



Photo-degradation of curcumin in the presence of TiO₂ nanoparticles: Fundamentals and application

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ABSTRACT

Photo-degradation of curcumin in the presence of TiO₂ nanoparticles has been studied in water–methanol and water–acetonitrile mixed solvents. Curcumin was found to form charge transfer (CT) complexes with TiO₂ nanoparticles. The binding constant of the CT complexes has been determined. Curcumin was found to undergo photo-degradation under UV–vis and only visible light irradiations. Photo-degradation was investigated in the presence of external electron quenchers like methyl viologen and dissolved oxygen and hole quenchers like iodide ions in a de-aerated condition. The presence of oxygen was found to enhance the photo-degradation processes. The photo-degradation was found to be completely quenched in the presence of iodide ions in both the solvent mixtures in a de-aerated condition. A reaction pathway for the photo-degradation of curcumin in the presence of TiO₂ nanoparticles has been proposed. This study has been successfully applied to remove the yellow turmeric stain from cotton fabrics.

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1. Introduction

Curcumin is an important molecule for its medicinal and several other usages [1–6]. Curcumin is a yellow coloured compound present in turmeric and accounts for only about 3–5% of its total constituents [7]. The photo-physical studies of curcumin have earlier been reported by our group [8]. Curcumin has two phenolic hydroxyl groups and two centrally located carbonyl groups, which can exist in keto-enol tautomers in solution. It has been now concluded by several experimental studies that these two groups predominantly exist in enolic form at room temperature [9,10]. The enolic form can also exist in two different forms, i.e. cis and trans, depending on the surroundings. The cis form has been suggested to be more stable as compared to the trans form [8,11,12].

The effect of light exposure towards the stability of curcumin is very important for exploring its medicinal applications for skin protection from sun-burns. The photo-degradation of curcumin has been reported by various groups in the recent years [13,14]. Canameres et al. have studied the photo-degradation of curcumin in aqueous solution in the presence of silver nanoparticles upon UV–vis light excitation [13]. They have identified the photo-degradation products mainly as phenolic compounds which

results from the breakdown of the chain connecting the two aromatic rings. Price et al. has reported the photo-decomposition of curcuminoid compounds present in turmeric. They have studied the effect of light, solvent and oxygen on the decomposition processes [14]. Thermal degradation of curcumin in methanol has been reported by Ahn and Obendorf [15]. They have analyzed the degradation products by gas chromatography coupled with mass spectroscopy. The major products include vanillin and its derivatives.

TiO₂ nanoparticles are well known to be very good catalysis for the decomposition of various organic molecules and dyes in aqueous as well as organic solvents [16,17]. TiO₂ nanoparticles are also recently being used as an effective UV-B radiation skin protective compound in sunscreens [18]. So it is important to know the effect of the presence of TiO₂ nanoparticles on the stability of curcumin molecules. There is no report available in the literature regarding the interaction between two such materials. In this study, we report the interaction between TiO₂ nanoparticles and curcumin molecules that leads to the latter's photo-degradation. A systematic investigation has been made on the photo-degradation of curcumin molecules in the presence of TiO₂ nanoparticles in two different solvent mixtures and two different types of exposures, UV–vis and only visible light. This study has been applied in removing the yellow turmeric stain from cotton fabrics, which was otherwise difficult to be removed by conventional methods using soap or detergents. The yellow coloured stains due to turmeric in

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the clothes are due to the binding of the curcuminoid compounds present in turmeric with cellulose fibres in cotton fabrics. When bound to fibres it becomes difficult to remove them by using common soaps or detergents. However, our method is very effective and simple to use.

2. Experimental

2.1. Chemicals

Curcumin was obtained from Sigma–Aldrich and its purity was verified by HPLC analysis. Locally available high purity grade potassium iodide (KI) and methyl viologen (MV^{2+}) were used as obtained. Commercially available turmeric powder was used for making the yellow stain on cotton fabrics. TiO_2 nanoparticles have been synthesized by acid hydrolysis of titanium isopropoxide [19,20]. Due to very poor solubility of curcumin in water, water–methanol (10–50%, v/v) and water–acetonitrile (10–50%, v/v) solvent mixtures were used for increasing its solubility. Freshly prepared solutions of 25 μ M curcumin was used in the photo-degradation experiments. Measured quantity of dry TiO_2 nanoparticle powders was added to the freshly prepared solution of curcumin, maintaining a concentration of 0.2 g/L.

