

PHOTOCATALYTIC TREATMENT OF INDUSTRIAL WASTEWATER

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معالجة المياه الصناعية الملوثة باستخدام الحفازات المنشطة ضوئياً

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معهد الطاقة الشمسية - هاملي ، اميرنال ، شارع سوكلبي ، هانوفر - المانيا

أستخدم مفاعل ذي مزايا نادرة إذ أن له القدرة على استخدام أشعة الشمس أو أشعة اصطناعية لمعالجة المياه الصناعية شديدة التلوث . استخدمت في هذا البحث طريقتين . في الطريقة الأولى أستخدم المحفز المنشط ضوئياً مع الماء الملوث وكانت النتيجة انخفاض كمية الملوثات من ٦٠٥ إلى ٣٧٣ جزء بالمليون وذلك في ٥٧,٤ ساعة من التعرض للضوء . في الطريقة الثانية تم معالجة المياه كيميائياً ثم استخدمت الطريقة الضوئية فانخفضت الملوثات من ٨٨٠ وحتى ١٩,٧ جزء بالمليون في ١٦,٧ ساعة .

Key Words : Photocatalytic treatment, industrial waste water.

ABSTRACT:

A novel Plexiglas double-skin sheet reactor (DSSR) able to use diffuse as well as direct sunlight for the detoxification of industrial wastewater was used. The efficiency of the photocatalytic treatment of a highly polluted industrial wastewater was studied. Two different sets of experiments were performed. In the first set of experiments the original wastewater was teated photocatalytically without any pre-treatment. The TOC decreased from 605 mg/L to 373 mg/L within 57.4 hours of illumination. In the second set of experiments the wastewater was pretreated by sedimentation after the addition of a flocculent followed by the photocatalytic oxidation process. The TOC was reduced from 880 ppm before treatment to only 19.7 ppm after treatment in 16.7 hours.

INTRODUCTION:

In third world countries water resources are limited and there is a great need to recycle water and to reuse it in agriculture and industry. Luckily solar energy is abundant in most of third world countries. Solar energy intensity in the gulf region is quite suitable and solar energy can be used as a source of energy for the photocatalytic deoxygenation of polluted water. This process may prove to be economically and technologically feasible [1-3] for water treatment and detoxification of wastewater [4].

A number of organic pollutants present in industrial and domestic wastewater resist biodegradation and they are poisonous even at low concentrations. A new method for removing these pollutants from wastewater is on heterogeneous photocatalysis using a semiconductor as the photocatalyst [5]. It was found that titanium dioxide, TiO_2 , is the best photocatalyst for the detoxification of water because it shows a high activity, and it is cheap, nontoxic, and easy to use and handle. The energy gap of TiO_2 is 3.2 eV [6] and thus it can be activated by light with wavelengths < 400 nm, i.e., by the UV portion of the solar spectrum.

Different reactors were developed to degrade organic pollutants photocatalytically [7]. In this work a novel Plexiglas, double-skin sheet reactor (DSSR) able to use diffuse as well as direct sunlight for the detoxification of industrial wastewater was used [8]. The efficiency of the photocatalytic treatment of a highly polluted industrial wastewater was studied. Two different sets of experiments were performed. In the first set of experiments the original wastewater was treated photocatalytically without any pre-treatment. In the second set of experiments the wastewater was pretreated by sedimentation after the addition of a flocculent followed by the photocatalytic oxidation process. A comparison of the two methods is presented.

Experimental:

The industrial wastewater provided was highly polluted by organic and inorganic compounds (Table 1). The total organic carbon (TOC) and inorganic carbon of the untreated

wastewater were 605 mg/L and 0 mg/L, respectively. The initial pH was 9.3; its color was brownish-black.

In all photocatalytic experiments TiO_2 Degussa P25 was used as the photocatalyst. All other chemicals used were of pure grade (Fluka).

