PCBS Journal

Volume 8   N° 1, 2 & 3   2014

PhytoChem & BioSub Journal

ISSN 2170-1768

Investigation of curcumin as sensitizer for anatase TiO₂ nanoparticles in photodegradation of of phenazopyridine with visible light

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Abstract. *This work describes a photodegradation catalyst, for water organic contaminants in visible light, based on curcumin (a natural dye) sensitized TiO₂ (anatase) nanoparticles. Phenazopyridine (a pharmaceutically active gradient) was used as a contaminant. A 400 nm, and shorter, cut of filter was used to confirm only visible light was used in photodegradation process with no UV radiation. The catalyst system was characterized by electronic absorption spectroscopy and XRD. The particle size forthe catalyst nanaprticles was calculated using Scherrer equation and found to be ~45 nm in average. Different reaction parameters were studied, such as effect of contaminant concentration, amount of loaded catalyst, and pH value on the photodegradation rate. Turn number (T.N.) and quantum yield (Q.Y.) values were calculated for comparative assessment of the catalyst effeciency. The results show the ability of curcumin dyes to sensitize TiO₂ anatase nanoparticles in photodegradation phenazopyridine under visible radiation.*

Key words: Curcumine; sensitization; photo-degradation; phenizopyridine; Anatase TiO₂.

1. Introduction

Different catalyst systems were suggested for photo-degradation of organic contaminants in water, using ultra violet radiations [1-4]. Despite the advantages of such photocatalyst systems, they demand UV rather than the freely abundant visible light. Because only a small fraction of UV exists in the arriving solar radiation [5, 6], researchers focus their efforts to sensitize their catalyst systems on visible solar light[7-14]. The most commonly used semiconductor in photo-degradation processes is the nano-sized titanium oxide TiO₂, by virtue of its stability to photo corrosion, low cost, abundance, safety and high photo-catalytic activity [4, 15-18]. Dye-sensitized TiO₂ particles were investigated in both light-to-electricity conversions (Graetzel cells) and in photodegradation processes [13, 14]. Different types of dyes are known including ruthenium complexes, CdS nano-particles and others [11, 19-22]. Natural dyes extracted from plants were also widely reported as sensitizers for TiO₂ particles in Graetzel cells. Examples of such dyes are chlorophyll derivatives, natural porphyrines, anthocyanins, and curcumin which exist in molecular form [23-28]. Unlike the case with solar cells, natural dyes have been used to a far lesser extent as sensitizers in water purification

studies [13]. In a previous study [29] we critically assessed using heavy metal based sensitizers, such as CdS particles, and demonstrated that such hazardous systems should be avoided in water purification strategies, unless their safety is manifested by preventing their degradation. We also highlighted the need to replace them with safer sensitizers. In this study we used curcumin dye, Scheme (1), as natural sensitizer. Curcumin is a phytochemical substance, that has many health values, and is found in the Indian spice turmeric, *Curcuma longa*, Scheme (1) [30].
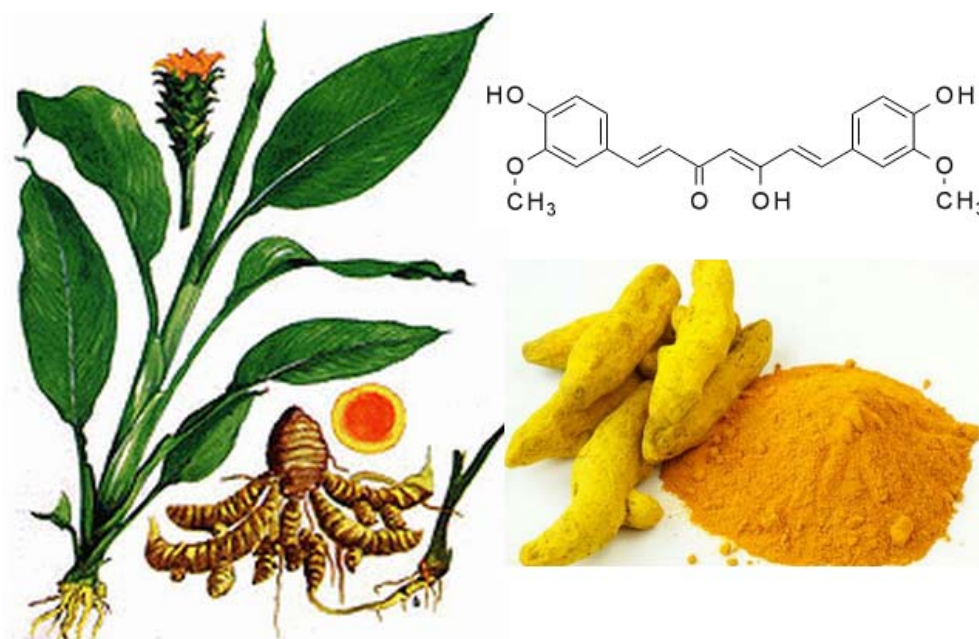
Scheme 1: *Curcuma longa* plant, curcumin powder, and curcumin molecular structure

