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Photocatalytic Degegradation of Bromocresol green by TiO_2/UV in aqueous medium

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Abstract

The synthetic dyes currently occupy an important place in the industrial sector. They are widely used in the textile, paper, plastic and leather. The release of large quantities of these dyes in the environment can lead to non negligible pollution of the latter. The heterogeneity of their composition makes it difficult or almost impossible, obtaining pollution limits lower than those imposed by the environmental standards after treatment with traditional techniques such as biodegradation. Thus, there is an urgent need for developing more efficient techniques, that among these techniques, there is the advanced oxidation processes. This study aims to investigate the discoloration of BCG photocatalysis by TiO_2 (PC 500) in aqueous solution. We then determined the optimum operating conditions such as the addition of H_2O_2, effect of catalyst concentration, type of TiO_2 and the initial concentration of the pollutant on the photodegradation rate. The experimental results show that the heterogeneous photocatalysis of TiO_2 was effective in discolors Bromocresol Green. In conclusion, it can be argued that the heterogeneous photocatalysis is an efficient technique for bleaching of the dye in an aqueous medium.

Key words: heterogeneous photocatalysis, TiO_2, BCG, Environment, Water**.**

Introduction

The intensive use of dyes in everyday life and in industry greatly increase,their presence in the environment which is a direct consequence of modern life. Organic dyes constitute one of the large groups of this effluent. However, the much research has been preformed to develop effective treatment for elimination of this type of pollutants because they are also very resistant to biodegradation. For instance,some conventional methods, such as precipitation,ion exchange [1-2], adsorption or various supports [3-6], membrane techniques, are widely applied to treat aqueous effluent. The degradation by UV radiation and advanced oxidation processes [7-8] are an excellent alternative for these pollutants degraded. One of these techniques: the heterogeneous photocatalysis is based on the absorption of radiation exciters (365 nm), by a semiconductor such as TiO_2, ZnO, Titanium oxide is the photocatalyst as used in the degradation of organic micropollutants [9.10]

In this work, we present results for the in photocatalysis of dye (BCG) in a particular support: TiO_2 in powder. We investigate also the effect of some parameters, on efficiency like: the influence of radiation UV, the addition of H_2O_2, the type of TiO_2 and the initial concentration of the pollutant on the photodegradation rate. These investigations will help to situate the effectiveness of these processes during the fading process.

2. Materials and methods

2.1. Material

Bromocresol Green (abbreviation BCG) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide (33% Fluka), solutions were prepared with ultra pure water from a Milli pure water.Millennium PC500 titanium dioxide (100% anatase, specific surface area of 320 m2 g−1) and other Millennium catalyst powders namely PC50, PC100 and PC105 were used for comparative study. The natural pH of the aqueous dye solution is 6.8 .The structure of our substrate is represented in figure (1).

2.2-Irradiation procedure

The irradiation experiments were carried out in a self-constructed Pyrex photoreactor (diameter of 2 cm) with a cooling water jacket placed in an elliptical stainless steel chamber. A fluorescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm was used. Light intensity ($I = 0.7$ mW cm^{-2}) was measured using a radiometer type VLX 3W. The lamp and the reactor are on both focal axes of the elliptical chamber. The reaction temperature was kept at 20 ± 1 ◦C by cycling water. The irradiated solutions and suspensions were magnetically stirred during whole experiments. The suspensions of Bromocresol Green (6×10^{-5} M) and 1 g L^{-1} of titanium dioxide were stirred in the dark for 15 min before irradiation to establish adsorption/desorption equilibrium. The particles of titanium dioxide were removed after irradiation by filtration (Millipore 0.45 μ m).

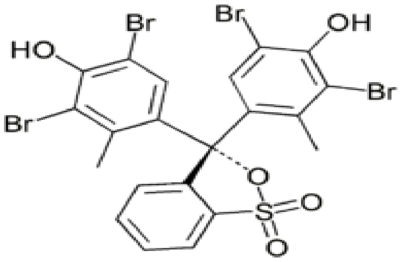

Figure 1. Molecule structure of Bromocresol Green (BCG).

