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Photocatalytic Degradation of Phenol and 1-Naphthalene Acetic Acid as a Representative Compounds of Industrial Waste Water Using Natural and Artificial UV-Light

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التكسير الضوئي المحفر لمادتي حامض 1- نفتالين أستيك والفينول كنموذج لملوثات مياه الصرف الصناعي باستخدام الأشعة فوق البنفسجية الطبيعية والاصطناعية

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تم دراسة تكسير مادتي حامض 1- نفتالين أستيك والفينول باستخدام نوعين مختلفين من ثاني أكسيد التيتانيوم كمحفزات ضوئية (ديجوسا P25 وهومبيكات UV100) ومتابعة التفاعلات باستعمال الشمس كمصدر طبيعي للضوء ومقارنته بالضوء الصناعي الناتج عن UV-lamp. ظروف التفاعل تم تغييرها للحصول على أفضل تفاعل من حيث الرقم الهيدروجيني وتركيز المادة المحفزة. بالنسبة لوسط التفاعل وجد أن أفضل وسط للتفاعل هو عند الرقم الهيدروجيني 5 لكل من المحفزين الضوئيين. أما بالنسبة لتركيز المحفز الضوئي ثاني أكسيد التيتانيوم ديجوسا P25 فقد وجد أن معدل التفاعل يكون في أقصاه عند تركيز 7جم/لتر وللمحفز الضوئي هومبيكات UV100 هو 10جم/لتر. معدل اختفاء مادة حامض أحادي النفثالين والفينول يكون أسرع عند استخدام ضوء الشمس مقارنة بالمصدر الصناعي للضوء UV-lamp مع كل من ديجوسا P25 وهومبيكات UV100.

التحطيم الكلى لحامض أحادي النفثالين قد تم بعد 5 ساعات من تعريض مزيج الديجوسا لضوء الشمس بينما بقي 23.43 جزء من المليون من تركيز المركب في مزيج الهومبيكات بعد 8 ساعات من التعريض المباشر لضوء الشمس. وبالنسبة لمادة الفينول لم يحصل التحطيم الكامل حتى بعد تعريض مزيج الديجوسا P25 والهومبيكات UV100 لضوء الشمس أو تحت UV-lamp لمدة 8 ساعات متواصلة. كما لوحظ أن المحفز الضوئي ديجوسا P25 اكثر فعالية في تكسير حامض أحادي النفثالين والفينول باستخدام ضوء الشمس مقارنة بالضوء الصناعي الناتج عن UV-lamp. تم تكسير أكثر من 90% من الكربون العضوي الكلي (TOC) الموجود بالمياه الصناعية الناتجة من مجمع راس لانوف في خلال 8 ساعات من تعريض المزيج للضوء (UV) باستخدام نوعين مختلفين من المحفز الضوئي (ديجوسا P25 وهومبيكات UV100) عند رقم هيدروجيني (pH) متعادل 6.55.

Abstract: *A photocatalytic detoxification of phenol and 1-naphthalene acetic acid was carried out using two different photocatalysts, Degussa P25 and Hombikat UV100. The degradation reaction was compared by using two sources of UV-light, sunlight and UV-Lamp. All degradation reactions were performed after first optimising the pH and catalysts concentrations. The optimal initial pH was found to be 5.0 for both catalysts. The optimal concentrations for Degussa P25 and Hombikat UV100 occurred at 7g/l and 10g/l, respectively. The degradation rate of 1-NAA and phenol is higher when using sunlight, compared to the artificial UV-light (UV-Lamp) for both photocatalysts Degussa P25 and Hombikat UV100.*

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A complete degradation of 1-NAA was achieved after 5 hours irradiation of Degussa suspension under direct sunlight while 23.43ppm of compound concentration was still in Hombikat suspension after 8 hours irradiation time. Phenol was not completely degraded even after 8 hours irradiation under natural and artificial UV-light by either catalyst. The degradation rate of 1-NAA is faster than that of phenol using the two sources of UV-light. Degussa P25 is the more efficient photocatalyst in degradation of 1-NAA and phenol using direct sunlight and artificial UV-lamp. About 90% TOC of RASCO waste water was completely mineralized within 8 hours of irradiation using the two-photocatalyst types at moderate suspension pH 6.55. Therefore, the solar detoxification process appears to be a good technique to treat the organic load of RASCO effluent treatment plant.

INTRODUCTION

Refinery and petrochemical waste water 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. Phenol and phenolic compounds are common contaminants in industrial waste waters. Their toxicity to mammalian and aquatic life is classified as moderate, but they have strong organoleptic effects[1].

The presence of phenolic compounds in the waste water can contaminate the sea water and, consequently, the drinking water produced from desalination processes. The chlorination of drinking water containing phenolic compounds could produce extremely toxic compounds like dioxin.

Polynuclear aromatic hydrocarbons, such as naphthalene and anthracene are well known hazardous by-products in the coal and petroleum industry[2]. There are several established methods for the removal of such contaminants. Biodegradation is probably the most frequently used technique[3]. However, many toxic mixtures are often lethal to microorganisms, which limit the applicability of the method to cases where well-defined and constant pollutant mixtures can be expected. Other important applied methods include adsorption on activated carbon, hydrogen peroxide/UV-light, Ozone/UV/ hydrogen peroxide and ã-radiolysis[4-7].

In the process of adsorption on activated carbon, some pollutants are either poorly adsorbed or not adsorbed at all. Pollutants transferred from the aqueous to the solid phase are desorbed by heat treatment, which may lead to the formation of new toxic products.

The application of hydrogen peroxide/UV is efficiently used to purify drinking water[5]. The hydroxyl radical produced from peroxide and UV-light is non-selective and can, therefore, oxidise all pollutants in the mixture[8]. The disadvantages of this method is the high cost of hydrogen peroxide and the undesirable adsorption of UV-light by contaminants that leads to the complete termination of the radical reaction.