Due to its strong coloring ability, curcumin is used in food, textile industries, and pharmaceutical applications [31]. Curcumin will be investigated here as a safe alternative sensitizer for TiO_2 photocatalyst in degradation of water organic contaminants. The yellow corcumin has an intense wavelength absorption wide visible range (420-580 nm) [8], with soundly high thermal and chemical stability. Charge transfer from dye to TiO_2 and effective anchorage of the curcumin dye to the TiO_2 surface anticipated by virtue of the ketol group [14, 32]. Phenazopyridine (PhPy) was chosen here as a well-known model drug species that may exist in water as a contaminant.

2. Experimental

2.1. *Starting materials*: All starting chemicals (TiO_2, HCl, NaOH) were purchased in pure form Sigma Aldrich, curcumin powder was purchased from local markets, and Phenazopyridine was kindly donated by Birzeit Pharmaceutical Co. BPC in a pure powder form.

2.2. Curcumin extraction: Curcumin was extracted from commercial turmeric powder prepared from the ground rhizome of Curcuma longa. The original dry sample (5.00 g) was refluxed in 100 mL of ethanol for 60 minutes. After extraction, the solid residues were filtered off. The absorption spectra of the extracted dye were measured on a Shimadzu UV-1601 spectrophotometer. The absorption spectrum matched earlier reports [12, 13, 14]. Depending on the molar absorptivity coefficient of curcumin in methanol at 428 nm as 48000 M^{-1} cm^{-1} [33], the molar concentration of the extracted Curcumin solution, in which curcumin was dominant species, was spectrophotometrically measured to be 1.75×10^{-3} M. The clear solution was used as prepared without any further purification.

2.3. Preparation of catalyst: Titanium dioxide TiO_2 (anatase) powder (40.00 g) was refluxed for an hour with 100.0 mL of curcumin/ethanol extract. After cooling to room temperature, suction filtration (with sintered glass) was used to isolate the prepared catalyst system, followed by washing with cold ethanol and drying under air in the dark. The TiO_2/curcumin system was then stored in the dark under dry atmosphere, for further use. The adsorption of curcumin on the TiO_2 surface by the carbonyl adjacent groups was described earlier [7, 14, 15].