2.2. Photo-irradiations

A 450 W xenon lamp was used for the UV–vis and only visible light irradiations for the curcumin photo-degradation studies. A 420 nm cut off filter was used to cut the UV light output from the xenon lamp for getting the visible light excitation and avoiding the absorption due to TiO_2 nanoparticles. The samples are photo-irradiated in a transparent cylindrical quartz cell of diameter 10 mm closed with a rubber septum. High purity nitrogen gas was purged in the samples for de-aerating the solutions. The optical absorption measurements were carried out in a Chemito Spectrascan 2600 absorption spectrophotometer. A visible light photo-reactor was used for the turmeric photo-degradation study. The light flux at the center of the chamber was 29,600 lux. Tungsten lamps were used for the stain removal study. Pictures of the photo-irradiated cotton fabrics were taken in a digital camera.

2.3. Analysis of photo-degradation products of curcumin

The organic products formed during photo-degradation of curcumin under different conditions were analyzed by Gas Chromatograph coupled with Mass Spectrometer (GC–MS) (Shimadzu), using AB1MS (30 m \times 0.25 mm \times 0.25 μ m) column with temperature programming from 50 to 250 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min. The products were identified by matching the spectral features with the reported mass spectra. Analysis of CO_2 product was carried out using Gas Chromatograph (Chemito) using Porapak Q (1 m \times 1/8 in.) in conjunction with flame ionization detector.

3. Results and discussion

3.1. Ground state interaction of curcumin with TiO_2 nanoparticles

The ground state optical absorption spectra of curcumin in the absence and presence of TiO_2 nanoparticles are shown in Fig. 1. The absorption spectrum of curcumin in the presence of TiO_2 nanoparticles was relatively broad and slightly red-shifted associated with an increased absorbance. This confirms the formation of a charge transfer (CT) complex between curcumin molecules and TiO_2 nanoparticles. The yellowish colour of curcumin solution was changed to reddish-yellow upon the addition of TiO_2 nanoparticles.

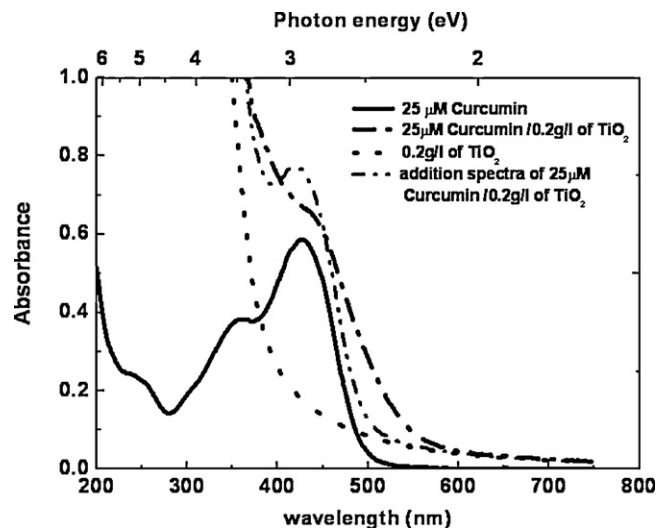
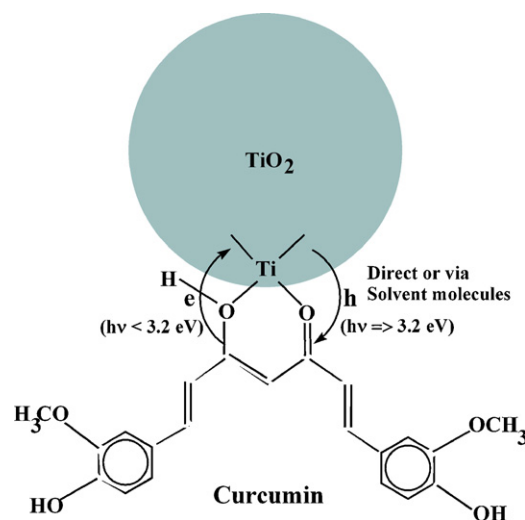


Fig. 1. Ground state absorption spectra of curcumin (25 μ M), TiO_2 nanoparticles (0.2 g/L), their mixture and the just addition spectra of only curcumin and TiO_2 nanoparticles in aqueous solution containing 10% (v/v) methanol.