Ozone/UV and hydrogen peroxide is another method for the detoxification of water, which employs two oxidising agents, ozone and produced hydroxyl radicals[9-10]. However, the treatment of water with ozone, in most cases, does not lead to complete mineralization. Therefore, the ozone/UV system was developed[11]. 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 waste water treatment is a more modern technique that does not require the addition of chemicals[7]. The high energy light ionises water molecules and produces hydroxyl radicals for the destruction of organic pollutants.

In recent years, much attention has been paid to photocatalytic detoxification as an alternative technique, where the organic pollutants are degraded by UV-irradiation of a semiconductor suspension such as titanium dioxide or zinc oxide[12-16]. Photocatalysis with titanium dioxide is based on the formation of pairs of electron/positive holes (e^-/h^+), when the photocatalyst is subjected to UV-light[17]. The electron holes may induce reduction, but in most cases, in the presence of oxygen, they lead to formation of superoxide anions[18]. Positive holes oxidise adsorbed organic substrates or react with water leading to the formation of hydroxyl radicals, which are powerful oxidising agents. The hydroxyl radicals produced are very reactive, and react rapidly and non-selectively with organic compounds leading to, in the last step of reaction, the total mineralization of the organic substrate[19].

There is the need to remove hazardous compounds such as naphthalene, phenol *etc*., which often persist in the final effluent of Ras Lanuf Oil &

Gas Processing Company (RASCO) treated waste water.

In the present work, the applicability of photocatalytic degradation for the destruction of 1-Naphthalene Acetic Acid and Phenol as representative compounds in the RASCO waste water, was studied, using two sources of light (natural sunlight and artificial UV-light), in the presence of two different photocatalysts (Degussa P25 and Hombikat UV100).

MATERIALS AND METHODS

Instruments

The total organic carbon (TOC) instrument used is manufactured by Skalar Company, Holland and equipped with IR-detector, TC+IC reactors, and an autosampler. The TC-reactor has been made of quartz glass, which is resistant to a temperature of 950°C. The TC-reactor tube is filled with Cobalt catalyst for analysis at 950°C, or with Platinum catalyst for analysis at 680°C. The injection volume used was 100µl.

The HPLC apparatus was manufactured by CECIL, UK. The instrument is equipped with a CE1100 pump and CE2020 UV-detector. The separation column used was a spherisorb 80A with a 25cm length and 4.6mm inner diameter. The mobile phase used was a combination of Acetic Acid: Water: Acetonitrile (1:44:55). The flow rate was 1ml/min. and the injection volume was 20µl.

pH-Meter 3071 Jenway type was used for pH measurements. The samples were centrifuged using Seta-IEC from Stan-Hop-Seta. The light intensity was measured using a UVA-meter from Dr Hoenle GmbH. The UV-Lamp used in the degradation experiments was manufactured by Philips, M44 GS-100M, 100W Mercuric Lamp, USA made, 365nm max. Wavelength.

Reagents

Sodium hydroxide, anhydrous potassium biphthalate, anhydrous sodium bicarbonate, nitric acid, phenol, orthophosphoric acid are supplied by BDH and purified before use. Anhydrous sodium carbonate is supplied by Riedel-Dehaen Seelze-Hannover. 1-Naphthalene acetic acid is supplied by Merck and used without purification. Titanium dioxide (Degussa P25, primary particle size 20-30nm, BET surface area 50±15m^2/g, 70% anatase and 30% rutile) was obtained from Degussa GmbH. Titanium dioxide (Hombikat UV100, primary particle size <10nm, BET surface area >250m^2/g, >99% anatase) was purchased from Sachtleben Chemie GmbH. The nitrogen gas used was obtained from nitrogen plant at RASCO with 99.99% purity. The water used in all experiments was distilled and demineralised by the RASCO utility plant. HPLC grade acetic acid, water and acetonitrile were obtained from Sigma-Aldrich. The oxygen gas was obtained from B.O.C. Ltd. With 99.999% purity, grade N4.8.

EXPERIMENTAL

Preparation of Phenol Stock Solutions

1.3053g (0.01387mol) of phenol were dissolved in one litre distilled and demineralized water in order to prepare 1000ppm carbon as a stock solution. 100ml or 25ml from the stock solution was pipetted into 900ml or 225ml water respectively to get 100ppm TOC and 130.5ppm phenol.

Preparation of 1-Naphthalene Acetic Acid (1-NAA) Stock Solution

1.2919g (0.00347moles) of 1-NAA were dissolved in 2 litre distilled and demineralized water to prepare 500ppm carbon as a stock solution. A 200ml or 50ml from the stock solution were pipetted into 800ml or 200ml water respectively to get 100ppm TOC and 129.2ppm 1-NAA.

Photodegradation Experiments

Variation of the photocatalyst concentration

The photoreactor was a 3 litre beaker made of Pyrex-glass, equipped with a magnetic stirring bar and an oxygen-purging device, consisting of two gas washing bottles and two sintered glasses. One bottle was filled with pure water to humidify the oxygen and to minimize evaporation of water in the beaker. In each of the performed experiments the photoreactor was filled with 100 ppm TOC (129.2ppm 1-NAA) and the required amounts of the photocatalyst as follows: (3g/l, 5g/l, and 7g/l for Degussa P25 and 5g/l, 7g/l, 10g/l, 15g/l, and 20g/l for Sachtleben Hombikat UV-100), the initial pH was adjusted to 5.0. The suspension was 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 sunlight and the suspension was irradiated for 8 hours.

15 mls sample was taken before the addition of photocatalyst directly before exposing the system to the sun and 15mls were taken at regular intervals (every 60 minutes) during irradiation. This was not returned to the bulk solution. Consequently there was a decrease in volume during the experiments, in which the TOC and HPLC was being measured. However, the number of analyses done and volume needed on a given run was limited so that the volume decrease in the illuminated solution was less than 15%.