2.4. Catalyst characterization: The extracted curcumin solution, Figure (1a), showed a typical absorption band at λ_{max} 530 nm, characteristic for curcumin. The solid absorption spectrum for TiO_2/Curcumin, Figure (1b), shows an absorption band at λ_{max} 550 nm for curcumin with a 20 nm-red shift, compared to curcumin solution band. The shift is attributed to chemisorption onto TiO_2 surface. An absorption edge for the solid TiO_2 at λ_{max} ~380 nm is also observed.
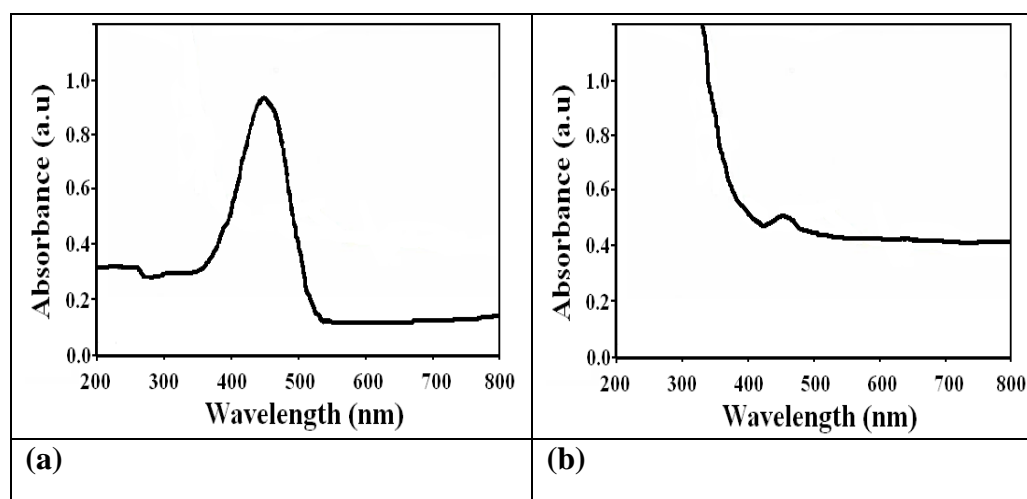
Figure 1: UV-visible spectrum for a) curcumin extracted solution b) TiO_2/curcumin nanoparticles

XRD measurements, for the powder TiO_2/curcumin system, were performed in the laboratories of ICMCB, University of Bordeaux, using a Philips XRD X'PERT PRO diffractometer with Cu Ka ($\lambda = 1.5418$ Å) as a source. The XRD pattern is shown in Figure (2). The average particle size of TiO_2 was calculated from the XRD pattern using Scherrer equation and found to be 45 nm.
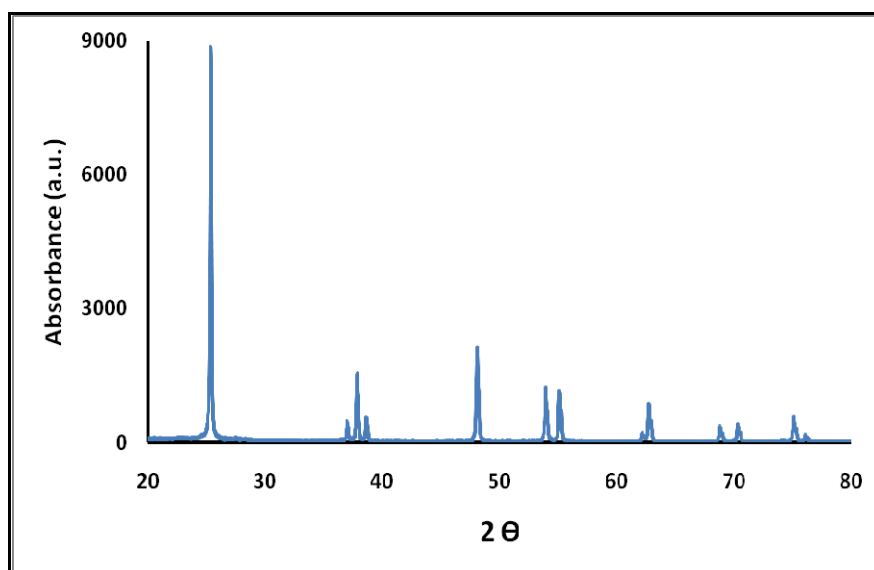
Figure 2: XRD pattern of TiO_2/Curcumin

