RECALCITRANT DYES PHOTODEGRADATION IN THE PRESENCE OF SENSITIZED TiO$_2$

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Introduction

TiO$_2$ is the most widely investigated photocatalyst due to high photo-activity, low cost, low toxicity and good chemical and thermal stability. In the past few decades there have been several exciting breakthroughs with respect to titanium dioxide. A key factor that favors the use ofphthalocyanines as dopants for semiconductor catalysts because they have LUMO orbital energy nearby the titanium oxide`s conduction band. The tetracarboxylphthalocyanines can interact on TiO$_2$ surface by two ways, first through a very strong physical adsorption and second through chemical adsorption of reaction of carboxylic acids with group Ti—OH on TiO$_2$ surface; phthalocyanines could be absorbed as carboxylates on the semiconductor surface.

Materials and methods

In our experimental work, we used three copper phthalocyanines, chlorinated α Cu phthalocyanine (phthalocyanine green G - αClCuPc), βCu phthalocyanine (heliogen blue A – βCuPc) and tetrasulfonated βCu phthalocyanine (C.I.Acid Blue 249 – βCuPc) for sensitizing TiO$_2$. The structures of phthalocyanins are presented in the following figure:

    a.αClCuPc   **b.** βSCuPc   **c.**βCuPc
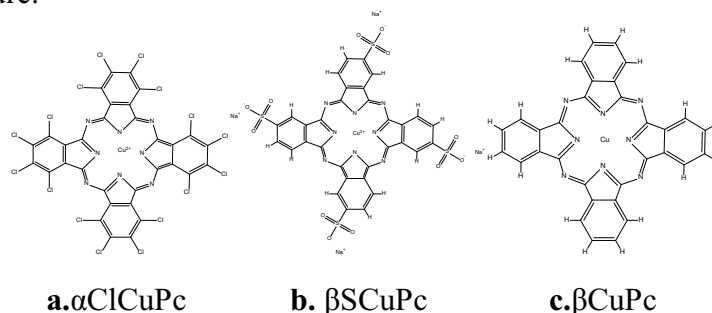
Figure 1. Structures of phthalocyanins used for TiO$_2$sensitization

First, we have tested a catalytic system in which the TiO$_2$ is the reference catalyst. We want to enhance its catalytic activity in the visible spectra domain by photosensitization with different copper phthalocyanines. As the preparation method, we used the wet impregnation method because it favors high dispersion of the precursors. The degradation of dyes was performed in a photochemical reactor; with a medium pressure mercury lamp emitting 400-450 nm and 550-570 nm.The proposed dye systems to undergo photocatalytic degradation are composed of: Brilliant Blue dye solution, SF Black solution, SF Brown solution and Fluorescein solution.We have

chosen different azo type dyes because they exhibit a great stability and because of this property they can be used as food or textile dyes. Ultraviolet–visible (UV–VIS) spectra of dye solutions before and during the degradation experiments were recorded between 200 and 900 nm using a Jasco V-530 spectrophotometer with a Peltier cell for temperature and stirring control.

Results and conclusions

The extent of dye degradation was estimated from the kinetic curve absorbance vs. time at the maximum absorption wavelength for each dye. The apparent first-order kinetic constants k were estimated through non-linear regression by fitting the exponential decay equation $A = A_0 \cdot \exp(-kt)$ on the experimental curves absorbance $A_{\lambda max}$ vs. time.
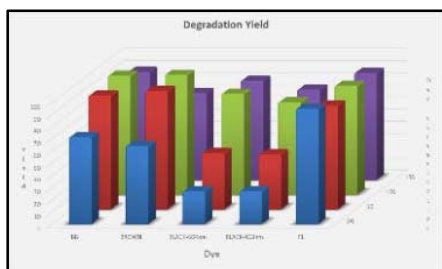
The degradation of textile dyes was also quantified by their degrees of degradation (%) calculated as:

$$D(\%) = \frac{A_0 - A_{fin}}{A_0} \cdot 100$$

where A_0 is the initial absorbance of the sample without permanganate and A_{fin} represents the final absorbance at the same wavelength after 4 h of reaction.
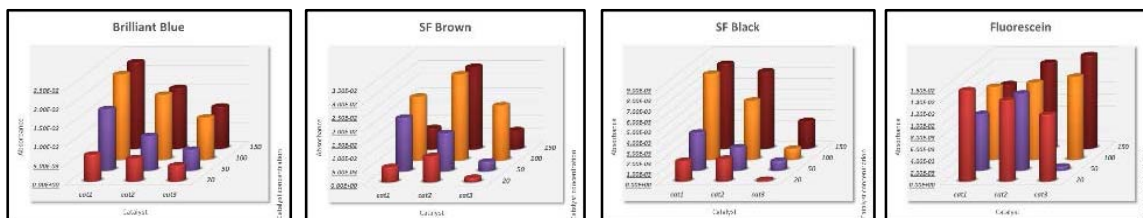
Figure 2. Rate constants for each reaction system

Figure 3. Degradation yield for each reaction system

The structure of our catalysts was determined using UV-VIS spectra on solids, FTIR, XRD measurements.

The degradation yield observed is quite high, being comparable to other advanced oxidation processes; the main advantage of this method is the use of visible light for irradiation.