The pH was measured immediately by a pH electrode before the samples were taken. TOC and the compound concentration (by HPLC) 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 using 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 concentrations were chosen as 7g/l for Degussa P25 and 10g/l for Sachtleben Hombikat UV-100, which were found to be the optimum concentration for the degradation of 1-NAA. The degradation of phenol was carried out at different pH (3.0, 5.0, and 8.0). The TOC and HPLC of the irradiated solution were performed as explained in the procedure above.

Photodegradation of phenol and 1-NAA

A small photoreactor was used that consisted of 300ml beaker made of Pyrex glass, equipped with a magnetic stirring bar and an oxygen purging device, which consisted of two gas washing bottles and two sintered glasses. One bottle was filled with pure water to humidify the oxygen and to minimize evaporation of water in the beaker.

A solution of one litre of 100ppm TOC (of 130.5ppm phenol or 129.2ppm *1-NAA*) and the required amount of the photocatalyst were filled into the reactor and the the initial pH was adjusted to the desired values (pH 5.0). The suspension was 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 sunlight and the suspension was irradiated for 8 hours.

Approximately 8mls were taken before the addition of photocatalyst, directly before exposing the system to the sun and about 8 mls also were taken at regular intervals (every 60 minutes) during irradiation. This was not returned to the bulk solution. Consequently there was a decrease in volume during the experiments. However, the number of analyses done and volume needed on a given run was limited so that the volume decrease in the illuminated solution was less than 15%.

The pH was measured immediately before the samples were taken. TOC and the compound concentration (by HPLC) was determined, after centrifuging the suspension for 15 minutes at 1500 rpm, according to a standard method ASTMD 1252 (ASTM, 1993). The UV-intensity was determined at regular intervals using a UV-meter (Dr Hoenle UV-A meter). The same procedure was followed when using the UV-lamp as the energy source.

TOC Experiments

2.1254g (0.01041mol) anhydrous potassium biphthalate was dissolved in 1 litre demineralised water to make a 1000ppm carbon as stock solution. The pH of the solution was adjusted to 2 using orthophosphoric acid.

A series of concentrations (20, 40, 60, 80, and 100ppm) were prepared and injected into the instrument in order to generate the TC calibration curve. For the inorganic carbon (IC) calibration curve 4.4122g (0.04163mol) anhydrous sodium carbonate and 3.4970 g (0.04163mol) anhydrous sodium bicarbonate were dissolved in 1 litre demineralised water to get 1000ppm inorganic carbon. Different concentrations were prepared (20, 40, 60, 80, and 100ppm) for the calibration curve. The TOC was calculated as the difference between TC and IC

TOC = TC – IC

Where,

TOC is the organic carbon that is converted into carbon dioxide after Oxidation; TC is the total carbon in a sample, this includes organic, inorganic, and volatile TC. It is represented as the total mass of carbon per amount of sample. IC is the inorganic carbon in a sample that after acidification turns into carbon dioxide. The TOC sample injection; 10 – 15 mls were collected from the suspension. The solution was acidified to pH 2, and centrifuged for 15minutes at 1500rpm to separate the catalyst. Aliquots were gently purged with nitrogen before analysis to remove any dissolved inorganic carbon.

HPLC Experiments

The HPLC was calibrated by the compound (Phenol and 1-NAA) which needs to be measured. The compounds standard solution used was: 50, 100, 150, and 200ppm. The concentration (Absorbance) of the pollutants was measured at 254nm. The samples injected into the HPLC equipment were from the same solutions used for the TOC experiments and the pollutant concentrations were determined using the calibration curve.

RESULTS AND DISCUSSION

The photodegradation of 1-NAA and phenol, with two different types of photocatalyst, utilizing solar energy as the energy source has been studied under optimum condition pH and catalyst concentration (pH 5, 10g/l Hombikat UV100 and 7g/l Degussa P25). When certain forms of titanium dioxide are illuminated by light of wavelength shorter than 380nm in the presence of water containing dissolved organic compounds and oxygen, powerful oxidation occurs. Many compounds are known to be oxidized to carbon dioxide under these conditions[20]. This work applies direct comparison of artificial and natural energy sources in order to degrade pollutants and apply this technique in the waste water treatment plant of Ras Lanuf Petrochemical Complex (RASCO).

Phenol and 1-NAA compounds have been selected as they are easily soluble in water, and representative of phenolic and condensate aromatic compounds respectively, which are the major organic pollutants in RASCO waste water [21]. To ensure that no degradation occurred in the dark or due to oxidation by oxygen two blank experiments were carried out. In the first one, a mixture of 100ppm total organic carbon (TOC) of 1-NAA and 7g/l Degussa P25 was stirred and bubbled with oxygen for 8 hours in the laboratory. The TOC was measured every 60 minutes. In the first hour the TOC decreased about 2%. This change in TOC was due to adsorption on the catalyst surface. During the next 7 hours the TOC remained constant. Sachtleben Hombikat UV-100 was also used, under the same conditions as the first experiment. More adsorption (approx. 4%) was observed in the first hour (Fig. 1). The dark experiment of phenol, gave the same results analogue to 1-NAA using the two photocatalyst type. The absorption of phenol on the catalyst surface has been also reported in the literature. It has been reported that there is no dark adsorption of phenol to TiO_2[22].

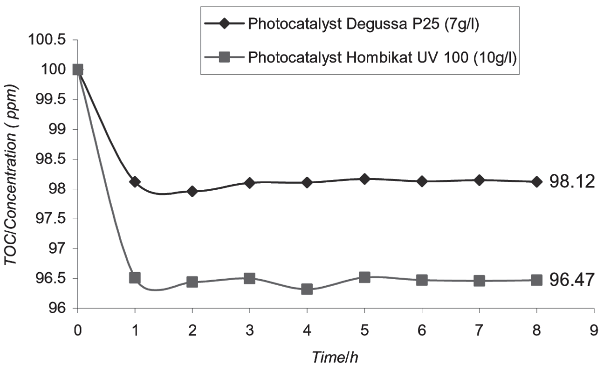


Fig. 1. Influence of the catalyst on the TOC/Co (Total Organic Carbon) reduction without irradiation.