Enediol ligands like catechols and aromatic molecules having two adjacent OH groups are known to form ligand-to-metal CT complexes with TiO_2 nanoparticles, forming a 5-membered ring with the surface Ti (IV) atom [20,21]. Some of the organic molecules like α -hydroxy quinizarins and salicylates have been known to form ligand-to-metal CT complexes with TiO_2 nanoparticles, forming a 6-membered ring with Ti (IV) [22,23].

In the present investigation, the β -diketo system in curcumin was found to form CT complexes with TiO_2 nanoparticles. This could be due to the co-existence of keto and enol groups in curcumin molecules. Such a system is very much similar to that of the α -hydroxy quinizarin molecules. A probable representation of such a complex is given in Scheme 1. The binding constant (equilibrium constant), K , of the CT complex has been determined by employing Benesi–Hildebrand analysis for molecular complexes [24]. The reaction between TiO_2 nanoparticles and curcumins is shown in reaction (1):



Scheme 1. A schematic representation of a curcumin molecule binding to TiO_2 nanoparticle forming a 6-membered ring between Ti (IV) and β -diketo moiety.

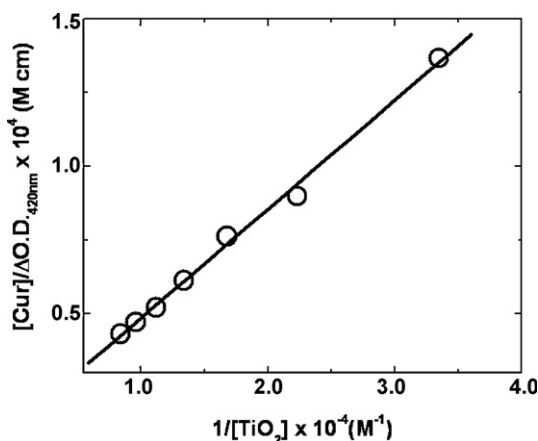


Fig. 2. Plot of $[\text{Cur}]/\Delta\text{O.D.}_{420\text{nm}}$ vs. $1/[\text{TiO}_2]$ in aqueous-methanol solution (10%, v/v).

$$K = \frac{[\text{CT complex}]}{[\text{TiO}_2][\text{Curcumin}]} \quad (2)$$

Using Benesi-Hildebrand analysis we get Eq. (3):

$$\frac{[\text{Curcumin}]}{\Delta\text{O.D.}_\lambda} = \frac{1}{\varepsilon_\lambda} + \frac{1}{K[\text{TiO}_2]\varepsilon_\lambda} \quad (3)$$

where $\Delta\text{O.D.}_\lambda$ { O.D._λ (CT complex) – O.D._λ (curcumin)} is the change in optical density (or absorbance) and ε_λ is the molar extinction coefficient, at a particular wavelength, in the present case it is 420 nm. The plot of $[\text{Curcumin}]/\Delta\text{O.D.}_{420\text{nm}}$ vs. $1/[\text{TiO}_2]$ in water-methanol (10% v/v) solvent mixture is shown in Fig. 2. Thus $K = 3.1 \times 10^3 \text{ M}^{-1}$ and $\varepsilon_{420\text{nm}} = 8.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ were obtained from these measurements. This K value is in comparison with that ($K = 6.4 \times 10^3 \text{ M}^{-1}$) between TiO_2 and quinizarin [22]. The molar extinction coefficient value in our case is also comparable to that in the TiO_2 and quinizarin CT complex [22].