2.6. Photocatalytic degradation experiments: A typical photo-degradation experiment was conducted in a magnetically stirred thermostated aqueous mixture of known phenazopyridine concentration and catalyst amount in a 100 mL glass beaker. Drops of dilute HCl and/or NaOH were added to control the pH of the reaction mixture. A visible solar simulator spot lamp was used to illuminate the reaction mixture. The spot lamp was placed above the reaction mixture, the reaction beaker was covered from outside with a reflecting aluminum foil to prevent loss of incident light. The measured irradiation intensity at the solution surface was measured to be 0.0212 W/cm^2. The beaker was then jacketed with a controlled temperature water bath.

A known amount of water, specific amount of contaminant and specific amount of catalyst were placed together inside the reaction beaker. In a control experiment, the reaction mixture was stirred in dark for 30 min in order to check any possible contaminant loss by adsorption onto solid catalyst or container surfaces. The reaction beaker was then exposed to light after taking an aliquot (~ 2 mL) from the mixture for the zero time reading. The reaction progress was followed up by syringing out aliquots (~ 2 mL) from the reaction mixture at different time intervals. The aliquots were centrifuged at 5000 r/m for 5 min. The liquid phase was pipetted out and spectrophotometrically analyzed (at 420 nm) for phenazopyridine azo group absorption. The reaction rate was calculated based on measuring remaining phenazopyridine with time. Values of quantum yield (Q.Y.) were calculated by dividing reacted contaminant molecules per calculated incident photons. Values of turn over number (T.N.) were calculated by dividing reacted contaminant moles by nominal TiO_2 mole after 60 min.

To confirm if contaminant photodegradation occurred in the visible light itself, a cut-off filter (400 nm) was used. The cut-off filter was placed between the reaction beaker and the spot lamp. To confirm if the phenazopyridine was totally degraded (mineralized) or just converted into other organic species, additional experiments were performed. Complete mineralization of the degraded phenazopyridine was confirmed by consistent lowering in absorbance band intensity in the range 200 and 400 nm. Such a band is typical for the aromatic ring. Spectral analysis indicated no traces of any new resulting organic species. No alcohols, carboxylic acids, ketones or aldehydes, appeared in the reaction mixtures after reaction completion. Moreover, the azo group of phenazopyridine, with absorption band at 420 nm decreased with

time, in parallel with lowering in the aromatic ring absorption band. The results indicate complete mineralization of the degraded phenazopyridine molecules.

3. Results and discussion

This work is focused on photodegradation of phenazopyridine organic contaminant in water with visible light using safe sensitizers. The visible light is more abundant in solar radiations while the UV light is less than 5% of the solar radiations [34]. Sensitization of TiO_2 with a suitable band gab ($E_g < 3$ eV) dye is needed. Curcumime is used hear as a safe dye.