In the second experiment, 100ppm TOC of 1-NAA and phenol were prepared in water and exposed to direct sunlight ($\lambda \geq$ 290nm) in the absence of catalyst and excess of oxygen (Fig. 2). The measured TOC of 1-NAA and phenol remained constant after two hours irradiation and after one day of sunlight, 1.5% of TOC was decreased from 100 to 98.5ppmTOC. These results indicate that no degradation of 1-NAA and phenol is recorded due to direct photolysis.

Variation of Photocatalyst Concentration and Initial pH

Concentration of the photocatalyst Degussa P25

To determine the optimum conditions for the photocatalytic degradation reaction of 1-NAA, the catalyst concentration was first optimized. Three

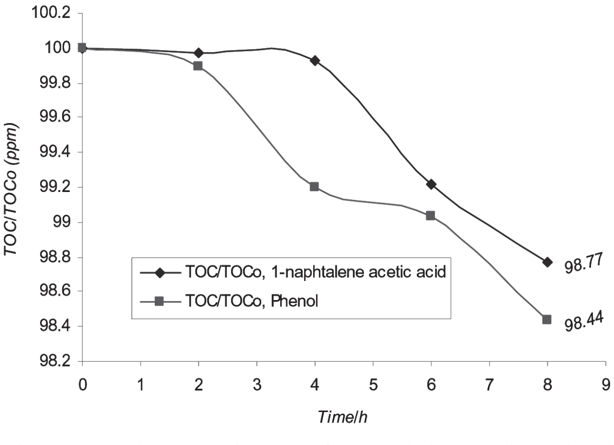


Fig. 2. Photolysis experiments of 1-naphthalene acetic acid and phenol without addition of photocatalyst.

suspensions of 100ppm TOC 1-naphthalene acetic acid with different amounts of the photocatalyst (3, 5, and 7g/l) were prepared, and continuously bubbled with molecular oxygen. All suspensions were left for one hour in the dark to reach adsorption equilibria before irradiation. The disappearance of the model compound (1-NAA) was monitored every one hour by HPLC, and the total organic carbon was measured using the TOC-analyzer.

The measured TOC and HPLC values (every one hour) at three different catalyst concentrations, are shown in Figures 3 and 4. The TOC results showed a non significant adsorption of 1-NAA at low catalyst load 3 and 5g/l, while at high catalyst concentration 7g/l, little adsorption (2.1ppm TOC) was detected after one hour of stirring in the dark. This effect is due to a high concentration of the active sites which are able to adsorb organic molecules.

The degradation of 1-NAA increased linearly by increasing the photocatalyst load. At the maximum catalyst load of Degussa P25 (7g/l), the compound disappeared after 4 hours of irradiation (Fig. 4), while 4 hours of irradiation were not enough for a complete degradation of the intermediate products (Fig. 3). The TOC decreased to 18ppm after 8 hours irradiation time, at the same catalyst load. In case of 3 and 5g/l catalyst load the TOC of 1-NAA showed 22 and 25ppm of total organic content after 8 hours irradiation, respectively. Contrary to these results, Figure 15, indicates a complete conversion of 1-NAA after 6 and 5 hours irradiation, for the two-catalyst concentration 3 and 5g/l, respectively. It has been reported that 3g/l was the optimum catalyst concentration for potassium hydrogen phthalate (KHP)[23]. The HPLC experiment showed that the concentration of 1-NAA decreased from 128.2ppm to 8ppm within 3 hours (Fig. 4). In the same period of time the TOC decreased from 98.7 to 82ppm. The TOC content of the sample is higher compared to the HPLC results. This is due to the presence of the intermediate products produced during the degradation process. After 6 hours the HPLC experiment showed a complete conversion of 1-NAA. At this time 40% of the original TOC was still in the solution. After one day of sunlight (8hours) the TOC of the solution reached 22ppm.

From Figure 3 and Figure 4 it is obvious that the increase of the photocatalyst concentration has an important effect on the conversion rate of 1-NAA. The 1-NAA disappeared from the suspension after 5 hours and 4 hours at 5 and 7g/l catalyst concentrations, respectively. It was also observed that the catalyst concentration has only a slight effect on the TOC of the suspension.

Concentration of the photocatalyst Sachtleben Hombikat UV-100

It is known from the literature that the particle size and the type of the photocatalyst play an important role in the degradation of organic pollutants. Therefore, the photodegradation of 1-NAA by direct sunlight was investigated using different concentrations of Sachtleben Hombikat UV-100 as an alternative photocatalyst. Sachtleben Hombikat UV-100 consist of <1% rutil and >99% anatase compared to Degussa P25 with 30% rutil and 70% anatase. Furthermore, Sachtleben Hombikat UV-100 possesses bigger particle size than Degussa P25. For this reason it was interesting to compare the degradation efficiency of both types of catalyst. Five mixtures of 100ppm TOC (129.2ppm1-NAA) and

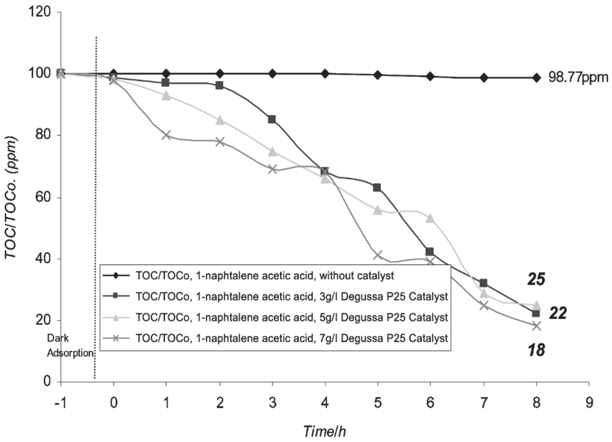


Fig. 3. The TOC comparison of 1-naphthalene acetic acid degradation using three different catalyst concentration of Degussa P25 and sunlight as energy source.

