Elimination of organic compounds in wastewater by advanced oxidation technologies

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Abstract

A rapid development of industry and other activities and the increment of population in last years is origining a serious problem of environmental pollution. Advanced oxidation technologies are proving to be important contributions to the treatment of water and air to remove harmful and toxic substances. These methods are very important because can degrade organic pollutants to non toxic substances, such as carbon dioxide and water, under moderate conditions.

A objective of this research work consists in a study of the yield of advanced oxidation on degradation of pollutants mixtures in water. The photoreactor designed is formed by a cylindrical recipient of 3 liters of volume. The UV radiation comes from a half-pressure (125 w) mercury vapour lamp with a cooling jacket around it to avoid any thermal influences affecting the chemical processes taking place inside the reactor. This lamp is placed traversely to the reactor. The reactor possesses a magnetic system of agitation and key to extract samples. It has an entrance of synthetic air of high purity at three different levels. The air flow is 5 ml/minutes. The system leading to the production of hidroxyl radicals in solution. The hidroxyl radicals are species strong oxidizers than attack and destroy chemically to water pollutants. In this work, mixtures of organic pollutants are treated by heterogeneous photocatalysis with titanium dioxide and effect photo-Fenton. The whole process is carried out ambient temperature.

On the other hand, it was realiced a analysis of effect adittion of oxidants agents in order to increase degradation of pollutants. After treatment for 120 minutes, total organic carbon initial (TOC) was reduced to 44%, 25% y 91% with titanium dioxide, potassium peroxodisulphate and titanium dioxide, hydrogen peroxide and titanium dioxide, respectively. Respect to photo-Fenton process, it leads to reduction of 87% total organic carbon initial in 120 minutes in the studied conditions. It is very important the high degradation conversion has been obtained in many of the studied cases. For this reason, advanced oxidation processes could be used for degradation of organic pollutants in wastewater.

The research work continues by application of photocatalysis with titanium dioxide and Fenton method to samples of urban wastewaters coming from a secondary biological treatment. We were carried out different experiences varying semiconductor concentration and solution pH to study the influence on degradation of organic matter contained in urban wastewater. In all cases, the degradation was evaluated by analysis of total organic carbon (TOC) and chemical oxygen demand (COD) in function of reaction time.

Comparing the two processes carried out, we can stress that the photo-Fenton method is faster during the early stages of reaction (0-40 minutes). For longer periods of operation (between 180 and 240 minutes) the degradation conversions of both methods tend to be similar and the final conversion of elimination of TOC is 90-95 %.

Keywords: wastewater, pollutants, elimination, photocatalysis, Fenton

1. Introduction

The fundamental goal of this research work is the breakdown of the organic pollutants present in urban wastewater via advanced oxidation treatment. In our particular case, we used and evaluated some of these techniques, such as heterogenous photocatalysis with ultraviolet light using titanium dioxide as a catalyst and the photo-Fenton process. We have applied these procedures to mixtures of organic pollutants and; subsequently, to urban wastewater samples which have been purified via secondary biological treatment and proceed to evaluate the elimination performance of each technique.

Follow-up monitoring of the degradation process is carried out via an analysis of the evolution of the Total Organic Carbon (TOC) in terms of the operation time and analytical determination of each individual pollutant via gas chromatography-mass spectrometry.

We aim to analyse the effectiveness of these procedures and, depending on organic material degradation performance, undertake a prior viability study of the aforementioned techniques in order that they might be used and implemented as a tertiary purification treatment system for urban wastewater. In this sense it is necessary to clarify that mentioned tertiary treatment is a phase of the investigation project that will be studied in the future according to the landmarks obtained and the planning of the investigation project. Our research work is developing at the present time to laboratory scale, in the first phase of the investigation. Depending on the obtained results and degradation yields of organic matter of the different oxidation advanced processes, a study will be carried out in plant pilot to develop this project of tertiary treatment of purification of urban waste waters. This tertiary treatment will be based on a technique of advanced oxidation, in combined techniques of advanced oxidation or in a mixed procedure of conventional biological purification and a process of advanced oxidation. Finally, we shall analyse the possibility of reusing the wastewater treated via these techniques.