3.1. Control experiments: The TiO_2/Curcumin catalyst was examined for visible light degradation of phenazopyridine by using a cut-off filter that removes 400 nm and shorter wavelengths. Cut of filter experiments with complete exclusion of UV radiation showed that TiO_2/Curcumin catalyzed the photodegradation of phenazopyridine, albeit with somewhat lower efficiency, Figure (3). Up to 10% of the phenazopyridine were degraded in the purely visible radiation (with turnover number (T.N.) $1.12X10^{-4}$ and quantum yield (Q.Y.) $2.04X10^{-5}$), while up to 16% were degraded in the absence of cut of filter(T.N. = $1.60 X10^{-4}$ and Q.Y. = $2.91X10^{-5}$). This means that in the absence of the cut of filter the catalyst works in two fold action, with UV excitation of TiO_2, and with visible light excitation of the sensitizing curcumin dye molecules [13].
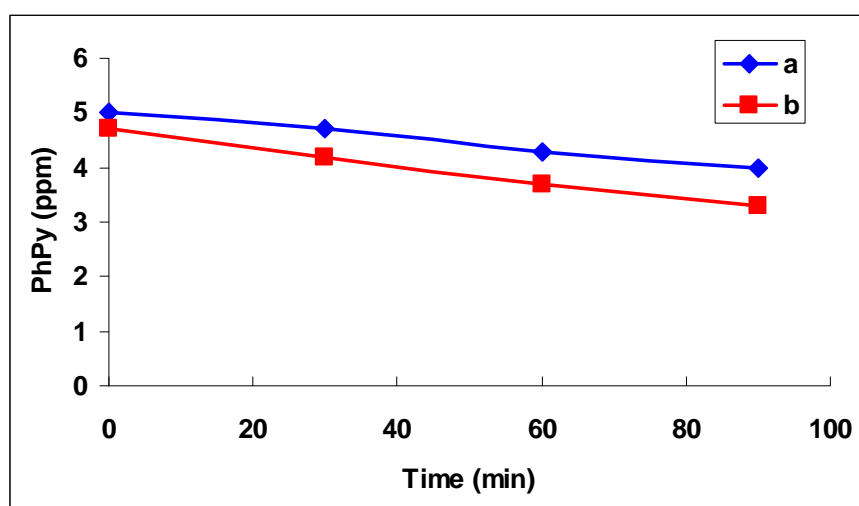

Figure 3: Photodegradation profiles for phenazopyridine in water, in 50 mL of 5 ppm contaminant using 0.1 g catalyst, a) TiO_2/Curcumin with cut off filter, and b) TiO_2/Curcumin with direct radiation

3.2. Effect of contaminant concentration: The effect of phenazopyridine concentration on the photodegradation reaction rate was studied. Three experiments with three different phenazopyridine concentrations (5, 7.5, 10 ppm) were conducted throughout 90 minutes of irradiation. Figure (4) shows the photodegradation results; the T.N. and Q.Y. values indicate that there is no consistent relation between the photodegradation rate and the contaminant concentration. The initial phenazopyridine concentration 7.5 ppm gives higher T.N. and Q.Y. values than other concentrations 5 and 10 ppm, Table (1). Literature showed that photo-degradation could be independent of the contaminant concentration, and in some cases, the rate is lowered with increased initial concentration [13, 35, 36]. Based on initial rate calculations, the reaction order was calculated with respect to contaminant concentration and found to be 0.36.
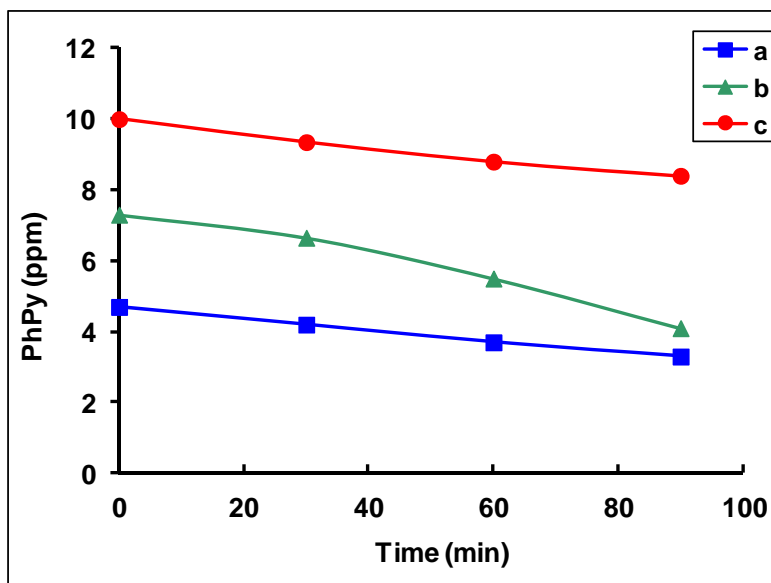
Figure 4: Effect of contaminant concentration on photodegradation of phenazopyridine using TiO$_2$/Curcumin, in 50 mL of contaminated solution using 0.1g catalyst. Contaminant concentrations were: a) 5 ppm   b) 7.5 ppm   c) 10 ppm .

