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Treatment heterogeneous photocatalysis; Factors influencing the photocatalytic degradation by TiO_2

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Abstract

In order to optimize the purification of water and sewage water, a new technique of degradation «the heterogeneous photocatalysis» of the organic matter was underlined. As catalyst we chose a semiconductor which is dioxide TiO_2 the titanium in the presence of a lamp UV as source of energy. One model substances present in many industrial effluents: the 4-iso propyl phenol was selected. The results of our experiments show that the adsorption of the pollutant (10^{-4}mol/l) on TiO_2 supported in absence of radiation UV is negligible. Compared to direct photolysis UV (365nm), the devolution of the pollutant is definitely faster in the presence of TiO_2 /UV for the same experimental conditions.

Keywords – degradation, heterogeneous photocatalysis, photocatalysor TiO_2 , UV, advanced Oxidation.

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1. Introduction

Photocatalysis has found several applications in the field of environment: destruction of aqueous pollutants [1], air purification, metal recovery, and especially more recently, production of materials such as self-cleaning glass surfaces [2]. Applications for photocatalytic decontamination of water have already arrived at the stage of pilot plant. Reactors are artificial radiation source on the market. Despite the small percentage of the absorbed solar radiation (3.5%) by TiO_2 solar processes have been developed [3].

Nomenclatures

e^- : Electron.

h^+ : Electronic gap (positive hole).

pHPZC : pH at the surface of a solid at zero charging.

TiO_2 : titanium dioxide.

UV: Ultraviolet.

2. The titanium dioxide (TiO_2): photocatalysor of choice

The catalyst is in the heart of the photocatalytic process. Since photocatalysis is based on the excitation of a photocatalyst with irradiation of light energy at least equal to that of the band gap (BI). These photocatalysts are more commonly called semiconductors. There are many semiconductor metal oxides represent a large part of the semiconductors used for photocatalytic properties namely: TiO_2 , ZnO , ZnS , WO_3 , CdS , SnO_2 , GaP etc.....

Among the list of semiconductors reported in the literature, TiO_2 has proven most suitable for most common environmental applications. Because it is biologically and chemically inert, resistant to chemical corrosion and can work at ambient temperature and pressure, without addition of chemical species.

3. Treatment heterogeneous photocatalysis

3-1-General reaction mechanisms

The principle of photocatalysis is based on the excitation of a semiconductor (usually titanium dioxide TiO_2) by light (UV or visible). Under the action of photons, the semiconductor (or catalyst) produces highly oxidizing free radicals allowing the destruction of compounds adsorbed on its surface [5].

The semiconductor TiO_2 converts photon energy into chemical energy by oxidation-reduction reaction. This causes the activation sites of TiO_2 and molecular degradation of the compounds present. The degradation process then consists in a succession of radical oxidations initiated by strong oxidants such as OH^\bullet .

The OH^\bullet are directly generated by the photolysis of water molecules adsorbed on the active sites of TiO_2 [5].

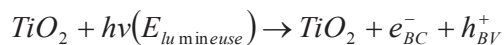
Organic pollutants adsorbed on the catalyst are then degraded by successive radical reactions in non-toxic mineral species. The degradation capacity of the semiconductor is related to several parameters: the nature and intensity of irradiation of the light source or the number of incident photons to the activation of TiO_2 and the nature of the reaction medium is the amount of TiO_2 (or active sites), the water content for the production of hydroxyl

radicals and the nature and concentrations of pollutants.

One can, in summary, schematize the process into four successive stages:

A. Activation of TiO_2

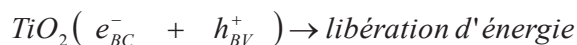
The activation step by irradiating the photocatalyst corresponds to the formation of electron-hole pair in the metal oxide



Reaction (1): Activation of TiO_2 by UV.

B. Separating electrons and holes

The life of the pairs (e^-/h^+) is of a few nanoseconds and their recombination is accompanied by a heat (reaction 2).



Reaction (2): release of heat

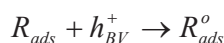
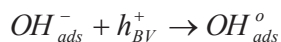
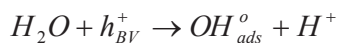
Therefore, in the absence of acceptor and electron donor appropriate, a recombination reaction hole / electron takes place very fast. For the photocatalytic oxidation is effective, it must of course avoid this recombination.

C. Oxidation and reduction

The charges created migrate to the surface of the catalyst and react with adsorbed substances that can accept or donate electrons. These are the reactions of oxidation or reduction which are interesting for the cleanup.



