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ORIGINAL RESEARCH PAPER

Photocatalytic Removal of Food Colorant E 131 VF from Synthetic Wastewater by Cu Doped TiO_2 Samples

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ABSTRACT

In this work, we studied the effect of various amounts (0.2-1.2 % mole ratio) of Cu doping to TiO_2 nanoparticles (Cu/TiO_2) on the photocatalytic removal efficiency of the food colorant E 131 VF. Two series of doped TiO_2 (P25) photocatalysts were prepared in two different media (50%ethanol-50%acetone and 5% surfactant (Tween 20)-95%H_2O) by using the impregnation method. The prepared samples were characterized by XRD, FTIR, Raman, diffuse reflectance spectroscopy and SEM/EDX analyses. The XRD results showed that the crystal dimension of TiO_2 increased from 23 to 35 nm and rutile/anatase ratio decreased from 16% to 9% after Cu doping in two different media. The photoactivity of TiO_2 was reduced in the presence of Cu even at a low molar ratio. The photocatalytic degradation rate constant of TiO_2 (P25) was 0.24 (au) but it decreased to 0.015 (au) in the presence of the sample containing 0.6% Cu. Several reasons were suggested to explain the dramatic decrease in the activity of the prepared Cu/TiO_2 samples.

Keywords: *Cu/ TiO_2, Photocatalytic removal, Impregnation, Surfactant, and E 131 VF dye, Kinetics study*

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INTRODUCTION

The food products may lead to numerous problems for human health because they are containing a number of harmful organic compounds. A number of studies have focused on the use of additives and their influence on humans and on the environment[1, 2].The food colorants have been found large applications in food industry. An environmental regulation applied in most countries requires discoloring industrial wastewater prior to its discharge. A number of techniques for dyed wastewater purification based on biodegradation [3], electrochemical treatment [4, 5], adsorption [6], and advanced oxidation processes [7, 8] are suggested as solution to remediate this problem. There are some reports about using photocatalytic degradation processes for the removal of dyes from wastewater [9–11]. Photocatalytic reactions based on semiconductor nanomaterials are started by absorption of radiation with energy that equals or higher than the band-gap energy of the catalyst. The absorption promotes an electron from the valence band (VB) of the photocatalyst to the conduction band (CB), thus generating a hole (h^+) in the valence band [12]. TiO_2 has been found to be the most suitable and very researched material due to the high chemical stability and non-harmfulness, physical, optical and electrical properties [10, 13]. It exists in three phases: anatase, rutile, and brookite [13]. Anatase phase is mainly used as a photocatalyst but rutile phase has low catalytic activity [13]. Several efforts have been made to increase the photocatalytic efficiency

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of TiO_2, such as doping it with metal[14–20]. The photodegradation of methyl orange (MO) was increased after doping of TiO_2 with Cu[21]. Complete degradation of crystal violet (CV) was observed by Au doped TiO_2, whereas for undoped TiO_2 was not observed [22].The effect of metal ions on the photoactivity of TiO_2 has been investigated for degradation of organic pollutants[23–25]. Some studies have suggested that improvement of the photocatalytic degradation rate was due to electron trapping by the metal ions leading to the inhibition of electron-hole recombination. However, high concentration of metal may have a detrimental effect on the photoactivity of TiO_2 [24].The nature of the metal and the dopant concentration have remarkable effect on the photocatalytic removal of the pollutant [25]. In contrast, some studies showed that the presence of some metals such as Fe(III) and Cr(III) in TiO_2 decreases the degradation rate constant of pollutants compared with pure TiO_2[26].The authors explained the dramatic decrease by a progressive loss of total crystallinity, partial transition from anatase to rutile phase. There are various experimental conditions that used for doped TiO_2 sample preparation and effect on photocatalytic activity, therefore experiments are necessary to point out these conditions on photocatalytic activity[15,24, 27- 28].

In this work, we prepared Cu doped TiO_2 (P25) containing different amounts of Cu in two different media for the degradation of the food colorant E 131 VF**.** The first set samples (1st procedure) were prepared in 50% ethanol- 50% acetone; another set (2nd procedure) were prepared in 5% surfactant (Tween 20) – 95 % water. The reason for using these two media was an attempt to overcome the nanoparticles agglomeration observed when using water alone as a solvent[29]. To the author's knowledge, use of two different media for the preparation of Cu doped TiO_2 samples and investigation of their performance for degradation of the food colorant E 131 VF has not been reported yet.