3.3. Effect of catalyst amount: The reaction rate increased with increasing the catalyst amount, Figure (5). The order of the initial reaction rate with respect to catalyst amount was calculated and found to be 0.59. The turnover number values decreased with increasing the catalyst amount, while the quantum yield values increased, Table (1). The results are consistent with earlier studies [13, 36]. The lowering in turnover number value indicates a lowering in relative efficiency, despite the increase in total arte. Such lowering is attributed to tendency of the catalyst particles to prevent penetration of light into the reaction mixture. This suggests that using small amounts of catalyst is more advisable for future water purification processes.
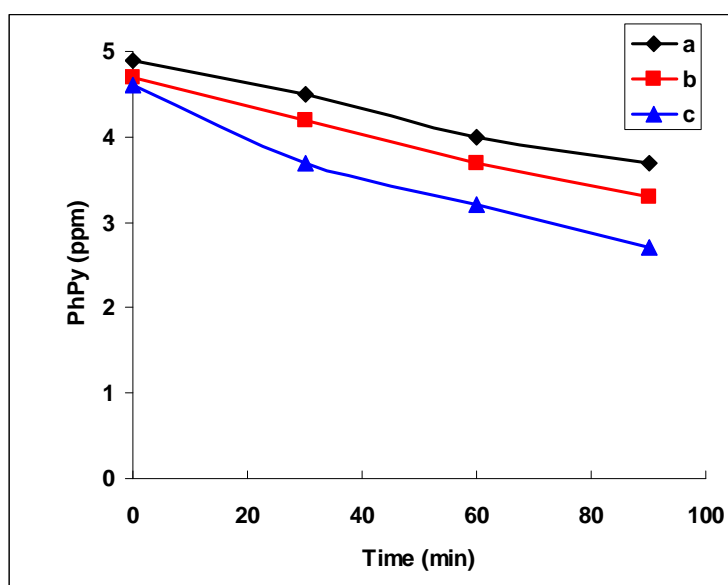
Figure 5: Effect of catalyst amount on photodegradation reaction rate in 50 mL solution of 5 ppm phenazopyridine solution. Catalyst amounts are   a) 0.05 g   b) 1.0 g   c) 2.0 g

3.4. Effect of pH on the photodegradation rate: The efficiency of TiO$_2$/Curcumin catalyst in photodegradation of phenazopyridine contaminant with visible light was investigated using different pH values. Figure (6) shows that the catalyst efficiency is higher in acidic and basic solutions than in the neutral solution. The acidic solution showed higher activity than basic solution. Turnover number and quantum yield values are higher for the acidic solution, and lower for neutral solution, as summarized in Table (1).
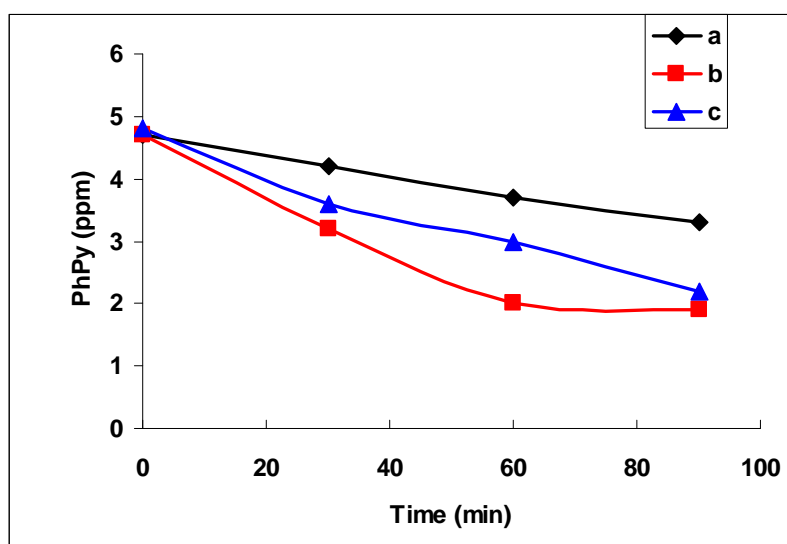