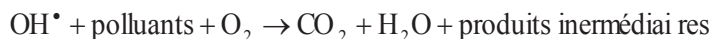
Reaction (3): Reduction reaction in photocatalysis



Reaction (4): Oxidations during the photocatalysis

3.2 Degradation of organic molecules

In turn, generated radicals (OH^\bullet , O_2^\bullet , R^\bullet) are oxidants and can break down compounds (refractory pollutants, pesticides, herbicides, dyes, etc...) Adsorbed on the surface of the semiconductor, up to mineralize. The final products of this mechanism are primarily water and carbon dioxide, intermediates [5]. It is possible to write the reaction of photocatalysis as:



Reaction (5): Photocatalytic degradation of pollutants

Finally, a pollutant in a liquid phase will, following a series of adsorption process and desorption, be degraded by the photocatalyst and activated by UV radicals generated.

We can say that the reaction mechanism of photocatalysis is characterized by two processes: one chemical and one physical. The chemical process is a chemical reaction of degradation itself, while the physical process comprises transport to the interface where the solid processing takes place.

In Fig. 1 gives details of all the processes outlined in the TiO_2 particle.

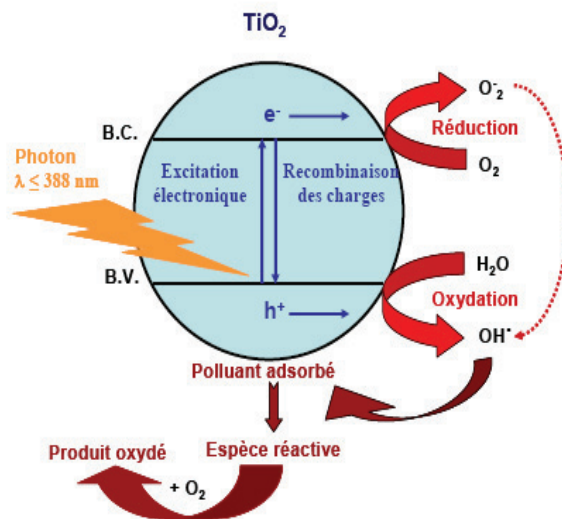


Fig. 1. Principle of heterogeneous photocatalysis

4. Application

Research done on the destruction of organic pollutants in aqueous phase is concerned mostly with poorly biodegradable compounds in physicochemical treatment [7], [8]. The pollutants selected for this study is the 4-iso propyl phenol.

5. Mode analysis

UV / visible spectrophotometry

We followed the technique photocatalytic, and determining the concentration of pollutant at different reaction times by spectrophotometry in the UV. The spectrophotometer we used is of type (Scan spectro 80DV-UV/Vis) spectral range of 190 to 1100 nm.

6. Results analysis; interpretation

6.1 Evolution of degradation by direct photolysis (365 nm) and by TiO₂ / UV

We conducted two tests in order to assess the effectiveness of photocatalysis and to ensure that degradation is not too important in the presence of UV only. We conducted the first test with the UV lamp only and the second with the UV lamp and the glass plates treated with TiO₂. The result represented on the fig. 2 shows that the degradation of the pollutant is much faster with TiO₂/UV than with direct photolysis UV for the reaction time considered (6 hours). This fact could be attributed to a relatively low substrate adsorption at this wavelength and the quantum yield of photolysis.

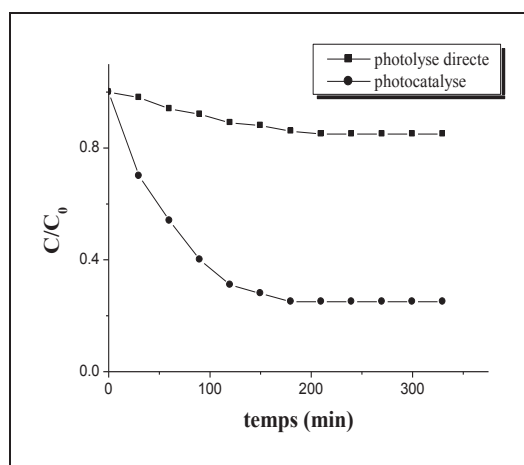


Fig. 2. Comparison between the degradation of the pollutant by direct photolysis (365 nm) and its degradation by TiO₂ / UV ($\lambda = 365$ nm)

This thus will enable us to locate well the clean effectiveness of the TiO₂/ UV system.