EXPERIMENTAL DETAILS

TiO_2 (P25) was provided from Degussa (Sigma Aldrich, Germany,) consists of 80% anatase and 20% rutile with a specific BET surface area of 50 $m^2\ g^{-1}$ and primary particle size of 23nm. The food colorant, E131VF dye selected as an organic pollutant model, was purchased from Sigma Aldrich ($C_{27}H_{31}N_2O_6S_2$-Na, purity: 50 %, M_W:565.67 g). $Cu(NO_3)_2\ 3H_2O$ was purchased from BDH (GPR).

Preparation of Cu doped TiO_2 samples

The impregnation method was selected to doping the metal according to the procedure in ref. [29].Several masses of $Cu(NO_3)_2\ 3H_2O$ (BDH, GPR) were added each time to 2 g of TiO_2 in order to have samples containing 0.2-1.2 % mole ratio of Cu(II)/TiO_2, and then 100 ml of equal volume of ethanol and acetone were added to each sample and stirred with a magnetic stirrer for 8 h, at room temperature. The solutions were allowed to stand at room temperature for 12 h and dried at 100 ˚C for another 12 h. The dried samples were ground in a mortar and annealed at 400 ˚C for 4h. In this impregnation method, the metal ion is deposited on the surface of TiO_2[18]. Another set (2^{nd} procedure) of the samples were also prepared with 100 ml of distilled water containing 5 ml of the surfactant Tween 20. 2 g of TiO_2 followed the same steps without the addition of metal ion in order to compare it with the doped catalyst (0 %Cu/TiO_2) was prepared. The prepared catalysts were named x% Cu,y, where x is the Cu/TiO_2 molar ratio and y is the medium where the impregnation was done. A stock solution of E 131 VF dye was prepared by dissolving 40 mg of the dye in 1000 ml distilled water. The concentration of the dye in the experiment was selected in such a way that the absorbance of the dye followed Beer's law.

Characterization

The X-ray diffraction patterns for crystallinity investigation were recorded on D8 Focus, Bruker, X-ray diffractometer operating at 50kV using Cu-Kα radiation (λ = 0.1541 nm). The measurement was performed over a diffraction angle range of 2θ = 10°–80°. The % of the rutile phase in the samples was determined with the following equation (Eq. 1):

$$\text{Rutile (weight \%)} = 1/(1 + 0.884 \times I_A / I_R) \qquad (1)$$

Where I_A and I_R are the diffraction intensity of the anatase and rutile phases, respectively[30].

FTIR spectra of the samples were recorded on Jasco FT/IR- 6300 spectrometers in the wavenumber range of 400 to 4000 $cm^{-1}$for functional groups identification. The FTIR study was performed by using KBr pellet. Raman spectra for characterization of surface functional groups were recorded on Horiba Scientific, operating

with green Laser at 532 nm. Scanning electron microscopy (SEM) images for investigation of the morphology corresponding to the achieved specimens were taken with Ametek materials analysis division (AIS 2300C series) instrument (working distance: 25 mm, voltage 20 kV). The optical band gap energies of the prepared materials were determined by UV-Vis DRS technique using Jasco V-570 spectrophotometer.

Photocatalytic degradation tests

The degradation of the food colorant E 131 VF was followed by measuring the absorbance (A) at the maximum absorption wavelength of E 131 VF dye (640 nm) with time. UV- visible spectra were recorded on a double beam UV-visible spectrophotometer. The determination of the order of the degradation reaction and the rate constant (arbitrary unit (au)) were obtained from the curve A vs time. Prior to commencing illumination, a suspension containing 0.08 g of the catalyst and 100 ml of aqueous solution of E 131 VF dye was stirred continuously at least for 15 min in the dark (for adsorption/desorption equilibrium), then the sample was irradiated under magnetic stirring by 4 UVB lamps (λ_{max}: 360 nm) positioned at 10 cm above the glass bowl (Luzchem LZC-4V, Canada). To quantify the decrease of the dye concentration, a sample of 3 ml was taken (with a pipette) at predetermined intervals of time and centrifuged at 4000 rpm.