3. Results and discussion

3.1. UV–vis spectrum of BCG

The UV–vis spectra of BCG are reported in figure (2). One observed mainly three absorption bands, each characterized by a molar absorption coefficient ε and located at 280nm (ε = 9165 l $mol^{-1}cm^{-1}$), at.444nm (ε = 16545 l mol^{-1} cm^{-1} being the most intense) and at 616 nm (ε = 7490 l $mol^{-1}cm^{-1}$) respectively. The pH influences the behavior of the substrate. Thus, in acid medium, one observes a color change (turning into yellow) but without a shift of all bands whereas in basic medium one observes a color change (turning into blue) again, but with a displacement of the most intense band (616 nm).This allowed the determination of the pKa where Its magnitude order was 5.1. (Inserted figure 2)

The results are well represented in figure (2) where we observe an isosbestic point. In this point the basic and acid form have the same unit absorbance and wavelength (515 nm). In these conditions, the pH would not have an impact on the measurement of BCG concentrations. In our case, the pH is not changing at the end of the oxidation process that is why all measurements were made at 444 nm.

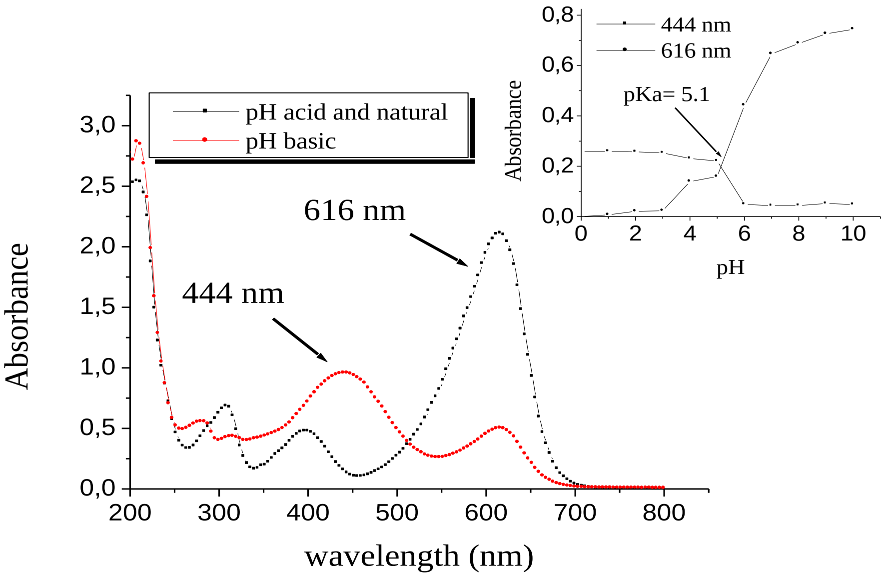

Figure 2. UV–vis spectrum of BCG, $[dye]_o = 6\ 10^{-5}$M ,influence of pH.

3.2. Preliminary experiments: photolysis and photocatalysis of BCG

Figure 3 shows the time course of dye concentration during irradiation of BCG solution under the following conditions: (i) UV irradiation without TiO_2 (photolysis), (ii) irradiation with PC500 (photocatalysis). This study has been investigated from 6 10^{-5} M concentration of dye at natural pH, catalyst loading of 1 g L^{-1} for both catalysts and a light flux of 2.5 mWcm−2. As can be seen in Fig. 3, the concentration of BCG remained unchanged after 180 min of irradiation in absence of TiO_2 (only18.4 %). This indicted no significant photodegradation by direct photolysis. However, the complete decolorization for PC500 was achieved at 180 min of irradiation time respectively.

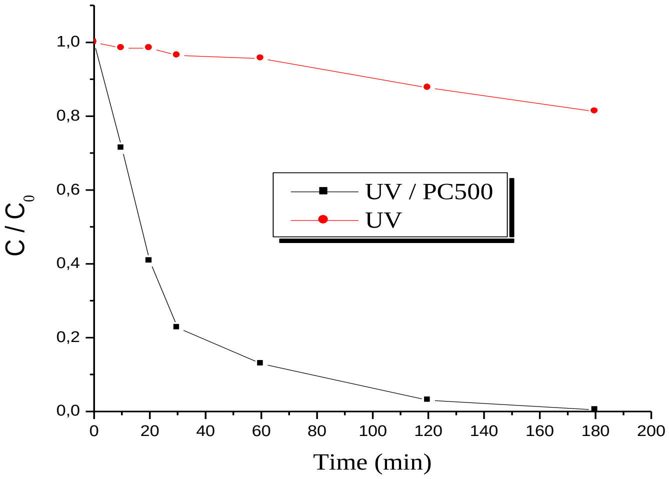

Figure 3. Photolysis and photocatalysis kinetics of BCG. ([PC500]=1 g L^{-1}, [BCG]=6 10^{-5}M, $pH_{natural}$=6.8, T+20°C.

