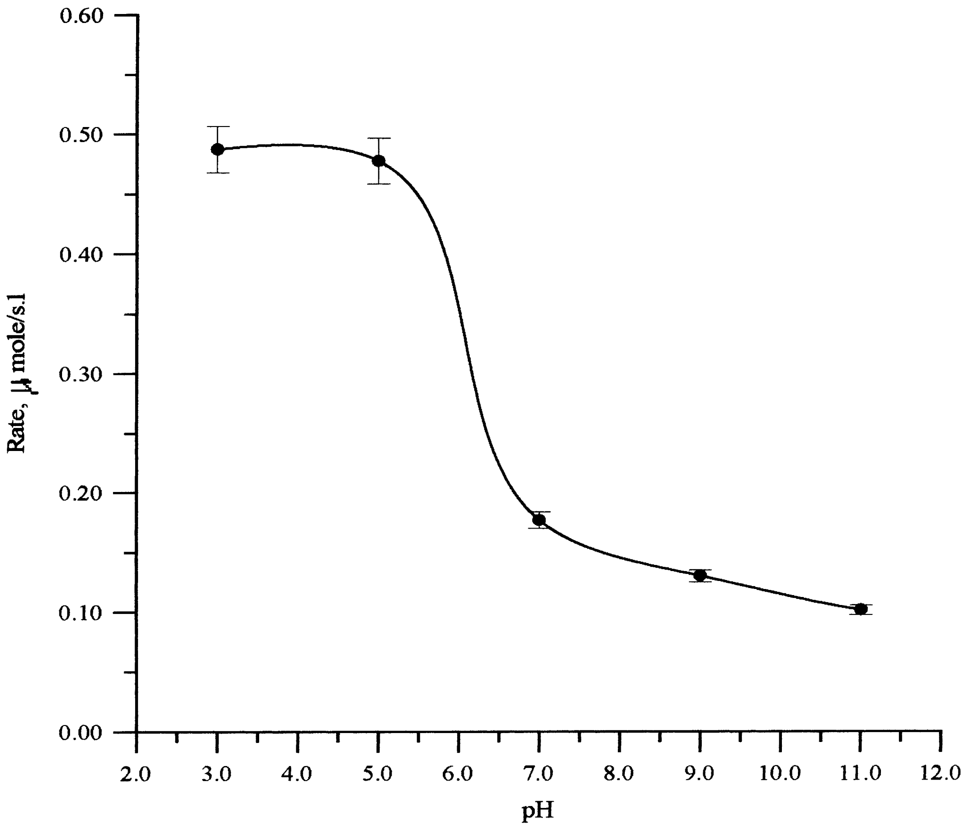


Fig. 7. The degradation rate of the KHP solution at different pH levels using 3 g/l Degussa P25 as catalyst.

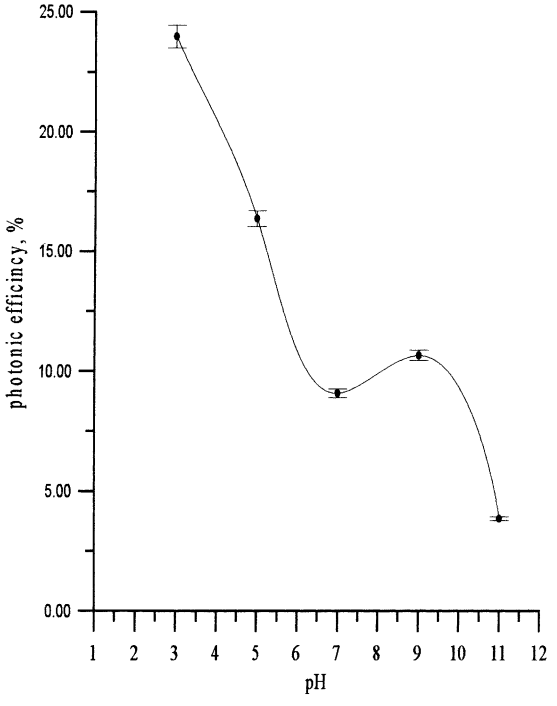


Fig. 8. Photonic efficiency against different pH values of KHP solution in 3 g/l Degussa P25 suspension.

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
Sulphate	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, indane, indene, 1,2,3,4-tetrahydronaphthalene, naphthalene, benzenecycloheptatriene, cyclopentanon, methylcyclopentanon, 2-hexanone, benzeneacetaldehyde, acetophenone, 1-indanone, 3,4-dihydronaphthalenone, phenol, *o*-, *p*-methylphenol

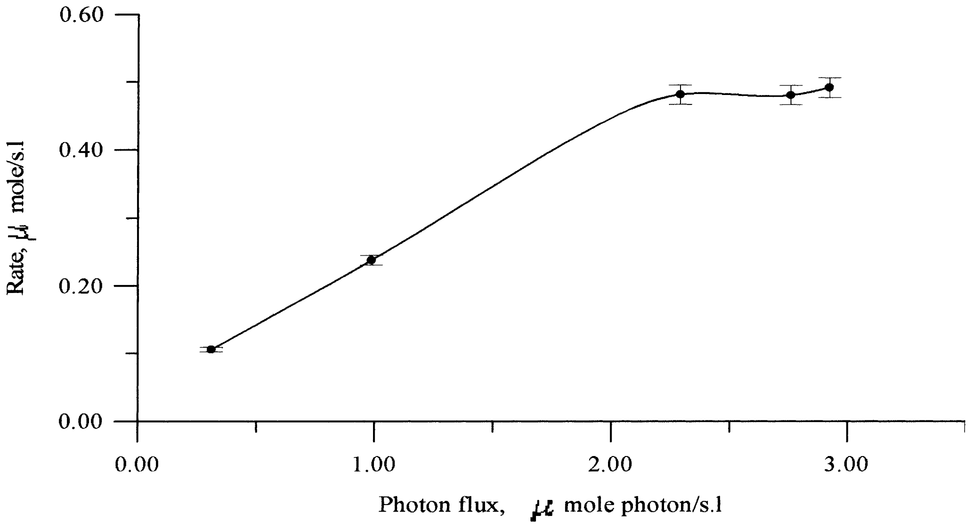


Fig. 9. The degradation rate of KHP against the photonic efficiency.