RESULTS AND DISCUSSION

Characterization of the prepared samples

The XRD patterns of TiO_2 and doped TiO_2 samples treated at 400 °C are shown in Fig. 1. They show five primary diffractions at 2θ =25.3° (100%), 38° (20 %), 48.2°(28 %) and 62.5°(10 %) which can be attributed to different planes of pure anatase form of TiO_2 [20,31]. Other diffractions at 2θ = 27.36° (100%), 36° (45%), 54.0° (53 %) and 69.0°(8 %) can be attributed to pure rutile form of TiO_2[32].The XRD patterns of the Cu/TiO_2samples almost coincide with that of the bare TiO_2(P25) or TiO_2 treated at 400 °C showing no new diffractions due to cupper doping thus suggesting that the small metal ion amounts are placed on the surface of the TiO_2 crystal (Fig. 1)[32]. The % of the two

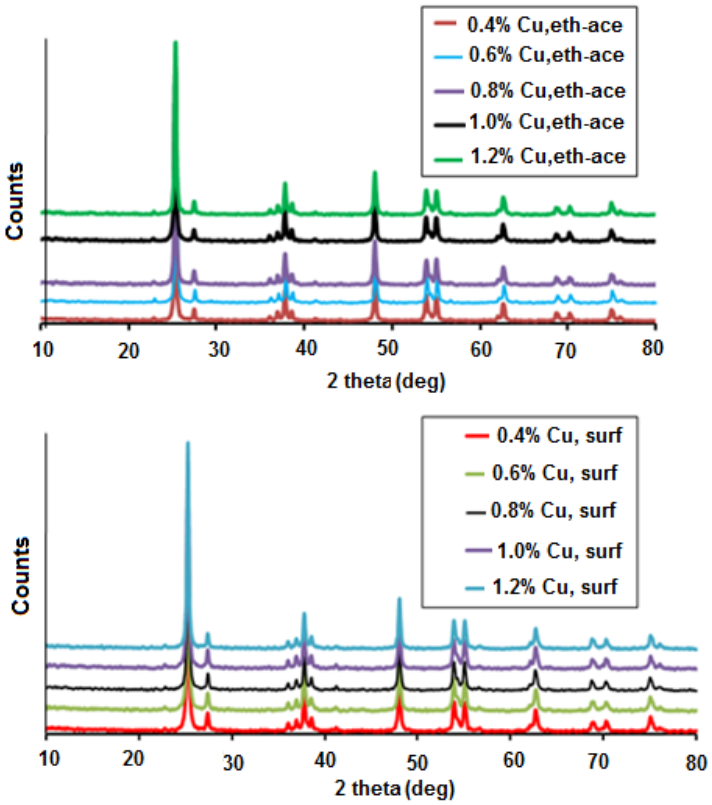

Fig. 1. The XRD patterns of the Cu/TiO_2samples prepared in two different media

diffractions at 2θ= 25.3° and 27.5°of the different samples are shown in Table 1.

The average size of the TiO_2 crystal was estimated by the Scherrer equation (Eq. 2) for all the samples[20] (Table 1):

$$D = k\lambda /(\beta \cos\theta) \quad (2)$$

Where, D represents the mean crystal dimension, λ is the X-ray wavelength (0.1541 nm), β refers to the diffraction full width at half maximum (FWHM) in radian for diffraction at 2θ=25.3°, K represents a coefficient (0.89) and θ is the diffraction angle. The doped samples did not have the same crystal size as the untreated one (P25) due to agglomeration of tiny particles. The % of the ratio of rutile to anatase in P25 is 16 % whereas it varies between 8.3% and 9.6% for the samples prepared in the ethanol-acetone medium. The ratio of rutile/anatase of the two samples of TiO_2: 0 %Cu, eth-ace and 0% Cu, surf are lower than that of the bare TiO_2 whereas the particle dimension (D) is higher in both cases (Table 1).

Fig. 2 shows the FTIR spectra of TiO_2 and Cu/ TiO_2 samples. The FTIR spectrum of TiO_2 shows

Table 1. TiO_2 crystal dimension and relative intensity of some characteristic peaks of P25 and the prepared samples, (Anatase (A), Rutile (R)).

