



Use of sunlight energy to eliminate pollutants in waste water from chemical laboratories

Luis Fernando Garcés Giraldo¹, Gustavo Antonio Peñuela Mesa²

Empleo de la energía solar para la eliminación de contaminantes en aguas residuales de laboratorios químicos

Emprego da energia solar para a eliminação de contaminantes em águas residuais de laboratórios químicos

RESUMEN

Introducción. El empleo de la energía solar para la eliminación de contaminantes en aguas residuales, mediante el uso de un fotocatalizador adecuado, permite aprovechar directamente la energía solar que llega a la superficie terrestre para provocar una serie de reacciones químicas que dan lugar a la eliminación de compuestos orgánicos en las aguas de vertidos urbanos, industriales y agrícolas y cambiar el estado de oxidación de los metales pesados de tal forma que pasan de estar disueltos a una forma insoluble.

Objetivo. Evaluar la degradación de aguas con azul de metileno utilizado para el análisis de algunas pruebas en laboratorios químicos por medio de un fotosensibilizador utilizando energía solar.

Materiales y métodos. Se llevó a cabo la degradación y mineralización de aguas residuales con azul de metileno por medio de la luz solar. Se realizaron diferentes ensayos con la combinación peróxido de hidrógeno, dióxido de titanio y aire, en concentraciones diferentes.

¹ Ingeniero Sanitario. Magíster en Ingeniería Ambiental. Investigador grupo GAMA. Decano de la Facultad de Ingenierías, Corporación Universitaria Lasallista. ² Químico. Ph.D en Química Ambiental. Profesor del Departamento de Ingeniería Sanitaria y Ambiental, Universidad de Antioquia.

Correspondencia: Luis Fernando Garcés G. email: lugarces@lasallista.edu.co

Fecha de recibo: 17/11/2009; fecha de aprobación: 7/12/2009

La degradación de esta agua residual se siguió por la disminución del color a una longitud de onda de 650 nm y para la mineralización se utilizó la técnica de la DQO.

Resultados. La concentración óptima de fotocatalizador y agente oxidante para la degradación del agua residual con azul de metileno en una concentración en el agua de 30 mg/L encontradas en esta investigación son: 20 mg/L de TiO_2 y 2 mL H_2O_2 /L con inyección de aire.

Conclusión. Se encontraron muy buenos resultados en la degradación del color en ocho horas de irradiación solar y más bajos porcentajes de mineralización en este mismo tiempo.

Palabras clave: Fotocatálisis, energía solar, laboratorios químicos, agua residual, degradación.

ABSTRACT

Introduction. The use of sunlight energy to eliminate pollutants in waste water, by the use of an appropriate catalyst, uses the sunlight that arrives directly to the Earth to produce several chemical reactions which allow the elimination of organic compounds in the water from urban, industrial and agropecuary effluents and change the oxidation state of heavy metals in a way that they pass from being soluble to an insoluble form.

Objective. To evaluate the water degradation with methylene blue used to analyze some tests in chemicals laboratories by the use of a photosensitizer, using sunlight.

Materials and methods. The degradation and mineralization of waste water with methylene blue by means of the sunlight was made. Different tests were made with the hydrogen peroxide, titanium dioxide and air combination. The degradation of this waste water was followed by the color reduction at a 650nm wavelength and the COD technique was used for the mineralization.

Results. The optimal concentration of photo catalyst and oxidation agent for the degradation of waste water with methylene blue in a 30 mg/L concentration rate in the water found in this research work are: 20 mg/L of TiO_2 and 2 mL H_2O_2 /L with an air injection.

Conclusion. Very good results in color degradation and lower mineralization percentages were found in an eight hour time of sunlight irradiation.

Key words: Photocatalysis, sunlight energy, chemical laboratories, waste water, degradation.

RESUMO

Introdução. O emprego da energia solar para a eliminação de contaminantes em águas residuais, mediante o uso de um foto-catalizador adequado, permite aproveitar diretamente a energia solar que chega à superfície terrestre para provocar uma série de reações químicas que dão lugar à eliminação de compostos orgânicos nas águas de vertidos urbanos, industriais e agrícolas e mudar o estado de oxidação dos metais pesados de tal forma que passam de estar dissolvidos a uma forma insolúvel.