illustrates the COD values of the degraded pollutants in the RASCO wastewater over a period of irradiation time of 900 min. 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 min of irradiation for both photocatalysts. Irradiation of the sample for a further 600 min produced no detectable degradation. The COD values remain in the range 47–49 mg O_2/l. These results indicate the possible existence of inorganic salts (chloride, ammonia etc.), which yield a corresponding COD value. The experiments showed that the pollutants in RASCO wastewater are completely degraded at the above-mentioned conditions within 300 min. Mechanistically, the study of the individual compounds in RASCO wastewater, such as naphthalene and anthracene, has been previously reported [21].

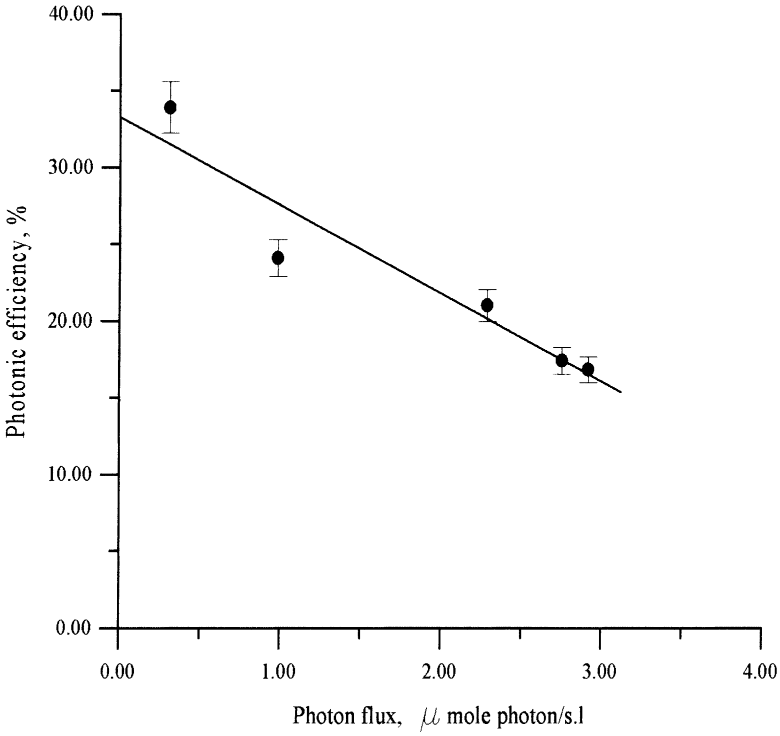


Fig. 10. The photonic efficiency against the calculated photon flux.

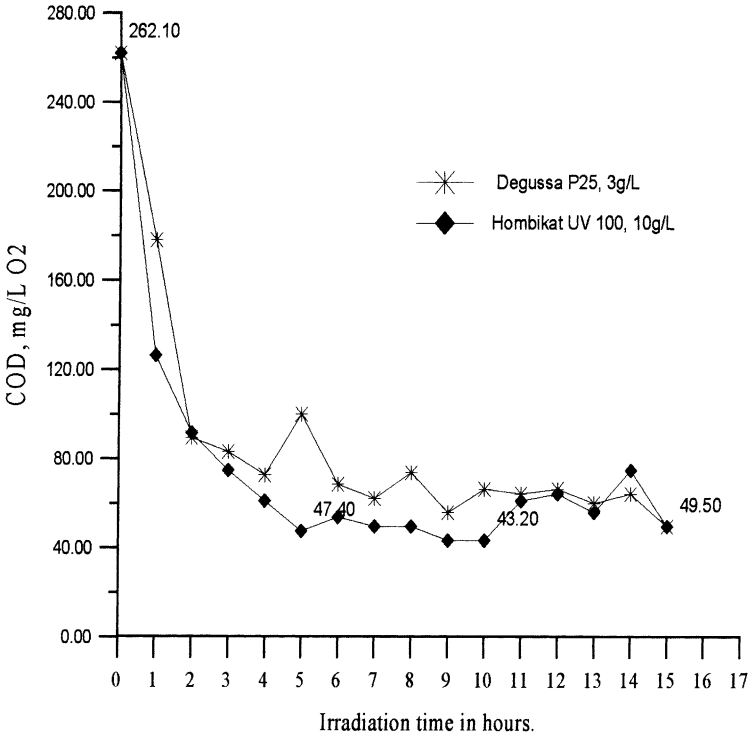


Fig. 11. The COD against the irradiation time for RASCO wastewater using Hombikat UV 100 and Degussa P25.

5. Conclusions

This work demonstrates that the optimal photonic efficiency of the KHP degradation process is reached at a pH level of 3.0 and a concentration of 5 g/l Degussa P25. Using titanium dioxide with smaller particle size does not improve the degradation rate, however, it offers higher absorption area. It was found that the degradation rate of KHP increased linearly with increasing light intensity up to a certain limit, where it reached a plateau indicating high recombination reactions. By applying the optimal experimental conditions, obtained from the model KHP experiments, to the real wastewater samples, it was observed that 5 h irradiation of the wastewater in 3 g/l Degussa P25 was sufficient in order to degrade the organic pollutants in the investigated wastewater. From these results, it was concluded that this could be a promising future process for RASCO wastewater treatment.

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