Sample	2θ = 25.3° (A)	2θ = 27.36° (R)	D (nm)	% (rutile/anatase)
P25	100	16.5	23.0	16.0
0% Cu, eth-ace	100	13.2	26.8	13.0
0% Cu, surf	100	12.6	27.8	12.5
0.4 % Cu,eth-ace	100	8.0	35.0	8.3
0.4% Cu, surf	100	10.3	32.2	10.4
0.8 % Cu,eth-ace	100	8.7	32.2	9.6
0.8 % Cu, surf	100	9.4	33.6	9.6
1.2 % Cu, eth-ace	100	9.0	33.6	9.3
1.2% Cu, surf	100	8.7	32.2	9.0

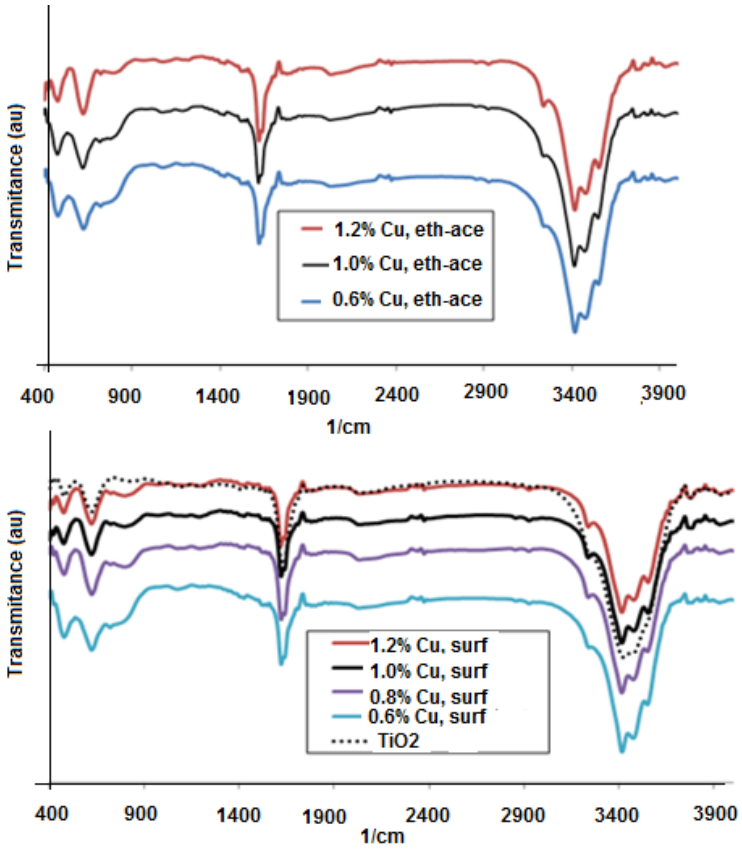

Fig. 2. FTIR spectra of TiO_2 and Cu/ TiO_2samples prepared in two different media

three bands: broad and intense one at 3420 cm^{-1}, the two other bands at 1620 and 620 cm^{-1}. The peaks at 3420 and 1620 cm^{-1}can be attributed to the O– H stretching and bending mode of hydroxyl groups of moister that is present on the surface of the catalyst [33, 34]. These are critical for photocatalytic reactions since they can react with photogenerated holes produced on the catalyst surface and generated hydroxyl radicals, which are powerful oxidant. The peaks of TiO_2 observe at 476 and 620 cm^{-1}can be assigned to the vibrations of Ti–O and Ti–O–Ti framework bonds of TiO_2 [33]. The zoom in the region between 400 and 600 cm^{-1} did not show any characteristic peak of Cu-O (432.3, 497, and 603 cm^{-1}) [35]. As the amount added of the metal salts are small, no new band and no shift is observed in the bands of the bare TiO_2 after Cu doping.

In the Raman spectrum of P25, the peaks centered at 145, 396, 514 and 636 cm^{-1} are attributed to the anatase phase, while the peaks, located at 245, 443 and 610 cm^{-1} are characteristic of the rutile phase of TiO_2 (Fig. 3)[35–37]. The Raman spectra of P25 and Cu/TiO_2 samples consisted of characteristic peaks of anatase (Fig. 3). No shift was observed after doping with 1.2 % Cu(II) [38].As in the case of XRD, the presence of copper oxide CuO or Cu_2O could not be detected by Raman spectroscopy [**35].** The non-detection of the corresponding metallic oxide by these techniques (Raman, XRD, and IR) does not mean its absence, due to the small amount of copper.