Objetivo. Avaliar a degradação de águas com azul de metileno utilizado para a análise de algumas provas em laboratórios químicos por meio de um foto-sensibilizador utilizando energia solar.

Materiais e métodos. Levou-se a cabo a degradação e mineração de águas residuais com azul de metileno por meio da luz solar. Realizou-se diferentes ensaios com a combinação peróxido de hidrogênio, dióxido de titânio e ar, em concentrações diferentes. A degradação desta água residual se seguiu pela diminuição da cor a uma longitude de onda de 650 nm e para a mineração se utilizou a técnica da DQO.

Resultados. A concentração ótima de foto-catalizador e agente oxidante para a degradação do água residual com azul de metileno numa concentração no água de 30 mg/L encontradas nesta pesquisa são: 20 mg/L de TiO₂ e 2 ML H₂O₂/L com injeção de ar.

Conclusão. Encontraram-se muito bons resultados na degradação da cor em oito horas de irradiação solar e mais baixas percentagens de mineração neste mesmo tempo.

Palavras Importante: Foto-catálisis, energia solar, laboratórios químicos, água residual e degradação

INTRODUCTION

The advanced oxidation processes allow destroying a great number of toxic and dangerous compounds, even at low concentrations, which have a high resistance to natural degradation. These processes have been being developed since the last decade and have proven their effectiveness for the destruction of many organic contaminants. Among the advanced oxidation processes, two photo-oxidative technologies are promising to treat waste water: Heterogeneous photo catalysis measured with semiconductors and photosensitization with ferric or ferrous ion¹⁻⁷.

The process of detoxification by solar photo catalysis is the use of the most energetic part of the solar spectrum, UV radiation, to boost a reaction of a very strong oxidation. This reaction takes place when an UV radiation activates a semiconductor catalyst with the presence of oxygen. Under these circumstances, any other substance (toxic or not) that is simultaneously in the same medium, is subjected to a vigorous process of oxidation⁵⁻¹³.

The present work is made to study the degradation and mineralization of methylene blue dye using photo catalysis with sunlight, which molecular formula is C₁₆H₁₈ClN₃S₂.2H₂O. This dye is used in the environmental analysis laboratories for determining the substances active to methylene blue, such as detergents, which is a routine test in this kind of laboratories. It is also used as raw material for making anti-malarial agents. It is used for the direct dyeing in order to make damp dyes like the alizarin blue, the indigo and the logwood more beautiful. It is also used for the printing of calico and the dyeing of silk under the name of D methylene blue marks. It dyes cotton with a fuller and redder tone, and brings a deep blue color to silk and printed items, with very bright tones^{14,15}.

METHODOLOGY

The sunlight collector used for the experiment had three modules. Each one was composed by eight 48 mm external diameter and 150 cm long glass pipes (Schott-

Duran) and an aluminum foil, which allows the reflection of UV irradiation of the sunlight. The whole system had a re circulation pump and a tank. The sunlight collector had a 6° inclination to the ground. It was facing North because it must match the geographical position of the place (Centro Nacional Agropecuario La Salada, SENA-Antioquia), in order to avoid the daily adjustment according to the sun elevation and to get the highest efficiency in the radiation recollection. The glass pipes were attached with PVC connections (picture 1).



Picture 1. Sunlight collector used for the experiment

In table I the experiments made for the methylene blue degradation are shown. Only one condition was varied in each experiment, aiming to study its influences in the dye's degradation.

Table I. Conditions of the experiments for the methylene blue degradation.

Experiment	Description	Dye concentration (mg/L)	TiO ₂ concentration (mg/L)	H ₂ O ₂ quantity (mL/L)	Aeration
F	Photolysis	30	0	0	No
E1	Oxidation with H ₂ O ₂ .	30	0	3	No
E2		30	0	5	No
E3	Heterogeneous photo catalysis	30	20	2	No
E4		30	20	3	No
E5		30	50	2	No
E6		30	20	0	Si
E7		30	50	0	Si
E8		30	20	2	Si
E9		30	50	0	No
E10		30	100	0	No

The statistical model used to analyze the experiments is the three level factorial (4x4x2), not balanced (because the number of observations by combined treatment is not equal), with an interaction between the photo catalyst and the oxidation agent. The response variable is the percentage of degradation in eight hours of sunlight irradiation.