The experimental set-up used in this work has been described recently [8]. It consists of a modified double-skin sheet reactor (SDP 16/32, Rohm, Darmstadt, Length = 680 mm, High = 980 mm, 30 Channels 28.5 x 12 mm, Volume = 7L) made from Plexiglas, which was connected with a reservoir. In typical photocatalytic experiments a known amount of TiO_2 was added to the industrial wastewater, resulting in the desired TiO_2 concentration of 5 g/L. The suspension was placed in the reservoir. In all experiments the system was run in a recirculation mode. The flow of the contaminated water was provided by a Sondermann centrifugal pump (M-PP 4450 B). The DSSR was illuminated with 16 fluorescent tubes (Cleo-Performance R 40 W, Phillips) aligned in parallel to the reactor surface [8]. The pre-treatment was performed by adding 0.4 g/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to 20 l of the wastewater (pH=9.3) followed by adjustment to pH 8 by the addition of dilute HCl. Then a saturated solution of $\text{Ca}(\text{OH})_2$ was added until the pH was 12.4. The precipitate formed was left to settle and the solution was decanted and filtered.

Samples were taken at appropriate time and analyzed after centrifugation. Inorganic carbon (IC) and total organic carbon (TOC) were measured with a Shimadzu TOC-5000 analyzer. UV/Vis spectra were recorded using an Omega Spektralphotometer (Bruins Instruments).

The pH values were measured with a Metrom pH meter.

Metal analysis was performed by inductively coupled plasma (ICP) and the atomic absorption spectroscopy (AAS) following German standard methods (DIN 38 406).

Results and Discussion:

The photocatalytic treatment of a sample (6 L) of the industrial wastewater under investigation in the DSSR resulted in a decrease of the TOC from initially 605 mg/L to 373 mg/L within 57.4 hours of illumination. The brownish-black color of the wastewater did not change during this treatment as can be seen in the UV-Vis spectra

of the original and the photocatalytically treated wastewater ICP and AAS measurements show the presence of metals (Fe, Ni, Mn, and Cr) in the wastewater (Table 2). The analysis of a TiO_2 sample, which was used in the photocatalytic degradation experiment, clearly show, that large amounts of these ions were adsorbed on the surface of the photocatalyst during the treatment (Table 2). It is well known that the presence of such ions (especially Mn) might cause the poisoning of the photocatalyst [9]. By washing the used catalyst with distilled water and stirring with 200 mL of distilled water for five hours it was found that some organic pollutants are adsorbed on the surface of the catalyst beside these adsorbed metal ions. To examine the photocatalytic activity of the used photocatalyst a dried sample (1 g) was used for the photocatalytic degradation of dichloro acetic acid (DCA) as a model pollutant. No DCA degradation was observed when following the standard procedure recently described [10]. These results clearly demonstrate that the photocatalytic activity of the photocatalyst is decreased during the photocatalytic treatment of this industrial wastewater by adsorption of inorganic and/or organic compounds. it seems to be necessary to reduce the concentration of the metals in the wastewater to improve the affectivity of the photocatalytic treatment proess. This was done by precipitation using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$. This pretreatment resulted in a significant reduction of the concentration of the metal ions in solution (Table 2). Additionally, the concentration of inorganic carbon (CO_3^{2-} , HCO_3^-), known as scavengers of the oxidizing hydroxyl radicals, was reduced from an initially 138 mg/L to a final 6 mg/L, and the concentration of the organic pollutants was reduced resulting in a decrease of the TOC from and initially 605mg/L to a final 537 mg/L. The color of the solution turned to a pale yellow and the intensity of the visible absorption spectrum decreased relative to the untreated one (Fig 1).

After this pre-treatment TiO_2 was added and the resulting suspension was transferred in the DSSR. An immediate decrease of TOC was noticed after the light was switched on. The TOC reached 19.7 ppm after 16.7 hours of irradiation. After four hours of exposure to light the Toc dropped to 124.3 ppm but at the same time the IC started to increase reaching 16.1 ppm and increased to 60.1 ppm

after 6.67 hours. At this time oxygen was bubbled through the solution for about forty minutes. This caused the IC to drop by a small amount (Table 3). The solution pH dropped from 12.4 in the beginning of the reaction to 7.46 after 9.33 hours of exposure. At this time the pH was adjusted again to 12.4 by adding a NaOH solution. After 10 hours of exposure to light and pH regulation the TOC reached 47.6 ppm and the IC value was 18.8 ppm. After 16.67 hours the reaction reached a steady state and the TOC was reduced to 19.7 ppm while the IC value reached 24 ppm.

The solution was colorless and it showed no absorption in the range 300-700 nm range (Fig 1).