The electronic band structures of the as-prepared samples were analyzed by UV–Vis diffuse reflectance spectroscopy (Fig. 4a). All the samples exhibited reflectance in the range of 250-400 nm that can be attributed to anatase and rutile phase of TiO_2. The Cu-doped sample indicated a redshift extending up to 600 nm that attributed to the presence of Cu in these samples. The successful doping of Cu was also evident from the change in the color observed in the samples, shifting from pure white to light yellow. The optical band gap energy of the prepared samples was determined by UV-Vis DRS analysis[31], and the obtained DRS results are reported as the Kubelka–Munk function where R is the reflectance, F(R) is the Kubelka–Munk function (Eq. 3):

$$F(R) = (1 - R)^2 / 2R \quad (3)$$

The optical band gap energy of the samples can be derived from UV-Vis DRS data by plotting F(R) against photon energy (E: hν), followed by extrapolation of the linear part of the spectra to the energy axis(Fig. 4b)[30]. The increase in the bandgap energy of the 1.0 and 1.2 % Cu, surf samples (3.25 and 3.21 eV) with respect to that of P25 (3.12 eV) may be due to rutile/ anatase ratio in these samples. The rutile/anatase ratio is 9.3%

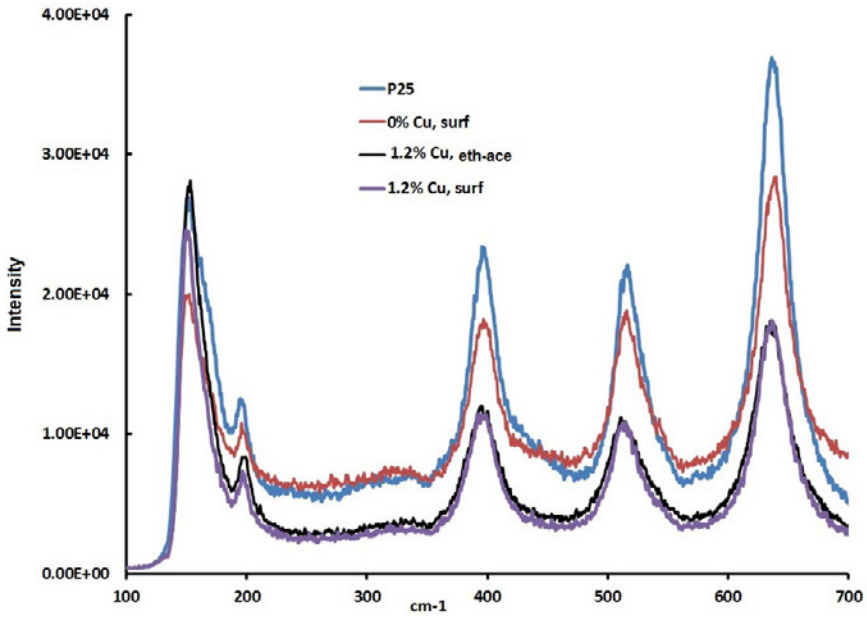

Fig. 3. Raman spectra of the samples prepared in two different media.

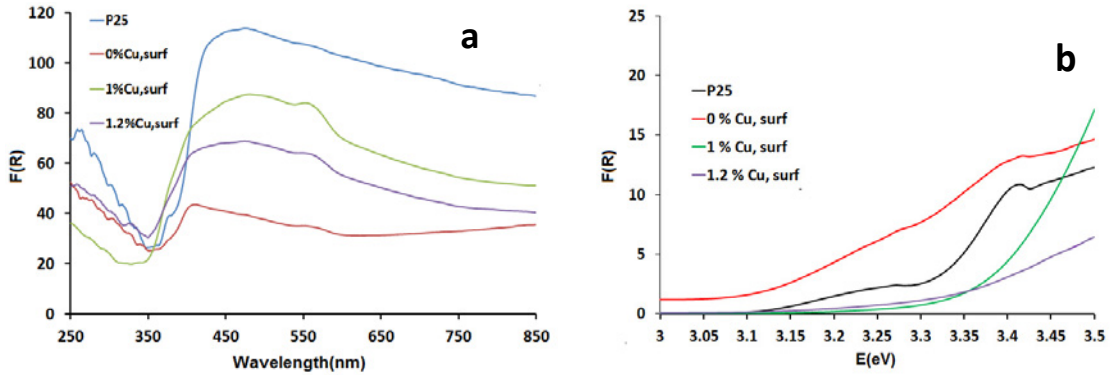

Fig. 4. a) Diffuse reflectance spectra and b) Kubelka-Munk curves of the samples for calculation of bandgap energy.