The statistical model proposed for the methylene blue degradation was analyzed with the SAS statistical package, and is:

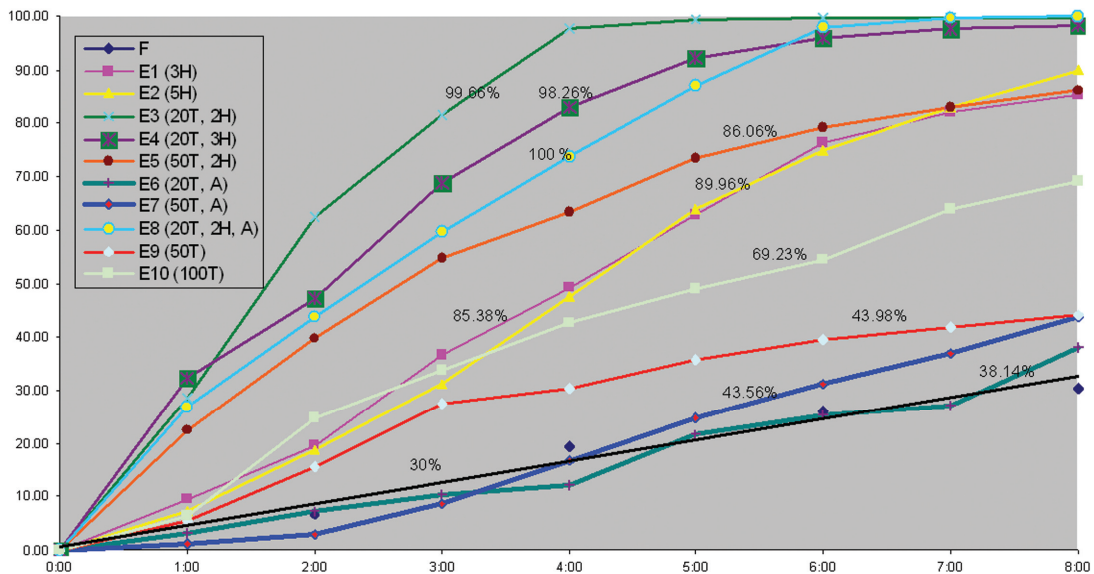
$$y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha\beta)_{ij} + \varepsilon_{ijkl}$$

Where μ is the global measure (medium degradation); α_i is the effect of TiO_2 in the degradation; β_j is the effect of H_2O_2 in the degradation; γ_k is the effect of air in the degradation; $\alpha\beta_{ij}$ is the effect of the interaction between TiO_2 and H_2O_2 in the degradation and ε_{ijkl} is the random error.

Each test was made three times. From the tests appearing in table I, three were chosen because they had the best methylene blue degradation percentages and were made again three more times, in order to determine the mineralization degree and making the follow up with the COD. Those tests are E4, E5 y E8.

RESULTS ANALYSIS:

% of dye degradation/time accumulated (hours)



Graph I. Test results of the tests for the methylee blue degradation

For the photolysis, in the three repetitions made the degradation percentages were very similar: 83.81, 76.64 and 74.76, and also a very similar behavior of the color degradation was observed during the 36 hours of sunlight irradiation. The degradation media of all the three repetitions was 78.04%, which is considered as high (graph 1).

The degradation percentage of the methylene blue using 3 mL/L of H_2O_2 (E1) was 85.38%, which is very good and higher than that reached in the photolysis (8 h), due to the H_2O_2 . This is very feasible, due to the high oxidation potential.

The degradation percentage of the methylene blue using 5 mL/L of H_2O_2 (E2) was 89.96%. Comparing the degradation percentage with that of the oxidation with 3 mL/L of H_2O_2 , it is observed that there is a 4.5% increase of the degradation media with the increase of the hydrogen peroxide quantity.

Compared with the use of only H_2O_2 , the use of 2 mL/L of H_2O_2 and 20 mg/L of TiO_2 (E3) increased the degradation percentage of the methylene blue, producing a media of 99.66%. This can be explained because the oxidation agent is the hydroxyl radical, easily produced from H_2O_2 because there is TiO_2 when it is activated by the UV light.