3.2. Photo-degradation studies of curcumin

The photo-degradation studies of curcumin were performed in water-methanol and water-acetonitrile solvent mixtures by irradiating the solutions with the light output from a 450 W xenon lamp. The overall light output from the xenon lamp was utilized in two different types of irradiations. In one case, the solutions were irradiated with the entire light output (UV-vis light) from the xenon lamp. In another case, the solution was irradiated with only the visible light, which is obtained by putting a 420 nm cut off filter in front of the xenon lamp output. In the former condition, the photo-excitation of the TiO_2 nanoparticles ($h\nu \geq 3.2 \text{ eV}$; $E_g = 3.2 \text{ eV}$) as well as the CT complexes ($h\nu < 3.2 \text{ eV}$) can occur. However, in the later condition, only photo-excitation of the CT complexes takes place.

The ratio of concentration of total curcumin present in the solution, in the photo-irradiated condition (C) to that in the un-irradiated condition (C_0), i.e. C/C_0 , was determined from the ratio of the absorbance values measured at 425 and 435 nm, respectively for the water-acetonitrile (v/v = 50:50) and water-methanol (v/v = 50:50) solvent mixtures. The photo-degradation results obtained in water-methanol and water-acetonitrile solvent mixtures are shown in Figs. 3 and 4 for UV-vis and only visible light excitations, respectively. It is clear from these two figures that on both the types of light irradiations, the photo-degradation of curcumin molecules is always higher in the presence of TiO_2 nanoparticles. The photo-degradation rates were almost similar in both the solvent mixtures in the presence of TiO_2 nanoparticles. Up to about 80% photo-degradation of curcumin molecules has been observed within just 6 min of irradiation in the presence of a 0.2 gram per litre (g/L) TiO_2 nanoparticles. The photo-degradation

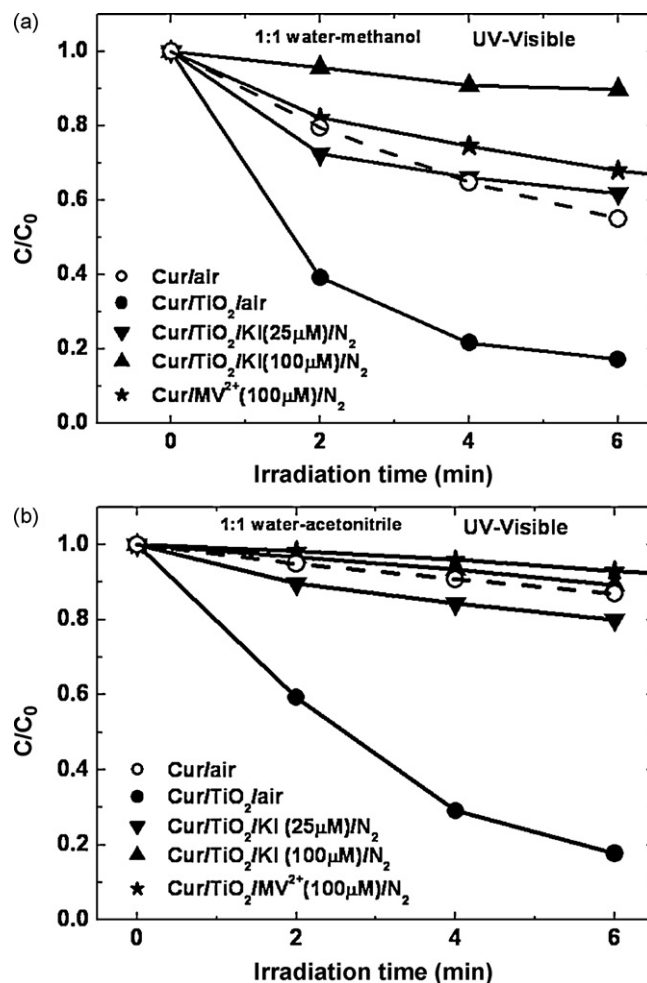


Fig. 3. Photo-degradation of curcumin in various conditions, mentioned in the figure, upon exposure to UV-vis light from a 450 W xenon lamp: (a) 1:1 water-methanol solvent mixture and (b) in 1:1 water-acetonitrile solvent mixture.