3-3-Effect of initial concentration of dye

The pollutant concentration is a very important parameter in wastewater treatment. The effect of various initial dye concentrations on the photocatalytic decolorization has been investigated from 4 10^{-5} to 8 10^{-5} M at natural pH and catalyst loading of 1 g L^{-1} for both catalysts. As shown in Figure. 4,

Figure (4) shows that, by irradiating the solution, the dye is almost completely eliminated for various concentrations. The time required for the total elimination is a function of the initial concentration. Furthermore, the higher the initial concentration of the dye, the greater the time required for its disappearance is long. Photocatalysis with TiO_2 is a suitable method for the degradation of pollutants in very low concentrations in aqueous solution

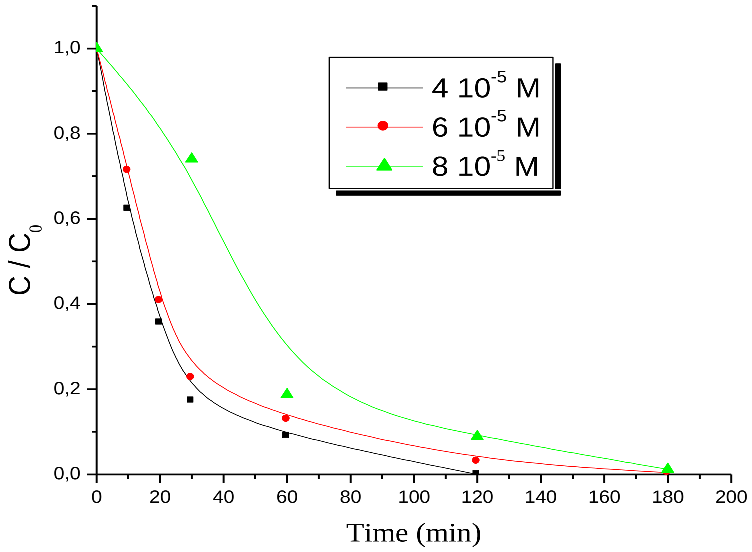

Figure 4. Effect of initial BCG concentration on the photocatalytic degradation. ([PC500]=1 g L^{-1}, $pH_{natural}$=6.8,T+20°C.

3-4-Effect of catalyst concentration

The effect of catalyst loading on the degradation of BCG was investigated using PC500 from 0.2 to 2 g L^{-1} keeping all other parameters constant. The apparent rate constant at varying TiO_2 concentrations are calculated from the initial slopes and are plotted against the TiO_2 concentrations, as shown in Fig. 5.

Experiments performed with different concentrations of catalyst (Table 2) showed that the rate increased with an increase in the amount of catalyst and that it remained almost constant above a certain level. As the concentration of catalyst is increased, the number of photons absorbed and the number of dye molecules adsorbed are increased owing to an increase in the number of TiO_2 particles. The density of particles in the area of illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of TiO_2 particles. Hence the additional catalyst powder is not involved in the catalyst's activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit. The aggregation of TiO_2 particles at high concentrations must also be considered, which causes a decrease in the number of surface active sites.