When this experiment was compared with 3 mL/L of H_2O_2 and 20 mg/L of TiO_2 (E4), there was no proof of the possibility that a higher presence of hydrogen peroxide could mean a higher degradation percentage of the dye, given the fact that with 2 mL/L of H_2O_2 the media was 98.26% and with 3 mL/L of H_2O_2 , it was 98.26%. Even though this difference is not statistically significant, for further treatments it is better to use lower doses of chemical reagents.

The E4 test was made again using H_2O_2 at 35%, to determine the mineralization percentage by the use of the COD. H_2O_2 at 35% accelerated the dye degradation, when compared to H_2O_2 at 30%. In the new test, with 4 hours of sunlight irradiation, the percentage was 100% and with the first, with the same 4 hours, it was approximately 82%. With H_2O_2 at 35% there was a mineralization, but it was not very high (44.72%).

The increase of TiO_2 when the E3 and E5 tests were compared (with the same H_2O_2 quantity) did not increase the methylene blue degradation percentage. In fact, the opposite happened, it was below 88.06%. This happens due to a TiO_2 concentration that starts a reduction of the sunlight pass inside the pipe.

The E5 test was made again with H_2O_2 at 35%, producing a 100% of degradation and 43.70% of mineralization. Like in the E4 repeated test, this E5 test had a remarkable increase in the degradation percentage and in the reduction for the methylene blue degradation using H_2O_2 at 35%. This is very meaningful, because it increases the efficiency of the process.

With the aeration, the idea was to increase the dissolved oxygen in the solution, so the quantity of reagent species was much higher. The methylene blue degradation

percentage with 20 mg/L of TiO_2 and air (E6) was very low if compared with the photo catalysis, TiO_2 and H_2O_2 : 38.14%. This means that with the air not enough hydroxyl radicals are produced to oxidize the methylene blue, or they are produced very slowly.

If the results of the E6 (20 mg/L of TiO_2 and air) and E7 (50 mg/L of TiO_2 and air) are compared, the increase of the TiO_2 concentration increased the degradation percentage of the methylene blue to 43.56%. The increase of TiO_2 allows the existence of more active places to produce hydroxyl radicals and, therefore, a higher probability of increasing the degradation percentage.

The methylene blue degradation with 20 mg/L of TiO_2 , 2 mL/L of H_2O_2 and air (E8), reached 100% at a time between 6 and 8 hours. When the E8 (100%) experiment was compared with the E3 experiment (99.66%) (20 mg/L of TiO_2 , 2 mL/L of H_2O_2), the degradation percentage was very similar for both of them. The effect of the oxygen injection could not be observed.

The E8 experiment was made again, changing the H_2O_2 value to 35%. A 100% of the methylene blue was reached in 4 hours, with a 42.50% mineralization. The methylene blue mineralization with 20 mg/L of TiO_2 , 2 mL/L of H_2O_2 and air (E8) reached 100% at a time between 6 and 8 hours.

With the results mentioned above, it is clear that a TiO_2 and H_2O_2 concentration improves and shortens the degradation percentage. However, it is interesting to determine if the TiO_2 photo activated in the sunlight collector can produce, from water, enough free hydroxyl radicals to degrade the methylene blue. For that reason, the photo catalysis was made without H_2O_2 .

For the E9 experiment (50 mg/L de TiO_2), the degradation in eight hours was 43.98% which, if compared with the photolysis in eight hours, shows that the one of the photo catalysis without hydrogen peroxide is higher in a 13.62%. The increase in the TiO_2 concentration from 50 mg/L to 100 mg/L (E10), using the photo catalyst only, increased the degradation percentage of the methylene blue to a 69.23%.