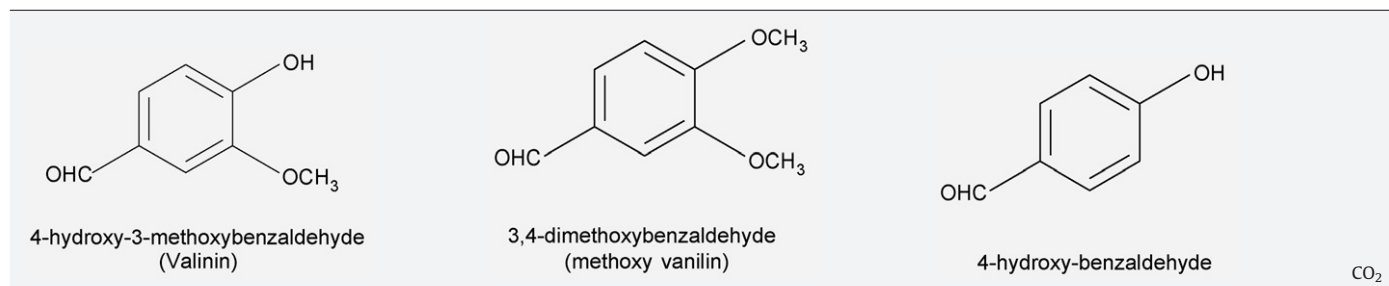
of the curcumin molecules in the absence of TiO_2 nanoparticles is higher in water-methanol solvent mixture as compared to that in the water-acetonitrile solvent mixture. This could be due to the involvement of methanol solvent molecules in the photo-degradation processes [25]. The photo-degradation products in the both the type of photo-excitations have been analyzed by GC and GC-MS. Vanillin was found to be the major product in both the cases, even though small concentrations of CO_2 , 4-hydroxy benzaldehyde and methoxy vanillin were also detected (Table 1). Some of the other probable products might be present in the bound form with the TiO_2 nanoparticles, which were difficult to be detected in the present analyses. The products obtained in this study fairly match with those reported in the literature [13–15].

3.2.1. Photo-degradation studies by UV-vis light

Upon UV-vis light excitation, both the TiO_2 nanoparticles and the CT complexes are likely to be photo-excited. In this section we will restrict ourselves to the photo-excitation of TiO_2 nanoparticles only, which will be supported at the end of this section. Electrons (e) and holes (h) are generated in the conduction band (CB) and valence band (VB), respectively, in the TiO_2 nanoparticles upon photo-excitation by a light with $h\nu \geq E_g$ (3.2 eV). The ground state redox potential of curcumin is +0.5 V vs. Ag/AgCl at room temperature [26]. This is close to the bottom of conduction band of TiO_2 potential, i.e. –0.52 V vs. Ag/AgCl [22] (shown in Scheme 2). Two possibilities may arise upon the creation of electrons (e) in the con-

Table 1

Stable products detected from the photo-degradation of curcumin in the presence of TiO₂ nanoparticles in 1:1 water–methanol and 1:1 water–acetonitrile mixed solvents upon irradiation with UV–vis and only visible light from a 450 W xenon lamp, analyzed by GC and GC–MS.



duction band (CB) and holes (h) in the valence band (VB) of TiO₂ nanoparticles. (1) The photo-excited electrons in the conduction band can cascade down to the surface states of TiO₂ and consequently reduce the ground state curcumin molecules leading to the formation of an anionic species. (2) The photo-generated holes in the valence band of TiO₂ nanoparticles can be captured either via the solvent molecules, e.g. methanol [27] and water or directly by the adsorbed curcumin molecules to form oxidized cationic species of curcumin [28]. These reactive intermediate species further undergo degradation in the presence of TiO₂ nanoparticles.

Photo-excitation of TiO₂ produced hot electrons in the CB, which are known to easily reduce dissolved oxygen to form super-oxide radicals (O₂^{•-}) [28]. The concentration of molecular oxygen in the aerated solvent mixtures is about 2.6×10^{-3} M. The redox potential of the dissolved oxygen is -0.33 V vs. Ag/AgCl (O₂ + e = O₂^{•-}) at room temperature [29]. These super-oxide radicals further produce hydroxyl radicals ([•]OH) in the presence of TiO₂, which oxidize the curcumin molecules. This process is known as radical mediated photo-degradation. The photo-degradation products in both the solvents mixtures have been found to be very much similar (see Table 1).