During illumination of the suspension the TOC was decreasing while the IC was increasing (Fig 2). This shows clearly that inorganic ions are formed while the organic pollutants were degraded, and the two reached nearly a steady state (Fig 2). This suggests that the there is a need to investigate the optimum pH, which cause the highest degradation of the organic pollutants.

The analysis of the catalyst after this combined treatment process shows that metals are adsorbed on the surface of the photocatalyst on a much lower content when compared with the amounts which were detected in photocatalyst samples which have been used in the photocatalytic degradation experiments with the original wastewater (Table 2). Only a trace amount of Al was detected and the catalyst did not change its color after use.

From Table 2 it is obvious that the concentration of Fe and other inorganic ions were reduced drastically. It seems that the amount of cations adsorbed on the photocatalyst before treatment was very high but chemical treatment caused a reduction in the concentration of those cations by two times for Cr, 5.3 times for Fe, 9 times for Ni. No change was noticed for V and 31.8 fold decrease for Mn.

In a recent study [9] it was noticed that the adsorption of some cations, especially Mn, causes a poisoning for the photocatalyst and it was difficult to regenerate it. The results obtained in this study whereby the TOC was reduced from 605 ppm before treatment to only 19.7 ppm after treatment in 16.7 hours in quite a pronounced

reduction of pollutants, also the Chemical Oxygen Demand (COD) was reduced from 2300 mg/l before photocatalytic treatment to 39.1 mg/l after treatment. There is a need to study the effect of all cations on the performance of the photocatalyst and to find method to regenerate it.

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Table 1: Analytical data of the industrial wastewater.

Parameter	Concentration (mg/l)
Oil and Fat	120.0
Phenols	247.0
Cyanide	10.0
Thiocyanate	150.0
Benzo(A) Pyrene	0.224
Ni	5.0
Cu	4.0
Fe	45.0
Hg	0.022
Sulfide	12.0
N in NO ₂	0.6
N in NO ₃	8.5
N in NH ₄	680.0

Table 2: ICP and AAS analysis of the industrial wastewater and the used photocatalyst.

	photo-catalyst after photocatalytic treatment	photo-catalyst after pre-treatment and photocatalytic treatment	wastewater, untreated	wastewater after pre-treatment	wastewater after pre-treatment and photocatalytic treatment
	mg/kg	mg/kg	mg/L	mg/L	mg/L
Cr	6.82	3.09	0.01	<0.01	<0.01
Fe	437.0	82.4	2.5	0.62	0.08
Ni	10.9	1.21	0.03	<0.01	<0.01
V	<10.0	<10.0	<0.1	<0.1	<0.1
Mn	20.3	0.64	0.01	<0.01	<0.01
Phenol	n.d.	n.d.	1.35	1.27	0.58

n.d. not determined

Table 3: Change of TOC during the photocatalytic treatment of the original wastewater.

Sample No	Time Hours	TOC ppm
1	0.0	605.1
2	4.5	608.7
3	19.1	518.7
4	27.5	482.4
5	28.0	540.3
6	31.8	489.3
7	38.6	448.5
8	54.4	396.6
9	57.4	372.9

Table 4: Change of IC and TOC during the photocatalytic treatment of a pre-treated wastewater.

Sample No	Time (hours)	IC (ppm)	TOC (ppm)	Remarks
1	0.0	8.7	536.7	pH 12.65
2	0.33	5.7	461.7	
3	0.67	9.6	455.7	
4	1.0	6.1	479.7	
5	1.33	9.3	382.2	
6	1.67	7.5	161.7	
7	2.0	7.4	168.9	
8	2.67	6.4	157.5	
9	3.33	7.8	142.0	pH 9.7
10	4.0	21.6	124.3	
11	4.67	36.5	117.3	
12	5.33	46.5	105.9	
13	6.0	55.7	97.9	
14	6.67	60.1	91.2	Bubble O ₂
15	7.0	56.9	88.2	
16	7.33	53.1	85.4	Stop bubbling O ₂
17	8.0	45.0	75.9	
18	8.67	45.9	68.7	pH 7.46
19	9.33	19.5	70.2	pH adjusted to 12.4
20	10.0	18.8	47.6	
21	10.67	21.8	42.0	pH 12.0
22	11.33	21.2	34.5	
23	12.0	22.4	33.0	
24	12.67	24.0	30.8	
25	13.33	31.2	29.2	
26	14.0	25.4	25.2	
27	14.67	24.1	31.6	
28	15.33	24.0	23.7	
29	16.0	25.0	24.6	pH 11.54
30	16.67	24.2	19.7	