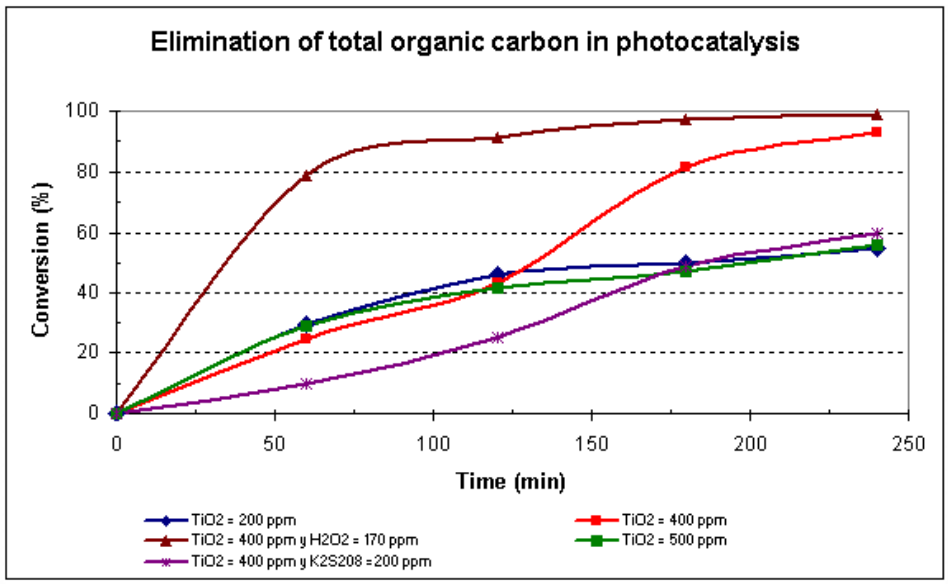
2. Experimental part and results

2.1 Titanium dioxide photocatalysis of mixtures of pollutants.

We have studied the influence exercised by the concentration of the catalyst (titanium dioxide) and the addition of oxidising agents to the reaction medium upon organic pollutant degradation performance. The results obtained are displayed in Table 1. The elimination conversion of the Total Organic Carbon (TOC) in terms of operation time is shown in Graph 1. In addition, follow-up monitoring of individual pollutant compounds was carried out via gas chromatography-mass spectrometry, with 90% of these disappearing within 30-40 minutes.

TOTAL ORGANIC CARBON CONCENTRATION (ppm)					
Time (min.)	**TiO_2 200 ppm**	**TiO_2 400 ppm**	**TiO_2 500 ppm**	**TiO_2 = 400 ppm H_2O_2 =170 ppm**	**TiO_2 = 400 ppm $K_2S_2O_8$ =200 ppm**
0	11,36	12,68	11	11.00	12.18
60	8,05	10,80	7,83	2.320	10.98
120	6,217	7,14	6,41	0.981	9.15
180	5,68	2,33	5,82	0.316	6.23
240	5,142	0,89	4,87		4.89

Table 1: Total Organic Carbon elimination in the tests carried out via heterogenous photocatalysis with titanium dioxide



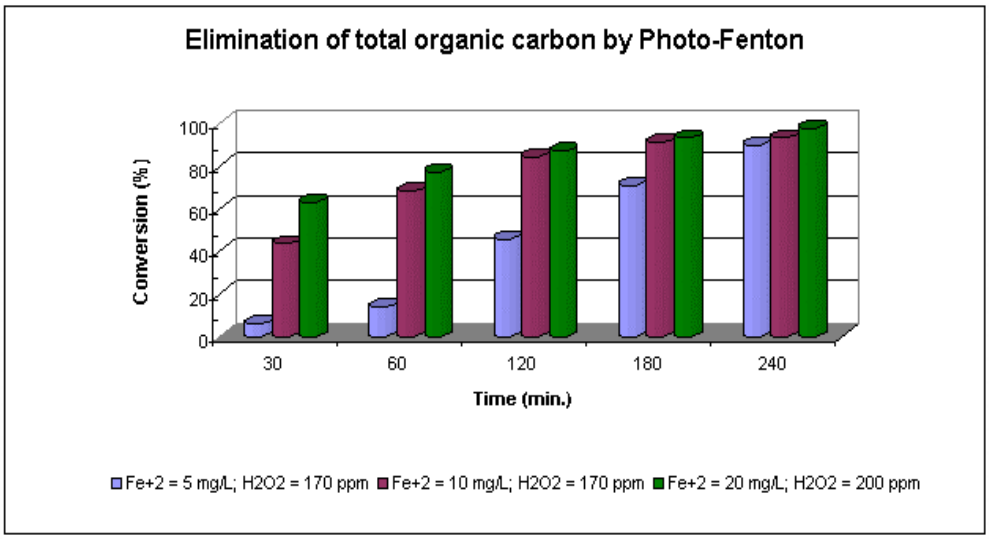
Graph 1. Variation in Total Organic Carbon degradation conversion according to quantity of titanium dioxide and oxidising agent used.

2.2 Photo-Fenton Method

The results of the tests carried out using the Photo-Fenton process are shown in Table 2. Graph 2 represents Total Organic Carbon degradation performance in terms of reaction time.

TOTAL ORGANIC CARBON CONCENTRATION (ppm)			
Time (min.)	**Fe^{+2} = 5 mg/L H_2O_2 = 170 ppm**	**Fe^{+2} = 10 mg/L H_2O_2 = 170 ppm**	**Fe^{+2} = 20 mg/L H_2O_2 = 200 ppm**
0	12.23	12.18	12.34
30	11.50	6.842	4.543
60	10.51	3.847	2.795
120	6.639	1.883	1.555
180	3.545	1.066	0.2504
240	1.225	0.05	

Table 2: Elimination of TOC in tests carried out using Photo-Fenton procedures



Graph 2. Variation in TOC elimination conversion (%) in terms of reaction time in tests carried out using the Photo-Fenton technique.