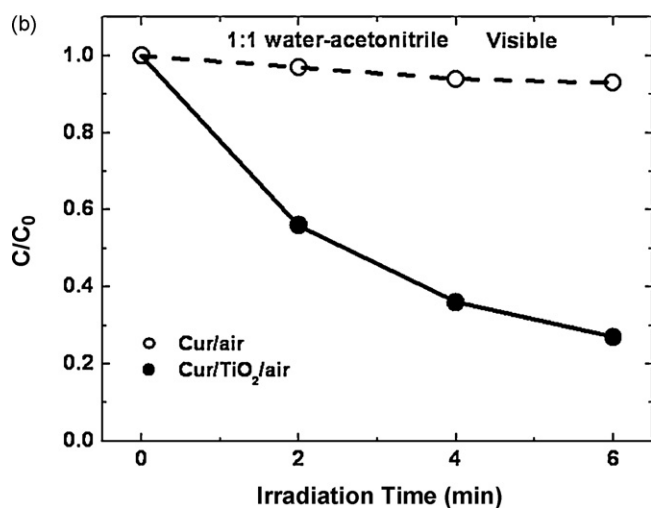
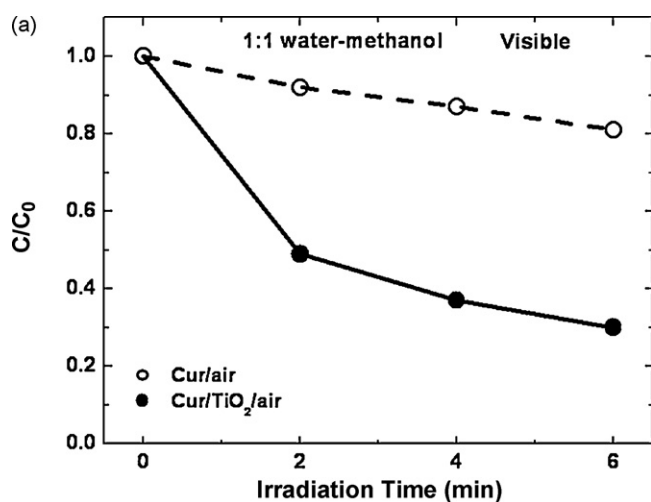
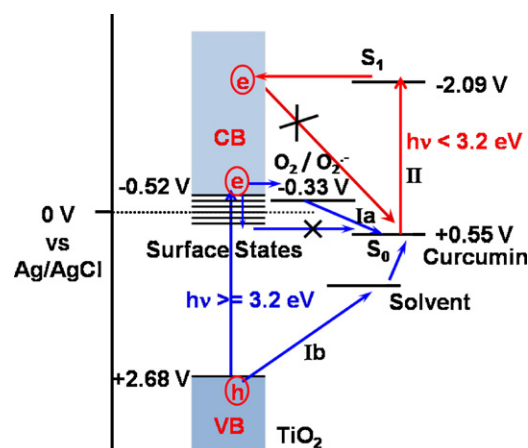


Fig. 4. Photo-degradation of curcumin in the absence (dashed lines) and presence (solid lines) of TiO₂ nanoparticles upon exposure to the visible light from a 450 W xenon lamp with a 420 nm cut off filter: (a) 1:1 water–methanol solvent mixture and (b) in 1:1 water–acetonitrile solvent mixture.



Scheme 2. A schematic representation of the electron and hole transfer processes in the TiO₂/curcumin systems.

Hence, the first proposition of the formation of an anionic species, as stated in the previous section is now ruled out. The possible reactive pathways involved in the photo-degradation of curcumin are represented in Scheme 2. The assumption of photo-excitation of TiO₂ nanoparticles with UV–vis excitation is also confirmed as there was no decomposition in the presence of KI. This is because if there would have an absorption by the CT complex then even in the presence of KI, some extent of decomposition should have occurred. The involvement of oxygen in the decomposition of curcumin is represented by the process, “Ia” in Scheme 2.