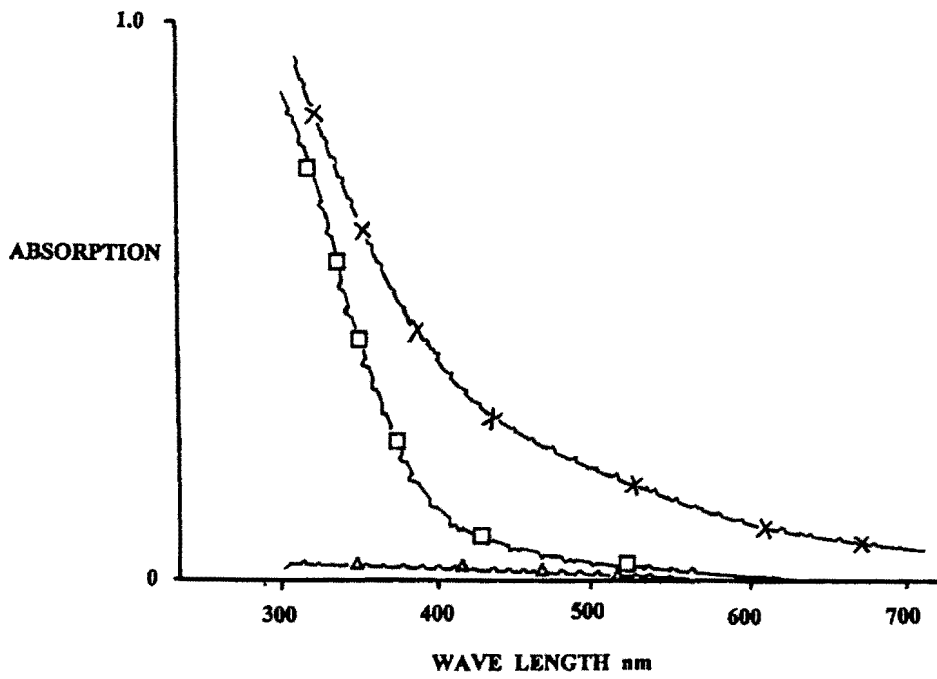


FIG1 ABORPTION SPECTRA OF WASTE WATER.

X UNTREATED □ CHEMICALLY TREATED
△ CHEMICALLY AND PHOTO CATALYTICALLY TREATED.

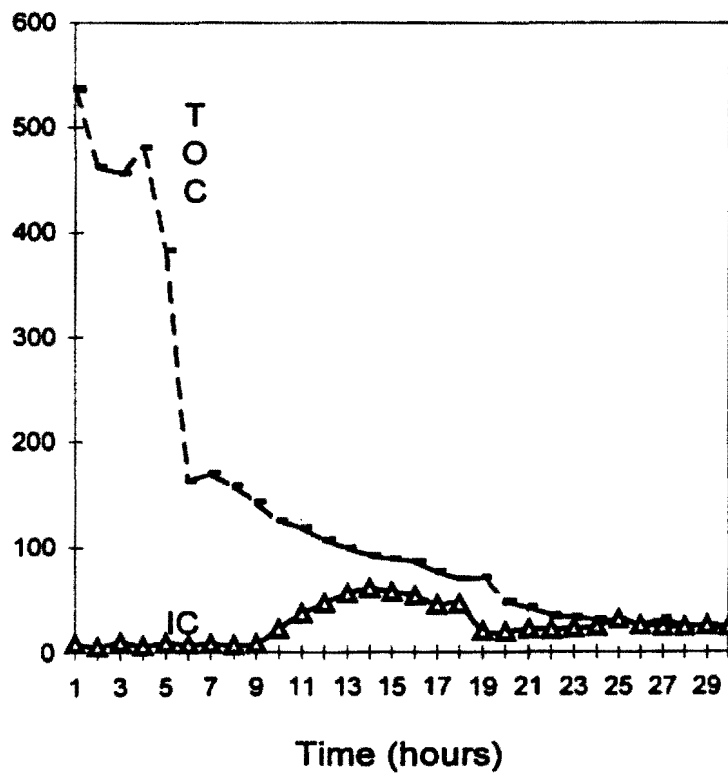


Figure 2: Change of TOC and IC with time.