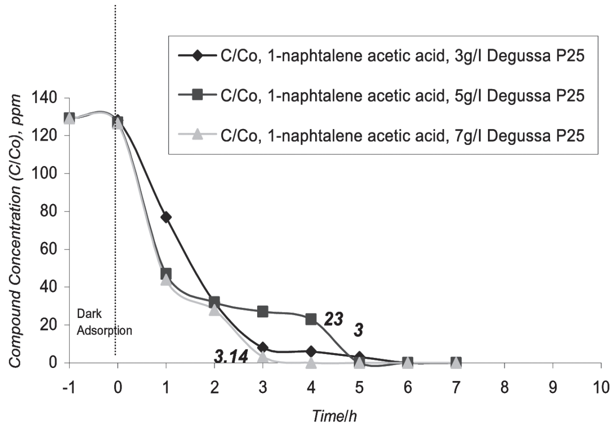


Fig. 4. Comparison of 1-naphthalene acetic acid degradation using three different catalyst concentration of Degussa P25 and sunlight as energy source.

different catalyst concentrations (5, 7, 10, 15, and 20g/l) were irradiated under continuous oxygen bubbling. The initial pH of the system was adjusted to 5.0. The mixture was stirred for at least one hour in the dark to allow equilibrium of the system. Figures 5 and 6 illustrate the behaviour of the TOC and HPLC reduction for different catalyst concentrations. At a catalyst concentration of 5g/l the adsorption of 1-NAA in the dark was low 97.8ppm TOC after one hour. Adsorption of 1-NAA was increased at higher catalyst loading. The TOC decreased at catalyst load 15 and 20g/l to 95.6 and 93.9ppm, respectively, at the dark experimental time (1hour). The disappearance of the organic pollutant in the dark is due to strong adsorption of compound (1-NAA) on the catalyst surface area.

At a catalyst concentration of 10, 15, and 20g/l of Sachtleben Hombikat UV-100, the adsorption of the organic pollutant reached a maximum value, which indicated that maximum coverage of the surface active sites with 1-NAA is achieved. The optimal 1-NAA conversion was obtained at 10g/l Sachtleben Hombikat UV-100 catalyst concentration. It can be seen clearly in Figure 5 that the best catalyst concentration for the degradation of *1-NAA* was 10g/l. The data indicate a 46ppm TOC after 8 hours irradiation, while the HPLC value (Fig. 6) showed that only 14ppm of starting compound was still in the suspension. The *1-NAA* concentration reached after 8 hours 24, 17, 14, 19, and 19ppm at 5, 7, 10, 15, and 20g/l catalyst concentration, respectively. On the other hand the TOC of the suspension was found to be at 46ppm at the best catalyst concentration 10g/l. That means the total degradation of intermediate products is slower in the Sachtleben Hombikat UV-100 than in the Degussa P25 suspension. The difference between the two catalysts can be explained by the different polarity of the intermediate and subsequently their effect on the adsorption/desorption on the catalyst surface.

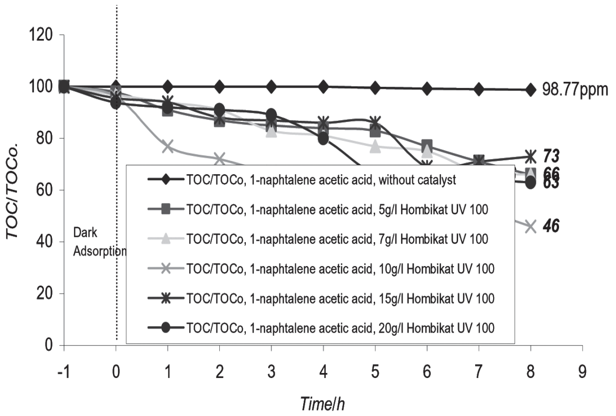


Fig. 5. The TOC comparison of 1-naphthalene acetic acid degradation using five different catalyst concentration of Hombikat UV 100 and sunlight as energy source.

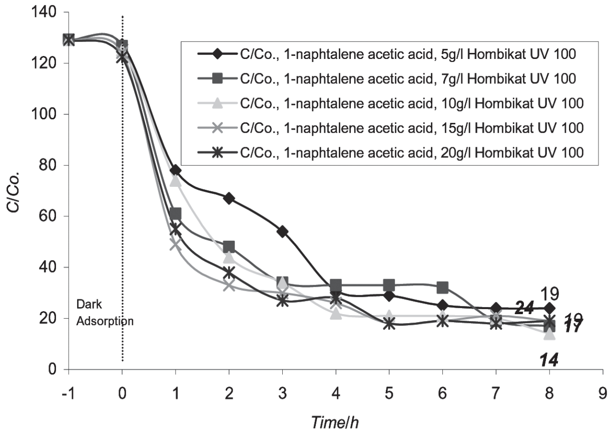


Fig. 6. Comparison of 1-naphthalene acetic acid degradation using five different catalyst concentration of Hombikat UV 100 and sunlight as energy source.

Influence of the initial pH

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 of phenol using direct sunlight and Degussa P25 as catalyst was studied.

In all pH experiments, the optimum catalyst dose 7g/l was chosen as the photocatalyst concentration. The degradation of phenol at different pH value (3, 5, and 8) was determined, and is shown in Figures 7 and 8. The TOC results (Fig. 7) show that the degradation of phenol is better in acidic medium (pH 3.0 and 5.0) compared to the basic media pH 8.

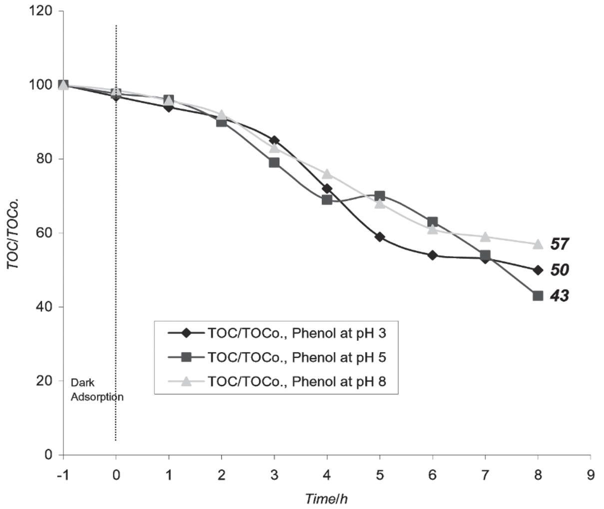


Fig. 7. The TOC comparison of phenol degradation at three pH values using 7g/l Degussa P25 and sunlight as energy source.