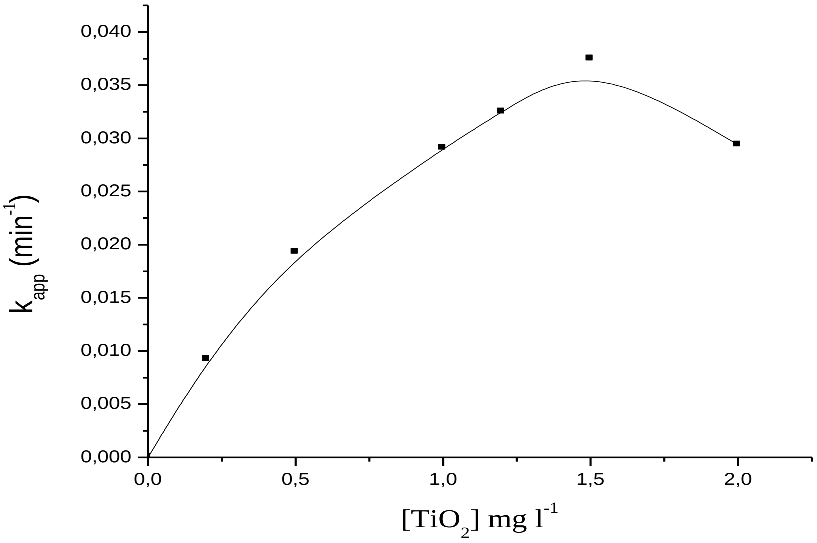

Figure 5. Effect of TiO_2 concentration on the photocatalytic degradation of BCG: $pH_{natural}$=6.8, T+20°C.,([BCG]=6 10^{-5}M

The optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface [11,12]. At high concentrations of catalysts, particle aggregation may also reduce the catalytic activity by reducing the specific surface.

3-5-Effect of addition of H_2O_2

The addition of hydrogen peroxide to the heterogeneous system increases the concentration of $OH^{\bullet}$, since it inhibits the electron–hole recombination, according to the following equation:

$TiO_2(e-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\bullet}$ (1)

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation [13]. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation, and it also forms $OH^{\bullet}$, according to Eq. (1).

The effect of addition of H_2O_2 on the photocatalytic oxidation has been investigated. The results are shown in Fig.6. To show the effectiveness of this process, we conducted a series of irradiation at 365 nm of solutions containing a fixed concentration of BCG (6 10-5 M), 1g / l of TiO_2 (PC500) and different concentrations of H_2O_2 (10^{-1} to 10^{-4} mol L^{-1}).It was observed that photocatalytic efficiency increases as the concentration of H_2O_2 increases and reaches an optimum at 10^{-2} mol L^{-1} and further increases in concentration up to 10^{-1} mol L^{-1} leading to a decrease in the photodegradation rate constant.

Therefore, high concentration of hydrogen peroxide inhibited the reaction rate of dye degradation by competing with BCG for available hydroxyl radicals [14, 28], as shown in Eqs. (2) and (3):

$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$ (2)
$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$ (3)

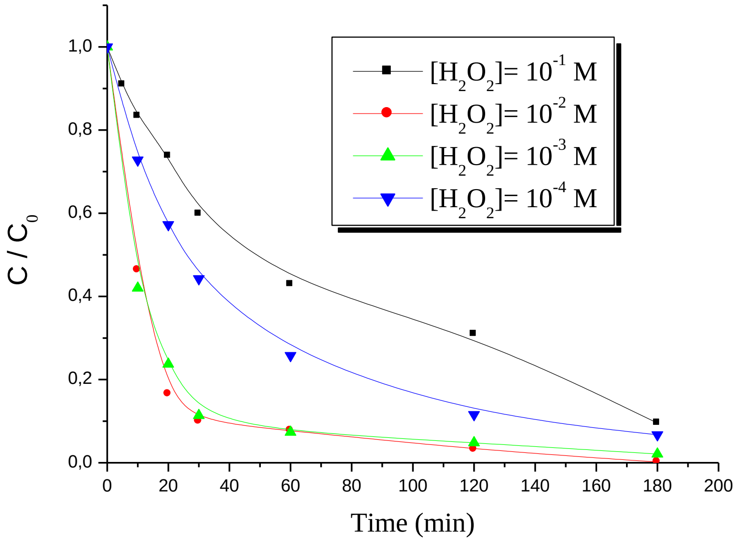

Figure 6. Effect of hydrogen peroxide concentration on the photocatalytic degradation of BCG: ([BCG]= 6 10^{-5}M, [PC500]=1 g L−1).

Conclusion

Heterogeneous photocatalysis using TiO_2 as photocatalyst was proven to be an effective method for the degradation and mineralization of BCG. This dye is easily degraded by TiO_2- PC500-Millennium assisted photocatalysis in aqueous dispersion.

The photodegradation depends on, effect of catalyst concentration, the initial concentration of the pollutant and hydrogen peroxide concentration. The decolourization rate goes through a maximum when increasing the concentration of the hydrogen peroxide. This effect could be ascribed to the competition for adsorption between the dye and the hydrogen peroxide

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