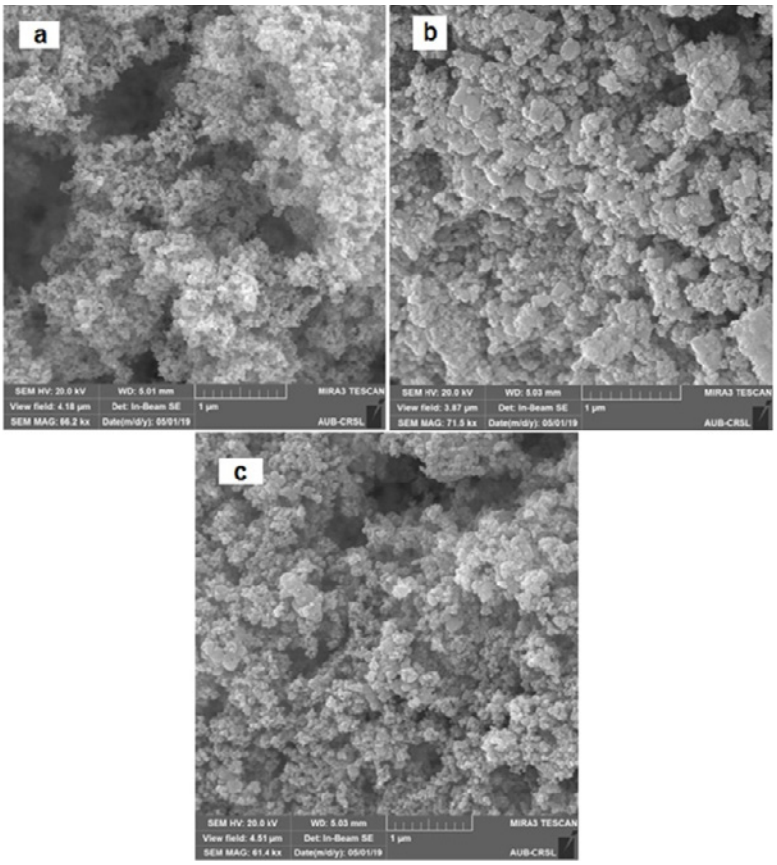

Fig. 5. SEM images of a) P25, b)1.2 % Cu, eth-ace, c) 1.2 % Cu, surf.

and 9.0% for 1.0 and 1.2% Cu, surf samples and the bandgap energy for anatase and rutile phase of TiO_2 are 3.20 and 3.00 eV respectively. The bandgap energy of Cu doped samples shifted to bandgap energy of pure anatase phase by decreasing rutile/anatase ratio.

SEM images of the TiO_2 and 1.2 % Cu/TiO_2 samples prepared in two different media are shown in Fig. 5. SEM images show that the samples prepared by the two procedures are agglomerated; also the particles are bigger than the bare TiO_2. The EDX patterns of Cu/TiO_2 samples (Fig. 6) show two peaks around 0.2 and 4.5 keV. The intense peak is assigned to the bulk TiO_2 and the less intense one to the surface TiO_2[20]. The peaks of Cu are observed at 0.7, 8 and 9 keV [34]. The results confirm the existence of Cu atoms in the Cu/TiO_2 samples (Table 2), but the XRD patterns did not show any