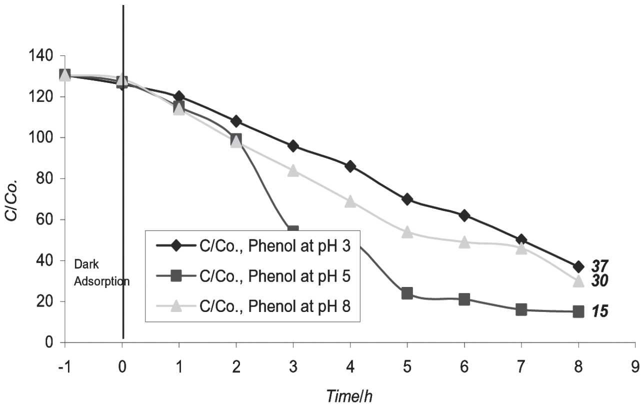
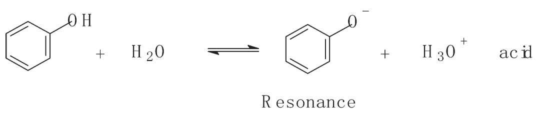


Fig. 8. Comparison of phenol degradation at three pH values using 7g/l Degussa P25 and sunlight as energy source.

An increase in pH (pHe≥ 8.0), lowered the degradation of phenol, this is due to negative charges on the catalyst surface and the phenol repulsion. The titanium dioxide surface is composed of amphoteric sites, which can become either positively or negatively charged[24]. At pH 5 the TiO_2 surface accumulates a net positive charge due to the increasing fraction of total surface sites present as $TiOH_2^+$ (equation 1). When phenol ionises, the phenoxide ion is resonance hybride (equation 2), and with strong alkalis, phenol behaves as a weak acid, forming phenoxide (equation 3).

$$\text{Ti-OH} + H^+ \rightleftharpoons \text{Ti-OH}_2^+ \tag{1}$$



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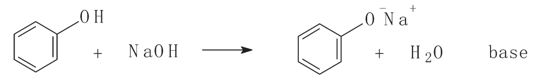


3

Since the surface of the photocatalyst is positively charged a good adsorption of the phenol can be expected. It can coordinate easily through the oxygen atoms with the positive surface. This leads to better adsorption and consequently effective degradation. At a pH above 5 the titanium dioxide has a net negative charge due to a significant fraction of total surface sites present as TiO^- (equation 4).

$$\text{Ti-OH} + OH^- + OH^- \rightleftharpoons \text{Ti-O}^- + H_2O \tag{4}$$

The HPLC data indicate that there are marginal differences in the removal of phenol with pH. A better degradation of phenol was observed with the suspension at pH 5 while at pH 3 and 8 the final concentration of phenol compound was 37 and 30ppm, respectively, after 8 hours of irradiation time. The pH 3.5 was found to be the optimum for the degradation of phenol[18, 25]. Howeever, it has been reported that there is no effect of pH on the degradation rate of phenol removal[26]. Differences between catalysts might be responsible for these disagreements.

For Sachtleben Hombikat UV-100, pH 5.0 was reported as the optimum pH-value using potassium hydrogen phthalate (KHP) as a model compound and sunlight as energy source[23].

Photodegradation of 1-NAA and Phenol

Photocatalytic degradation of *1-naphthalene acetic* acid and phenol was carried out using two sources of UV-light. Sunlight with an average light intensity 3.2±0.5W/cm^2 and artificial UV-light from the UV-lamps, 3.2±0.5W/cm^2 light intensity which is equal to the average light intensity from sunlight. The photoreactor was surrounded with aluminium foil when exposed to direct sunlight to avoid penetration of irradiation through the side walls, since only the top area of the reactor is considered for the degradation rate calculation. Figures 9 and 10 show the degradation rate of 1-NAA. TOC and HPLC

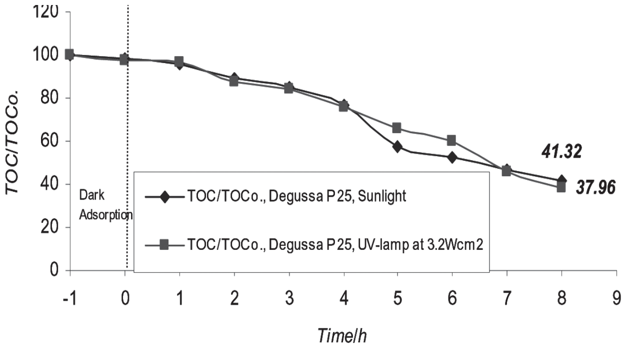


Fig. 9. The TOC comparison of 1-naphthalene acetic acid degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 7g/l Degussa P25.

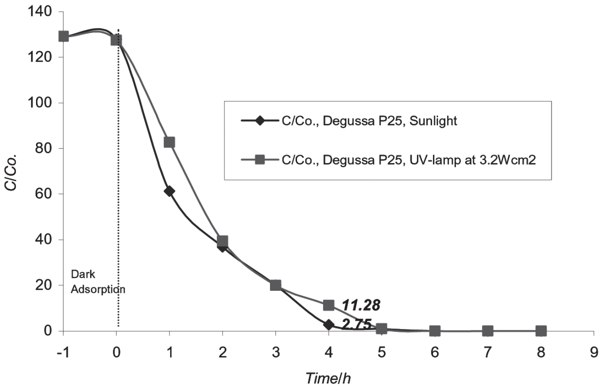


Fig. 10. Comparison of 1-naphthalene acetic acid degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 7g/l Degussa P25.

results indicate higher degradation when using sunlight as the energy source. Increasing the light intensity of UV-lamp to 19.2 W/cm^2 gave a little improvement in degredation of 1-NAA. The HPLC data indicate complete conversion of 128ppm 1-NAA after four hours of irradiation, when exposed to the direct sunlight, while five hours was required for complete degradation of 1-NAA using the UV-lamp of same light intensity. At the same irradiation time the degradation of intermediate products reached about 75ppm TOC with both sources of UV-light. The slow degradation of total organic carbon was due to the partial oxidation to intermediates and not complete destruction of the model compound. Further irradiation gave a decrease in TOC, which reduced 41ppm in the case of direct sunlight and 38ppm by using UV-lamp at 3.2±0.5W/cm^2 light intensity.