The extent of photo-degradation in the curcumin/TiO₂ solutions containing 25 μM KI is almost similar to that in the de-aerated curcumin/TiO₂ solutions. The photo-degradation in the curcumin/TiO₂ solutions in the absence of oxygen is very close to that observed in the aerated curcumin solutions. This clearly indicates that the iodide ions with a concentration of 25 μM are unable to quench the holes in the VB of TiO₂ nanoparticles. The photo-degradation in the de-aerated condition in curcumin/TiO₂ solution can only be thought of occurring via the holes in the VB of TiO₂. The holes could be either trapped by the solvent molecules like methanol [25] or by directly by the adsorbed curcumin molecules, forming a cationic intermediate species, which causes its degradation. This is shown as the process “Ib” in Scheme 2. Therefore, the extent of photo-degradation in these systems was higher in the water–methanol solvent mixture as compared to that in the water–acetonitrile solvent mixture.

3.2.1.2. Effect of external electron quencher. The photo-degradation mechanism in the case of UV–vis light excitation has also been investigated by adding external electron quencher, methyl viologen (MV²⁺) as shown in Fig. 3a and b. In the presence of 100 μM MV²⁺, which is an electron quencher, the photo-degradation was found to be different in these two solvent mixtures. In the case of water–methanol mixed solvent, the photo-degradation is slightly improved, whereas it is comparable to that observed in the case of 100 μM KI in the water–acetonitrile mixed solvent. This indicates that upon quenching of the electrons in the CB of TiO₂, the free holes in the VB of TiO₂ get trapped by the solvent molecules, like methanol in 1:1 water–methanol mixed solvent, which leads to the photo-degradation of curcumin. This process is shown as “Ib” in Scheme 2. On the other hand, in the water–acetonitrile mixed solvent, this process was absent and hence, the extent of photo-degradation was very much similar in the presence of both hole and electron quenchers.

3.2.2. Photo-degradation studies by visible light

The photo-degradation of curcumin by the visible light excitations is shown in Fig. 4a and b. It is expected that upon visible light excitation, only the CT complex is photo-excited. The photo-excited electrons in the complex can be transferred to the CB of the TiO₂ nanoparticles [20,22] leading to the formation of cationic radicals of curcumin molecules, which further get decomposed in the presence of TiO₂ nanoparticles. Redox potential of the S₁ state of curcumin is –2.09 V vs. Ag/AgCl, which is calculated from the E₀₀ value [8] and its ground state redox potential [26]. This level is well above the bottom of the CB of TiO₂. This is represented as the process, “II” in Scheme 2. The photo-degradation takes place through the cation radicals before any other reaction channel starts. Thus in both the type of photo-excitations, i.e. UV and visible, similar intermediate species are involved in the photo-degradation of curcumin molecules. Hence, the photo-degradation products should be also very much similar. Surprisingly, the photo-degradation products were found to be very much similar to those obtained in the UV–vis excitations (see Table 1). The overall movement of electrons and holes in the above system is represented with arrows in Scheme 1.

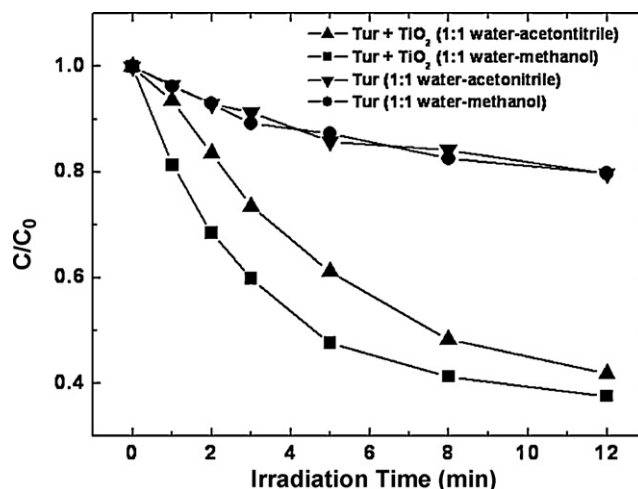


Fig. 5. Photo-degradation of turmeric in the presence of TiO₂ nanoparticles upon exposure to the visible light from a visible light photo-reactor.

