Kinetic Model for Photocatalytic Degradation of Alizarin Red-S by Polypropylene coated nano-TiO₂

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The aim of study is optimize and clarify the total mechanism of adsorption/ visible-photodegradation of Alizarin Red S Polypropylene coated nano- TiO_2 Degussa P-25 and TiO_2 Anatase as photocatalysts. The characterization of Alizarin Red S and its chemical interaction with TiO_2 surface has been studied. The acid dissociation constants of Alizarin Red S are determined. Adsorption and photodegradation steps were simultaneously studied in order to propose a simple kinetic model which can describe the process in an adequate way. The results obtained from this kinetics model are in good agreement with experimental data.

Dyes are an important class of synthetic organic compounds which are found in water bodies coming from different sources such as textile industries, paper and pulp industries, pharmaceutical industries, tannery, etc.

Residual dyes from these sources are considered as a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems. The discharge of dyes into the water environment is undesirable, not only because of their color, but also because many released dyes and their breakdown products are toxic, carcinogenic or mutagenic to life forms [1]. It is necessary that water contaminated by dyes undergoes treatment before wastewater disposal.

Because of their synthetic origin and their complex structure many dyes are difficult to decolorize and, as a result, it is more difficult to destroy contaminants containing large, stable and refractory compounds of dyes [2].

The most important families of dyes are: Azo dyes which is characterized by at least an azo bond (-N=N-) connected to aromatic or heterocyclic rings, but can contain two, three, or, more rarely, four or more azo groups and Anthraquinone dyes which are derivatives of substituted anthraquinone and have two carbonyl groups (-C=O-) in their structure [3]. An important example of anthraquinone derivative is Alizarin Red S [sodium salt of 1,2-dihydroxyanthraquinone-3sulfoacid, ARS], which bears two hydroxyl groups in positions 1 and 2 and a sulfo group in position 3. ARS belongs to the group of the most durable dyes. These dyes cannot be completely degraded by general chemical, physical and biological processes. This resistance to degradation is due to the complex structures of the aromatic rings.

A wide range of technologies have been developed to remove dyes from wastewaters; one of these methods is advance oxidation process and in particular the photocatalysis is more useful for the photodegradation of organic contaminant in the wastewater using UV or visible light. Photocatalytic oxidation is one of the most effectively clean technologies. TiO_2 is the most efficient photocatalyst used in the photocatalytic degradation of different pollutant as dyes [4].

In this study, with the aim to optimize and clarify the total mechanism of adsorption/ visiblephotodegradation of ARS by Polypropylene (PP) coated nano-TiO₂ Degussa P-25 and TiO₂ Anatase as photocatalysts has been used. ARS has been spectrophotometrically characterized at different pH conditions and has been observed that this dye exists in three different forms, H₂ARS, HARS⁻ and ARS²⁻ in acidic, neutral and alkaline conditions respectively. In Figure 1 the spectral change of ARS at different pH is reported.



Figure 1. Absorption spectra of ARS in water at different pH values.

Only H_2ARS , present at acidic pH, favorably bind on TiO₂ surface as reported in the scheme of Figure 2.



Figure 2: Bond between H₂ARS and TiO₂ surface.

At this pH only the sulfonic group owns a negative charge that binds positively charged on TiO_2 surface. The ARS acid dissociation constants are determined.

The adsorption of ARS dye molecules on PP-TiO₂ film is a time dependent process and in particular, the major adsorption rate is obtained in acidic conditions. In Figure 3, as example, decrease of the solution concentration in time for TiO_2 Anatase is reported.



Figure 3. Decrease of the solution concentration in time for TiO_2 Anatase.

In order to obtain a kinetic model for the photocatalytic degradation of ARS, the adsorption and visible-photodegradation were simultaneously studied using PP coated TiO₂.

The mechanism of photocatalytic degradation of dyes by visible radiation (figure on the top) suggests that excitation of the adsorbed dye takes place to appropriate singlet or triplet states, subsequently followed by electron injection from the excited dye molecule onto the conduction band of TiO₂ particles, whereas the dye is converted to cationic dye radical that undergoes degradation to yield products as follows:

$ARS + TiO_2 \rightarrow ARSTiO_2$	k_{I}
$ARSTiO_2 + h\nu \rightarrow ARS^{+} + TiO_2(e^-)$	k_2
$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{-}$	k_3
$D^{+} + O_2^{-} \rightarrow mineralized \ products$	k_4

This model considers two steps consecutive reactions: the adsorption of ARS on TiO_2 surface and the photodegradation of ARS and permits the description of total process.

In conclusion, the results obtained from this kinetics model are in good agreement with experimental data and can predict the profiles of ARS and photoproduct concentrations during the process. In Figure 4, as example, the graphical validation of models for photodegradation of ARS by TiO₂ Anatase is reported; the graph show that the photodegradation process of ARS catalyzed by TiO₂ Anatase reflects perfectly the kinetic model.



Figure 4. Validation model for photodegradation of ARS at 20 ppm by TiO_2 Anatase.

References

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