The degradation of 1-NAA was better when sunlight was used as energy source compared to UV-lamp of same light intensity. By increasing the light intensity of UV-lamp to 19.2+0,5W/cm2 an improvement occurs.

The photodegradation of *1-NAA* was investigated using Sachtleben Hombikat UV-100 as an alternative photocatalyst. Sachtleben Hombikat UV-100 possesses bigger particle size than Degussa P25. The TOC and HPLC data of *1-NAA* show similar degradation rate using the two sources of UV-light. No significant differences in TOC and HPLC values in the degradation of 1-NAA by using the two sources of UV-light. Figures 11 and 12 indicate that the Sachtleben Hombikat UV100 has the same behaviour in degradation of 1-NAA using the three sources of UV-light. The 1-NAA concentration reduced to 23ppm with Sachtleben Hombikat UV100 while 61ppm TOC was still in the suspension after 8hours irradiation using sunlight as energy source. That means the total degradation of intermediate products is slower in the Sachtleben Hombikat UV100 than in the Degussa P25 suspension. However, the degradation rate of *1-NAA* was better when using Degussa P25 as photocatalyst compared to Hombikat UV100. The difference between the two catalysts can be explained by the different polarity of the intermediates and subsequently their effect on the adsorption/desorption on the catalyst surface. Generally, the use of Sachtleben Hombikat UV100, 1-NAA and sunlight as source of UV-light show a complete destruction of 36% TOC, which is slower when compared to Degussa P25 at the same experimental condition.

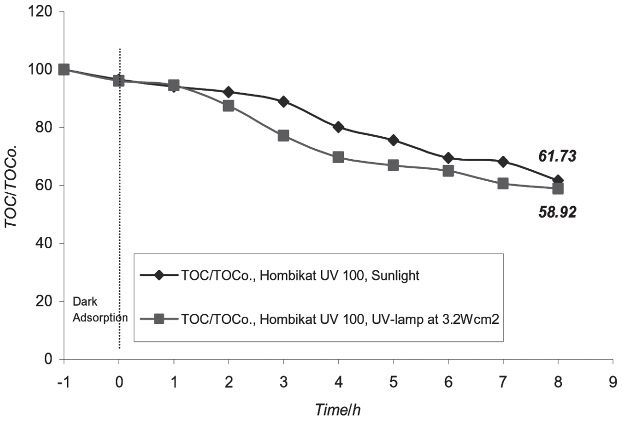


Fig. 11. The TOC comparison of 1-naphthalene acetic acid degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 10g/l Hombikat UV 100.

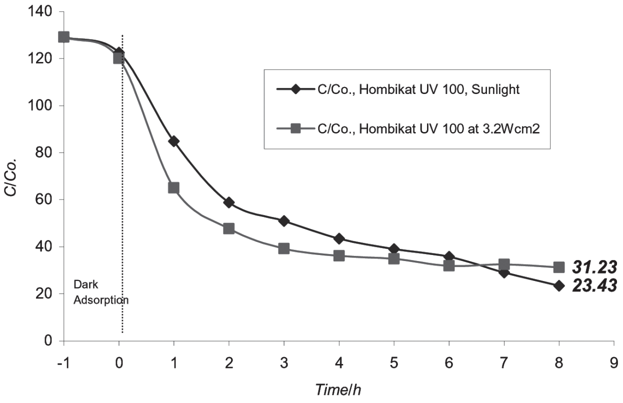


Fig. 12. Comparison of 1-naphthalene acetic acid degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 10g/l Hombikat UV 100.

The degradation rate of phenol was also carried out using two catalyst types with two sources of UV-lights. Phenol was selected due to its presence in the RASCO waste water received in the effluent treatment plant having formed during the ethylene production process. A solution of 130.5ppm phenol (100ppmTOC) was prepared in suspension with titanium dioxide. When using Degussa P25 as photocatalyst and sunlight as energy source, it was observed that the degradation of phenol and other intermediate compounds that are formed during the conversion process is faster compared to the UV-lamp at same intensity of 3.2±0.5W/cm^2. Increasing intensity of UV-lamp to 19.2±0.5W/cm2 shows a better conversion of phenol and its intermediate organics. The HPLC results (Fig. 14) show that the total conversion of phenol was not reached after 8 hours irradiation using both sources of UV-light. Using direct sunlight more than 65% of phenol was degraded after 8 hours of irradiation time while about 56ppm TOC was still in the solution. There is a clear observation (Figs. 13, 14) that the use of direct sunlight was better in destruction of organic compounds compared to UV-lamp of the same light intensity (3.2±0.5W/cm^2). The best conversion of phenol was obtained with Degussa P25 and reached 45ppm after 8 hours irradiation (Fig. 14). The slow conversion of phenol compared to 1-NAA under the same conditions is due to the adsorption of phenol itself and also its intermediate products. It is obvious from the structure of both molecules; 1-NAA is more polar and consequently has stronger interaction with the titanium dioxide surface. This will increase the conversion rate of the molecules. The total conversion of organic matter (TOC) inside the suspension reached 56% with Degussa P25 catalyst (Fig. 13). The explanation for this is the slow adsorption effect of the phenol molecule on the catalyst surface. Low adsorption means low degradation, and high adsorption means high degradation.