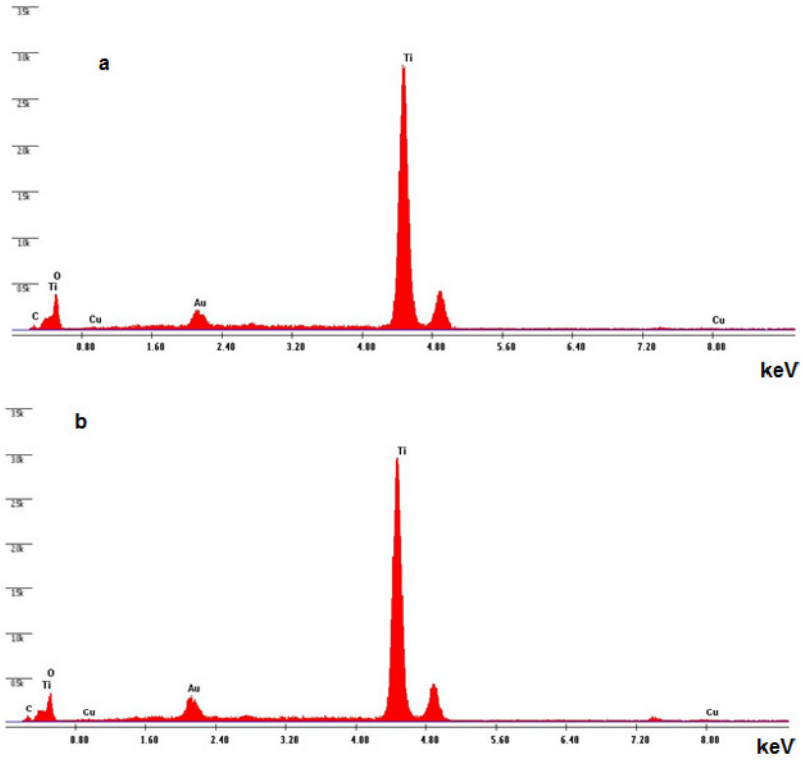

Fig. 6. EDX pattern for sample a) 1.2% Cu, eth-ace and b) 1.2% Cu, surf.

Table 2. Chemical composition of the prepared samples (At%: atomic%).

Sample	C (At%)	O (At%)	Ti (At%)	Cu (At%)
P25	5.00	50.0	45.0	-
1.2% Cu, eth-ace	35.5	43.0	21.0	0.50
1.2% Cu, surf	39.53	50.0	10.0	0.47

diffractions related to Cu. EDX analysis shows that some zones contain high atomic % of C. It may be due to organic molecules adsorbed chemically on the surface of the TiO_2nanoparticles.

Photocatalytic activity of Cu doped TiO_2

The variation of the UV- visible spectrum of the dye versus time shows a decrease of all the spectra with time. The photocatalytic degradation of E 131 VF dye in the presence of the bare TiO_2 follows perfectly the pseudo-first-order kinetics (Fig. 7).Also the photocatalytic degradation reaction order obtained in the presence of TiO_2 with 0 % and 0.2 % Cu in the two media (calcined at 400 ˚C) were pseudo-first-order, but it became zero order for higher % of Cu (Fig. 7).There is a blue shift of the maximum wavelength (indicated by dotted line in Fig. 8) that proving a successive degradation of dye during irradiation. A similar result was obtained with Baraka [40]. The time needed to decrease the absorbance from 1.6 to 0.1 for the bare P25 was 12 min whereas it was 20 min for 0% Cu, eth-ace and 28 min for 0% Cu, surf. The impregnation of TiO_2 in the acetone-ethanol and in the aqueous solution of surfactant affected the surface of TiO_2 may be by adsorption of these organic molecules at the surface of TiO_2 or by agglomeration of the nanoparticles of P25.The rate constants of TiO_2 with 0 % Cu in the two media were for the 1st procedure: 0.14 and for the 2nd one:0.098,which are both smaller than the bare TiO_2 (k_o=0.24 (au)) and P25 heated at 400 °C without addition of any solvent for 4 h (k_o=0.23 (au)) (Fig. 9).The decrease in the activity of TiO_2 after solvation is due to increase in agglomeration of the nanoparticles of TiO_2 and maybe also due to the adsorption of organic solute (ethanol/acetone or surfactant) on the surface of TiO_2 which prevent the absorption of the radiation and therefore the