STATISTICAL ANALYSIS

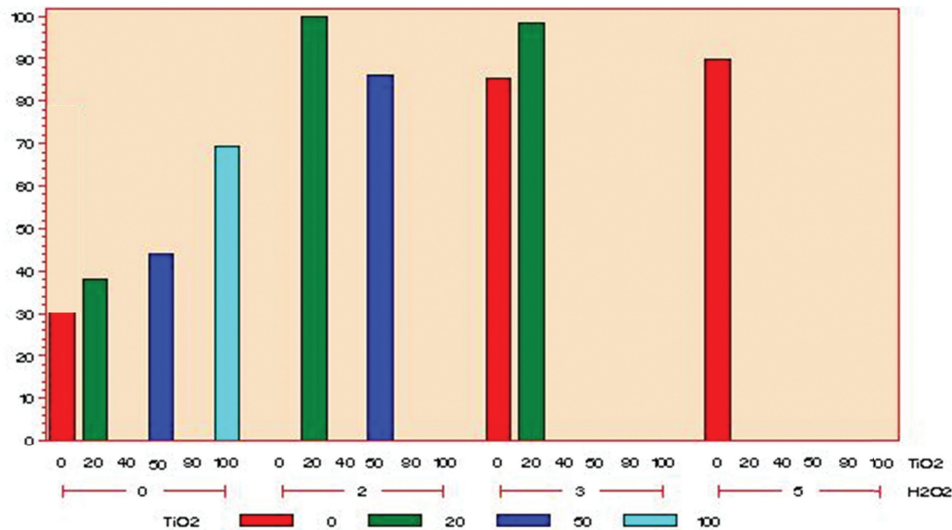
The ANOVA for the statistical model used in the analysis was calculated in order to prove if the model used is useful to explain the dye degradation. According with the meaning of the effects analyzed, the ANOVA for the model proposed is significant ($p < 0.0001$). Therefore, the model is useful to explain the degradation of the methylene blue according to the factors defined.

The ($R^2 = 0.9226$) value means that 92.26% of the variation in the methylene blue is explained by the model proposed, which includes the effects of TiO_2 , H_2O_2 , air and

their interactions among them. The variability level due to not controlled factors is not very high (10%). This coefficient indicates a good control of the experimental error; hence the model is good to explain the degradation of methylene blue.

The analysis of effect significance shows TiO_2 , H_2O_2 and their interaction is significant ($p < 0.0001$). This means that a change in the concentration of each one and the combination of the concentrations between them affect, statistically, the degradation. The air is not significant ($p = 0.09953$), which means that with or without aeration, there is no effect due to it.

According to the statistical model proposed, a graph of the interactions between the titanium dioxide and the hydrogen peroxide was made (graph 2). It indicates that the differences between the degradation level medias, when hydrogen peroxide is not added for titanium dioxide concentrations between 20-50 mg/L, have a significant change when 2 mL/L of hydrogen peroxide with titanium dioxide concentrations within that same rank (20-50 mg/L) are added. When hydrogen peroxide is not added, and is combined with 20mg/L of titanium dioxide, a lower degradation media than that with 50mg/L is obtained, while for a concentration of hydrogen peroxide of 2mL/L with 50mg/L of titanium dioxide, a lower degradation media is obtained if compared with that of 20mg/L.



Graph 2. Interaction between titanium dioxide and hydrogen peroxide for the degradation of methylene blue

From this graph it can be read that the highest degradation rates of the dye are obtained when there is a combination between 2-3 mL H_2O_2 /L and 20 mg/L of TiO_2 . Proving that the optimal concentration for the degradation of methylene blue is located within this rank, (E3, E4 and E8 tests), it can be observed that there is a slight reduction of the degradation when the hydrogen peroxide is increased

from 2 to 3mL/L. This is why the optimal concentrations for the degradation of methylene blue in 30 mg/L concentrations are: 20 mg/L of titanium dioxide in combination with 2 mL/L of hydrogen peroxide without air injection.

CONCLUSIONS

In the methylene blue photolysis, a high degradation percentage of the dye was reached. The media of the three repetitions made was 78.04%, in 36 hours of sunlight irradiation. Therefore, methylene blue is not photo stable before sunlight radiation.

The percentage and speed of methylene blue degradation were higher when the quantity of hydrogen peroxide or titanium dioxide was increased, when only hydrogen peroxide or titanium dioxide were used respectively. When titanium dioxide and air were mixed, the degradation percentage was higher when more photo catalyst was added. No significant difference was observed either in the degradation percentage, or in the degradation speed in the tests in which the oxidation agent was air. The highest degradation speeds and the shortest degradation times were reached with the lowest concentrations of photo catalyst and hydrogen peroxide (2 and 3 mL of H_2O_2/L with 20 mg/L of TiO_2), tests E3, E4 y E8.

With the hydrogen peroxide at 35%, comparing with that at 30% and using the same hydrogen peroxide volumen, a considerable reduction of the time required to reach a high percentage of methylene blue was achieved. This can be explained by the fact that a higher quantity of hydrogen peroxide was used, and this was done with a much cheaper source (commercial peroxide, not analytical).