3.3. Photo-degradation studies of turmeric

Curcumin and its derivatives are the only yellow pigments present in the turmeric. Hence, it is expected that the photo-degradation of these compounds will lead to the de-colouration of turmeric. In order to confirm this, we have systematically studied the photo-degradation of turmeric. Turmeric was dissolved in 1:1 aqueous–methanol and 1:1 aqueous–acetonitrile solvent mixtures due to its very poor solubility in water. Desired quantity of TiO₂ nanoparticles was dispersed in these solutions. The final solutions were photo-irradiated in a closed chamber of a visible light source. The change of absorbance at the absorption peak positions 435 and 425 nm wavelength, respectively, for the above two solvents systems was monitored at different time intervals. The ratio of concentrations of turmeric in the presence (C) and absence (C₀) of TiO₂ nanoparticles was plotted against exposure time of photo-irradiation, as shown in Fig. 5. Thus, it is clear from this figure that the photo-degradation of turmeric is much faster in the presence of TiO₂ nanoparticles as compared to that in its absence. This observation has finally led to an application discussed in the following section.

3.4. Removal of turmeric stain from cotton fabrics

Turmeric often puts stains on clothes during its use, which is very difficult to be removed by ordinary soap and detergents. The yellow stain on cotton fabrics is due to the binding of the yellow pigments which are mainly curcumin and its derivatives with the cellulose present in these fabrics. We have already investigated that curcumin gets degraded upon exposure to both UV and visible lights in the presence of TiO₂ nanoparticles. This is the main cause of the photo-bleaching of the yellow coloured turmeric solution to a transparent colourless solution upon exposure to the visible light in the presence of TiO₂ nanoparticles. Hence, we have utilized this observation to remove the yellow stains from cotton fabrics.

White cotton clothes were made yellow coloured with turmeric powders. These yellow coloured clothes were photo-irradiated with 40, 60 and 100 W tungsten lamps in the presence and absence of TiO₂ colloidal solution. The pictures of the photo-irradiated samples taken at different exposure times are shown in Fig. 6. It was observed from this investigation that the yellow colour in the white cotton fabrics gets completely removed in 2 h of photo-irradiation by 60 and 100 W lamps in the presence of aqueous colloidal TiO₂ nanoparticles. Whereas the yellow colour still remains long after 2 h of similar photo-irradiation in the absence of TiO₂ nanoparticles.

























Light Source	Condition	0hr	1/2hr	1hr	2hrs
40 W Tungsten Lamp	Turmeric &TiO ₂				
	Turmeric				
60 W Tungsten Lamp	Turmeric &TiO ₂				
	Turmeric				
100 W Tungsten Lamp	Turmeric &TiO ₂				
	Turmeric				

Fig. 6. Camera ready pictures of the photo-irradiated cotton cloth (which was made yellow colour by turmeric) in the absence and presence of TiO₂ nanoparticles upon exposure to the visible light sources at different exposure times.

We have successfully demonstrated an easier method of removal of turmeric stain from cotton fabrics.

4. Conclusion

Curcumin forms CT complexes with TiO₂ nanoparticles in water-organic mixed solvents and gets decomposed upon exposure to either UV-vis or visible light. Upon visible light excitation, the CT complexes are photo-excited and the subsequent photo-degradation of curcumin takes place through electron transfer from the photo-excited CT complexes to the CB of TiO₂ nanoparticles. In the case of UV-vis excitation, the photo-excited holes in the VB of TiO₂ nanoparticles found to play an important role in the photo-degradation of the curcumin molecules. The involvement of photo-excited holes in the photo-degradation of curcumin molecules was confirmed by adding external hole quencher, KI and electron quencher, MV²⁺ in the solution. The photo-degradation of curcumin takes place through the photo-excited electrons in the CB of TiO₂ nanoparticles by involving the dissolved oxygen present in the solution. The photo-degradation products in both the type of photo-excitations were analyzed by GC and GC-MS. The yellow coloured turmeric stain on cotton fabrics was easily removed upon exposure to visible light in the presence of an aqueous colloidal solution of TiO₂ nanoparticles.

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