2.3 Photocatalysis of urban wastewater

Samples of urban wastewater that had undergone secondary biological treatment were subsequently taken from a wastewater purification plant outlet and subjected to heterogenous photocatalysis using titanium dioxide. We studied the effects of varying catalyst concentration and pH value upon organic material degradation performance. Follow-up monitoring of Total Organic Carbon (TOC) in terms of reaction time was also carried out.

2.3.1 Influence of operational pH

Different tests were carried out using constant titanium dioxide (400 ppm) and hydrogen peroxide (200 ppm) concentrations while varying operational pH with the aim of studying the influence of the acidity of the medium on the degradation of pollutants present in wastewater via advanced oxidation processes. The results can be seen in Table 3.

TOTAL ORGANIC CARBON CONCENTRATION (ppm)				
Time (min.)	**pH = 7.5**	**pH = 5.6**	**pH = 4**	**pH = 3.2**
0	20.17	13.03	11.61	20.60
60	20.06	10.56	10.52	17.12
120	19.94	9.32	8.05	15.28
180	19.6	8.94	6.50	13.66
240			5.25	13.10

Table 3.- Influence of operational pH value in photocatalysis

2.3.2 Influence of titanium dioxide concentration

In order to study the effects of titanium dioxide concentration, we carried out a series of experiments in which the quantity of hydrogen peroxide (200 ppm) and the pH value of 4 were

constant while the concentration of titanium dioxide was varied between 400 and 1000 mg/L. The results are contained in Table 4.

TOTAL ORGANIC CARBON CONCENTRATION (ppm)			
Time (min.)	**TiO_2 = 400 ppm**	**TiO_2 = 500 ppm**	**TiO_2 = 1000 ppm**
0	19.50	11.61	9.2
60	17.30	10.52	7.67
120	14.58	8.05	5.65
180	12.65	6.50	4.83
240	11.45	5.25	3.38

Table 4.- Influence of titanium dioxide concentration.

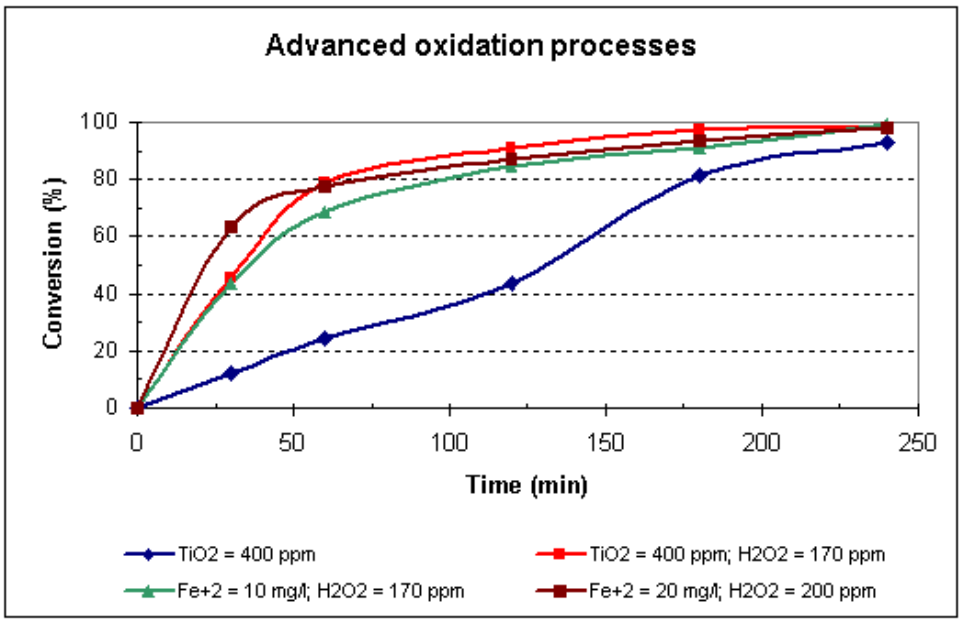
3. Conclusions

a) The optimal concentration of titanium dioxide to be used in carrying out photocatalytic tests on the mixtures of pollutants studied has been found to be 400 ppm (0,4 g/L).

b) The addition of oxidising agents during photocatalytic tests significantly increases organic compound degradation performance. The best of these was found to be hydrogen peroxide, which achieved much higher TOC elimination conversions than did titanium dioxide alone: a TOC elimination conversion rate of 12.10% in 30 minutes for the latter compared to 45.50% in the same time when the former was added, with a constant 400 ppm of titanium dioxide used throughout.

c) Comparing the two processes carried out to date (Graph 3), we can stress that the Photo-Fenton method is faster during the early stages of reaction (0-40 minutes) in the case of the mixtures of pollutants analysed. For longer periods of operation (between 180 and 240 minutes) the degradation conversions of both methods tend to be similar.

d) As far as photocatalysis of urban wastewater samples produced by secondary biological treatment is concerned, better organic substance elimination performances are obtained using pH = 4 acid values. Also, longer operation times (180-240 minutes) are required to achieve organic material elimination rates of around 60%.



Graph 3: Degradation conversion in photocatalytic and Photo-Fenton tests.

4. References

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