A Sachtleben Hombikat UV100 photocatalyst was also used in the degradation of phenol using UV-lamp and sunlight as source of UV-light. TOC and HPLC results indicate that the Hombikat UV100 has the same behaviour as the Degussa P25 catalyst in the degradation of phenol compound (Figures 15 and 16). The two sources of light and Sachtleben Hombikat UV-100 as photocatalyst show only 25% of the TOC was completely mineralized while about 65% of the phenol compound was degraded after 8 hours irradiation.

Degussa P25 as photocatalyst appears to have a better phenol conversion and degradation of its intermediate compound compared to Sachtleben Hombikat UV100. Phenol has slower and non-linear degradation using Hombikat UV100 due to the pH of suspension and the effect of adsorption/desorption process. The degradation process of phenol started at certain pH and during the degradation the pH changes and promotes the adsorption process, which decreases the phenol concentration in the suspension. Continuing the degradation causes again some change in the pH which increases the desorption process and releases non-degraded phenol molecules to the suspension, and consequently increases the phenol concentration in the solution. The degradation of 1-NAA using two photocatalyst types and two sources of UV-light are faster than degradation of phenol compound. This significant observation is explained by the structure of both molecules. 1-NAA is more

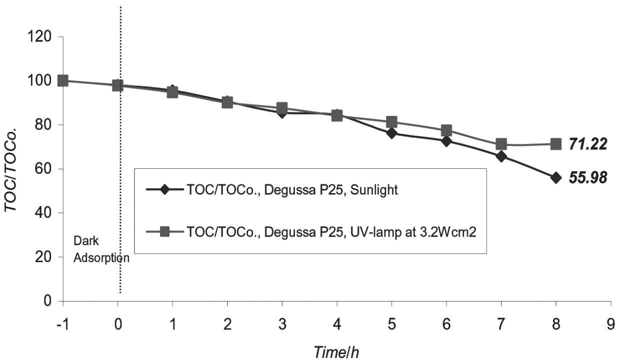


Fig. 13. The TOC comparison of phenol degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 7g/l Degussa P25.

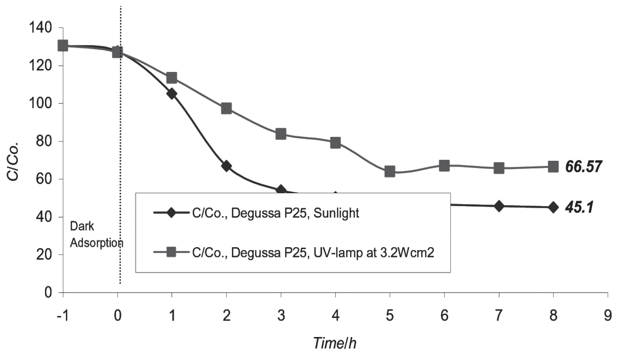


Fig. 14. Comparison of phenol degradation using sunlight and UV-lamp at pH 5 and catalyst 3.2,concentration 7g/l Degussa P25.

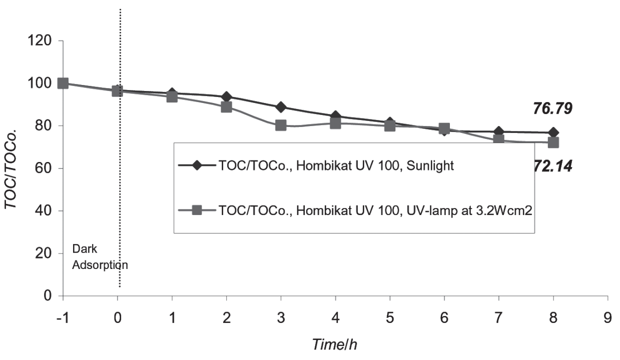


Fig. 15. The TOC comparison of phenol degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 10g/l Hombikat UV 100.

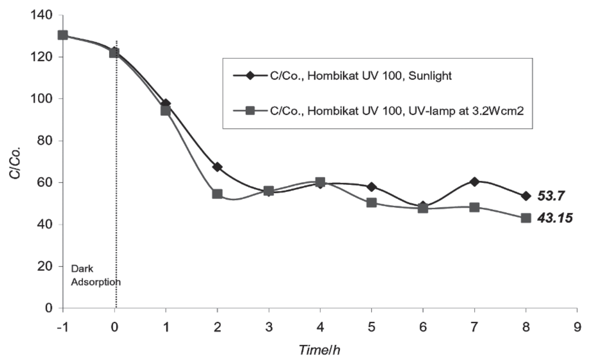
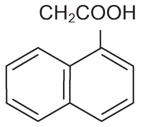


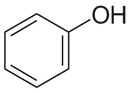
Fig. 16. Comparison of phenol degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 10g/l Hombikat UV 100.

polar and consequently has stronger interaction with the titanium dioxide surface, and this will increase the conversion rate of the molecules.

In addition, 1-Naphthalene acetic acid has two benzene rings while phenol has only one benzene ring. The resonance energy of benzene is 150.6KJ/mol. The actual resonance energy of naphthalene is 255.2KJ/mol, and, hence, naphthalene is less aromatic than benzene (each ring in naphthalene has a resonance energy of 127.6KJ/mol). Consequently, naphthalene will have less aromatic character than benzene, and so will be more reactive.



1-naphthalene acetic acid compound



Phenol compound

CONCLUSION

The degradation of 1-NAA and Phenol is better when sunlight, at average light intensity of 3.2±0.5W/cm^2 , was used as energy source, compared to artificial UV-light at the same light intensity. The degradation of 1-NAA is faster than phenol compound. Degussa P25 catalyst is more efficient in the degradation of 1-NAA and Phenol than Sachtleben Hombikat UV100. The total conversion of 1-NAA was reached after 4 hours irradiation time using Degussa P25 as catalyst, while 8 hours was not enough for complete destruction of Phenol at the given catalyst concentration and initial pH of 5 due to structure of both molecules.

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