6.2 influence of some physic-chemical parameters on transformation photocatalytic of the pollutant in the presence of TiO₂

A-Effect of pH of the solution

The pH is an important parameter in photocatalytic reactions, because it affects the one hand, the load on

the catalyst and, on the other hand, on the species present in the compounds to be oxidized (or dissociated form molecular form). The analysis results, shown in Fig. 3 show that the degradation is best for acidic pH.

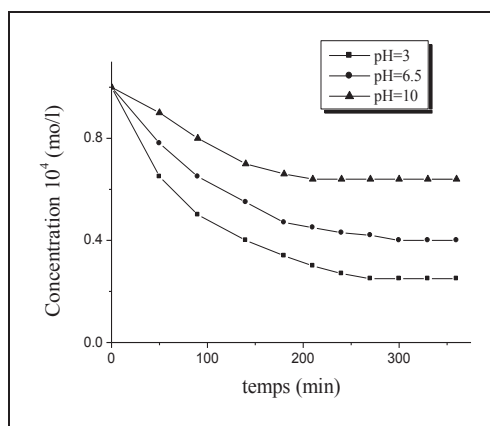
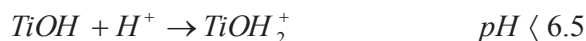


Fig.3. Effect of solution pH on the photodegradation of the pollutant

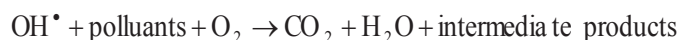
In fact, the pH in aqueous solution can significantly affect the TiO_2 on its surface charge and size of aggregates. The pH at which the surface charge of the oxide is zero is called Zero Point of Charge (pHPZC) [9]. Before and after this pH, the surface of the oxide is responsible



The photocatalytic degradation is initiated by the attack of the adsorbed molecule by free radicals OH^\bullet which strongly depend on the pH of the solution. For acidic pH, the amount of OH^\bullet formed increases, which accelerates the degradation [10].

B-effect of oxygen

In the water purification by heterogeneous photocatalysis, the pollutants are usually organic. The equation for the reaction in the presence of oxygen:



Oxygen is essential for complete degradation and should not be in competition at the level of adsorption with other reactive species on the catalyst for this, we studied the photocatalytic degradation of pollutants in the presence and absence of oxygen. The results are shown in Fig. 4:

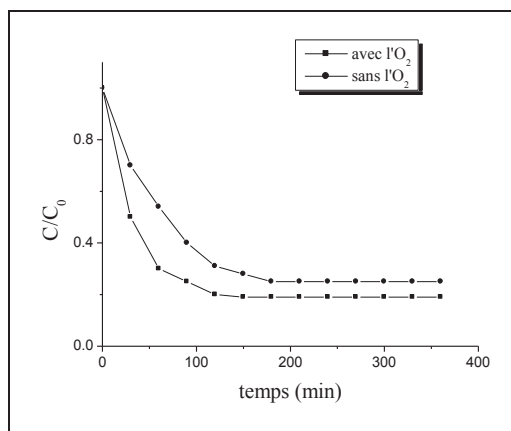


Fig. 4. Effect of the presence of oxygen on degradation photocatalytique

We note that in the presence of oxygen in the heterogeneous medium (TiO_2/UV), there is acceleration of the decrease in the concentration of the pollutant. This acceleration may be related to inhibition of the recombination of electron-hole pair and also by the production of more radicals OH^\bullet in the middle, so we conclude that oxygen (O_2) here plays the role of a catalyst but since it is not regenerated at the end of the reaction, it affects the performance of the degradation reaction by increasing, so we can conclude that reacts with the pollutant

7. Conclusion

We sought to include/understand the fundamental mechanisms of photocatalytic degradation, study some, for example, the influence of the adsorption of the molecules on the titanium dioxide (TiO_2) in absence of the radiation, the effectiveness of the photocatalysis compared to the photolysis, the presence of O_2 in the heterogeneous medium (TiO_2/UV), will accelerate the photocatalytic reaction, the rate of degradation decreases with the increase in the pH, and thus shown that the reaction of degradation is favorable in acid medium.

The study showed that the photocatalytic degradation of the substance chosen model in the presence TiO_2 / UV irradiation under artificial, is satisfactory. In raising the possibility of easy reuse of TiO_2 support-which is an important advantage. It is also possible to adapt this process to a larger scale with a power of immediate use of treated water.

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