Figure 6: Effect of pH on the photodegradation reaction rate of 50 mL (5 ppm) phenazopyridine:
a) neutral   b) pH = 4.5   c) pH = 11

Table 1: Turn number and quantum yield values for TiO$_2$/curcumin catalyzed photodegradation of phenazopyridine in water under different experimental conditions

Catalytic experiment		
	TiO$_2$/Curcumin with cut off filter	TiO$_2$/Curcumin with direct radiation
T. N.	1.12×10^{-4}	1.60×10^{-4}
Q. Y.	2.04×10^{-5}	2.91×10^{-5}
Effect of contaminant concentration on the photo-degradation rate		
	5 ppm	7.5 ppm	10 ppm
T.N	1.60×10^{-4}	2.88×10^{-4}	1.92×10^{-4}
Q.Y.	2.91×10^{-5}	5.24×10^{-5}	3.49×10^{-5}
Effect the amount of loaded catalyst on the photo-degradation rate		
	0.05 g	0.10 g	0.20 g
T.N	2.88×10^{-4}	1.60×10^{-4}	1.12×10^{-4}
Q.Y.	2.62×10^{-5}	2.91×10^{-5}	4.08×10^{-5}
Effect of pH on the photo-degradation rate		
pH	7	4.5	11
T.N	1.60×10^{-4}	4.33×10^{-4}	2.89×10^{-4}
Q.Y.	2.91×10^{-5}	7.86×10^{-5}	5.24×10^{-5}

3.5. Photo-degradation proposed mechanism: Semiconductor particles may absorb photons with (energy $\geq E_g$). This absorption generates electrons in the conduction band and holes in the valance band. The TiO_2 needs UV radiation due to its wide band gap. The attached dye with the suitable band gap between HOMO and LUMO (400-800 nm) can sensitize the TiO_2 in the visible region. The Curcumin molecules attached to TiO_2 particles absorb suitable visible photons, where the electrons are excited from HOMO to LUMO. The excited electrons in LUMO are directly transferred to the conduction band of the TiO_2 particle. On the other hand electrons and holes are generated in TiO_2 molecules by absorption of a small fraction of UV radiation which is present in the solar radiation, Scheme (2).
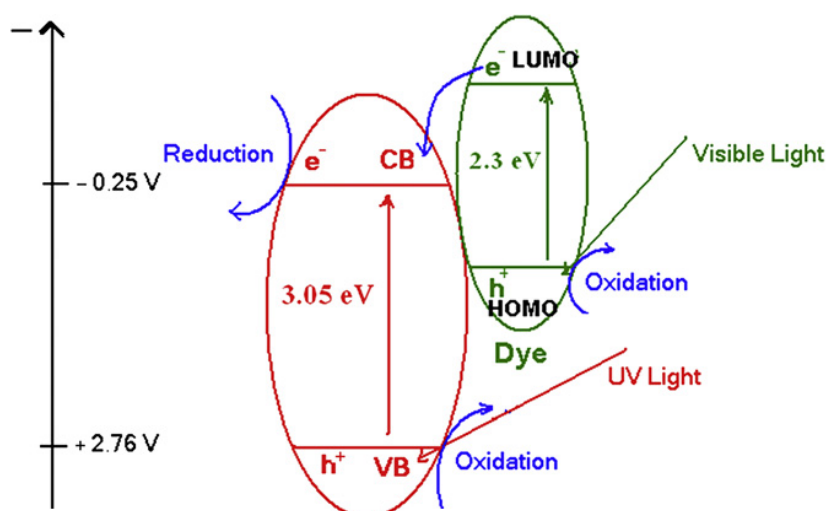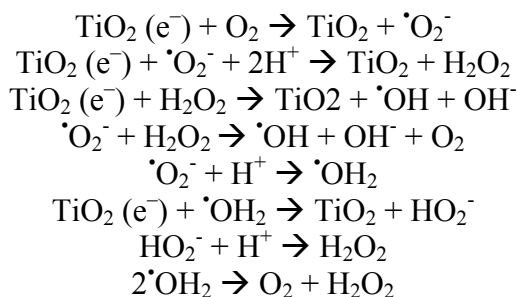