The optimal concentrations of photo catalyst and oxidation agent for the degradation of methylene blue (30 mg/L) found in this research work are: 20 mg/L of TiO_2 and 2 mL/L H_2O_2 , without an air injection, given the fact that this is not meaningful for the treatment and, also, can increase its costs.

REFERENCES

1. MÁRQUEZ LONA, Héctor y TISCARENO LECHUGA., Fernando. La foto-oxidación en el tratamiento de aguas residuales. En: Ingeniería Química. Junio, 1999, vol. 31, no. 358, p 101-108. Madrid.
2. BLANCO GALVEZ, Julián y MALATO RODRÍGUEZ, Sixto. Descontaminación de aguas residuales mediante fotocatalisis solar. En: Ingeniería Química. Enero, 1993, no. 316, p.129-137.
3. VALLADARES, Julio Eduardo. Fotocalizadores y energía solar en la detoxificación de aguas contaminadas:Aplicaciones potenciales. México:

- Centro de Calidad Ambiental. Universidad Tecnológica de Monterrey, 1998. 6 p.
4. BLANCO GALVEZ, Julián, et al. Tratamiento de efluentes con fotocatalisis solar. En: Ingeniería Química. Septiembre, 1995, vol. 27, no. 316, p.125-133. Septiembre, 1995. Madrid.
 5. PEÑUELA MESA, Gustavo Antonio. Fotólisis y fotodegradación sensibilizada con Fe³⁺ y TiO₂ de pesticidas en aguas naturales. Tesis doctoral Química Analítica del Medio Ambiente y de la Polución. Barcelona: Universidad de Barcelona. Departamento de Química analítica, 1998. 149 p.
 6. MALATO RODRÍGUEZ, Sixto, et al. Low contrating CPC collectors for photocatalytic water detoxification: comparison with a medium concentrating solar collector. En: Water Science & Technology. 1997, vol. 35, no. 4, p.157-164.
 7. LI, XZ. y ZHAO, Y.G. Advanced treatment of dyeing wastewater for reuse. En: Water Science & Technology. 1999, vol. 39, no. 10-11, p. 249-255(57)
 8. ----- y ----- . On-site treatment of dyeing wastewater by a bio-photoreactor system. En: Water Science & Technology. 1997, vol. 36, no. 2-3, p.165-172.
 9. INCE., N.H. y TEZCANLI, G. Treatability of textile dye-bath effluents by advanced oxidation: preparation for reuse. En: Water Science & Technology. 1999, vol. 40, no. 1, p.183-190.
 10. PEÑUELA MESA, Gustavo Antonio. Destoxificación solar de aguas mediante la fotocatalisis o fotosensibilización. En: Revista Facultad de Ingeniería. Diciembre, 1999, no. 19. p. 24-28.
 11. MALATO RODRÍGUEZ, Sixto, et al. Photocatalysis with solar energy at a pilot-plant scale: an overview. En: Applied Catalysis B: Environmental. 2002, April, vol. 37, no. 1, p. 1-15.
 12. BLANCO GALVEZ, Julián, et al. Purificación de aguas por fotocatalisis heterogénea: Estado del arte. En: Eliminación de contaminantes por fotocatalisis heterogénea. La Plata, Argentina: Collective text by CYTED Network VII-G, 2001. p. 51-76.
 13. ----- y MALATO RODRÍGUEZ, Sixto. Tecnología de fotocatalisis solar.: Cuadernos monográficos, 31. Spain: Ciemat Almería, 1996. 210 p.
 14. OTHENWER, Kirk. Enciclopedia de tecnología química. México: Limusa Wiley, 1998. p 357-379.

15. EUROPA. COMISIÓN ECONÓMICA EUROPEA. Directiva 91/155. (5, marzo, 1991). Por la que se definen y fijan, en aplicación del artículo 10 de la Directiva 88/379/CEE del Consejo, las modalidades del sistema de información específica, relativo a los preparados peligrosos. [en línea]. Diario Oficial. Europa: Eurlex, no. L 076 de 22/03/1991 p. 0035 – 0041. [citado 20 noviembre 2009]. Disponible en:
<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0155:ES:HTML>