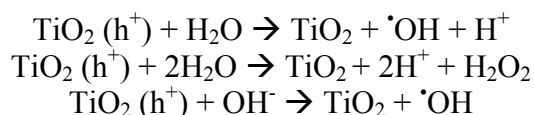**Scheme 2:** the dye sensitized TiO_2 suggested mechanism [13]

The fundamental process involved in photocatalysis is represented as:

$$TiO_2 + h\nu \ (\lambda < E_g) \rightarrow TiO_2 \ (e^- + h^+)$$
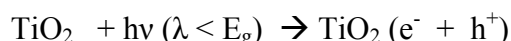
The generated electrons lead to formation of ($^\bullet O_2{}^-$),(H_2O_2), ($^\bullet OH$), ($HO_2{}^-$) and ($^\bullet HO_2$) [37, 38] as shown in the following reaction series:

$$TiO_2 \ (e^-) + O_2 \rightarrow TiO_2 + {}^\bullet O_2{}^-$$
$$TiO_2 \ (e^-) + {}^\bullet O_2{}^- + 2H^+ \rightarrow TiO_2 + H_2O_2$$
$$TiO_2 \ (e^-) + H_2O_2 \rightarrow TiO2 + {}^\bullet OH + OH^-$$
$${}^\bullet O_2{}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- + O_2$$
$${}^\bullet O_2{}^- + H^+ \rightarrow {}^\bullet OH_2$$
$$TiO_2 \ (e^-) + {}^\bullet OH_2 \rightarrow TiO_2 + HO_2{}^-$$
$$HO_2{}^- + H^+ \rightarrow H_2O_2$$
$$2{}^\bullet OH_2 \rightarrow O_2 + H_2O_2$$

On the other hand, the photo-generated holes initiate oxidization reactions as follows:

$$TiO_2 (h^+) + H_2O \rightarrow TiO_2 + {}^{\bullet}OH + H^+$$
$$TiO_2 (h^+) + 2H_2O \rightarrow TiO_2 + 2H^+ + H_2O_2$$
$$TiO_2 (h^+) + OH^- \rightarrow TiO_2 + {}^{\bullet}OH$$

Then the reactions are terminated as follows:

$$^{\bullet}OH + H^+ + 2e^- \rightarrow H_2O$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
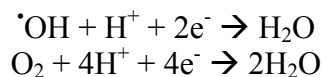
Thus photoexcited TiO_2 molecules (which are directly excited by small fraction of solar UV light or by corcumine sensitization in visible region) can decompose and mineralize the organic contaminant molecules in a series of oxidation reactions leading to carbon dioxide and water [37, 38].

Conclusion

This study shows the ability of natural dyes like curcumin (yellowish color, stable, not expensive, and nontoxic dye) to sensitize TiO_2 (3.2eV) in photodegradation of water organic contaminants under visible radiation. Curcumin is thus a promising replacement for hazardous sensitizing dyes such as CdS and Ru-compounds.

Acknowledgement:

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