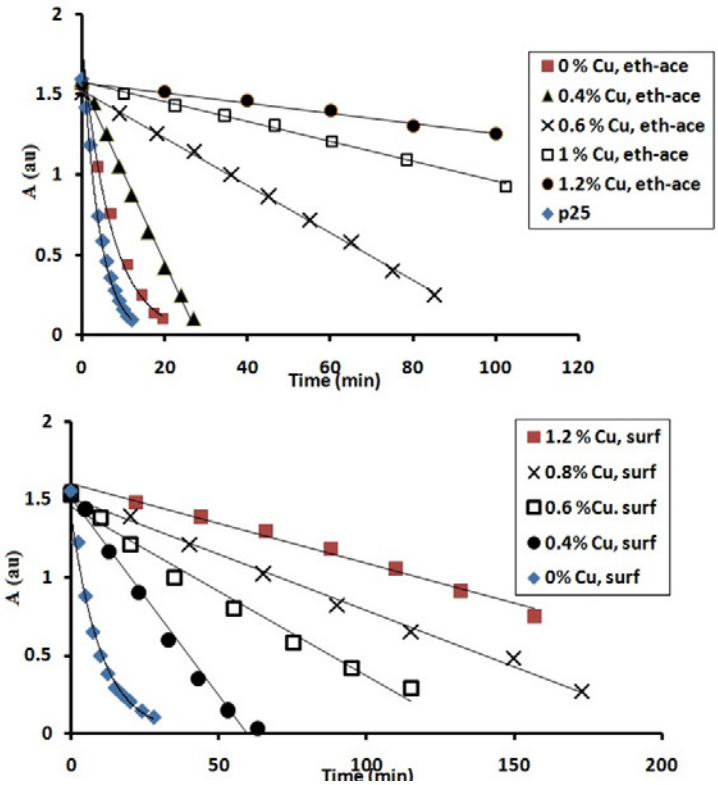

Fig. 7. Variation of the absorbance as a function of time for various Cu doped TiO_2 samples prepared in two different media.

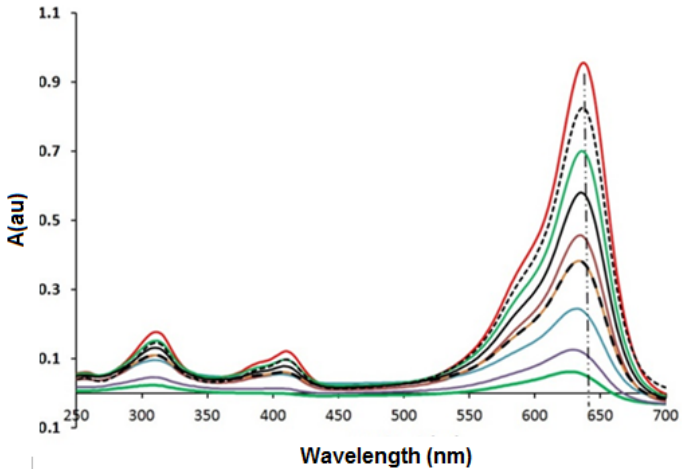

Fig. 8. Variation of the UV-Visible spectrum during the photocatalytic degradation of E 131 VF dye in the presence of P25.

good function of TiO_2. The rate constant in the acetone –ethanol medium is higher than that in the surfactant medium. For higher % of Cu the rate constant k_o is approximately the same (Fig. 9). For all the doped samples (including 0 % Cu), the rate constant is smaller than that of P25. The results of several works show a decrease in the photoactivity after doping with Cu(II) (Table 3). There are several factors which inhibit the photoactivity of TiO_2:

1) The adsorption of the organic molecules (surfactant or ethanol) on the surface of TiO_2

2) The agglomeration of the TiO_2 nanoparticles during solvation, so the particles of these catalysts are not well distributed in the food colorant solution as was the case with P25. The surface area available for photon absorption would be reduced.

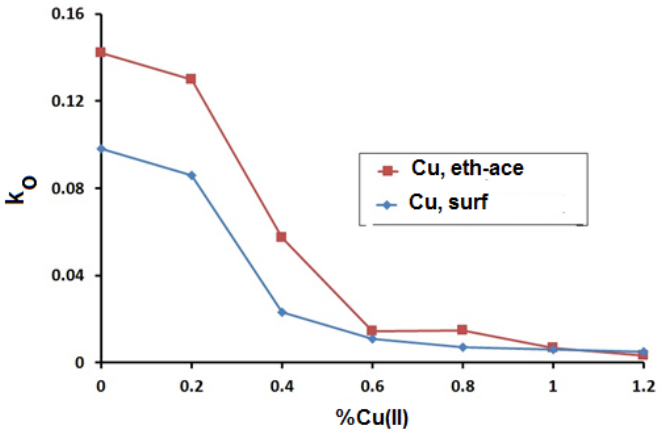

Fig. 9. Variation of the rate constant of k_o vs the Cu(II) molar ratio %.

Table 3. Effect of doping Cu(II) to TiO_2 on the photocatalytic degradation of the organic pollutants.

Pollutant	Range of doping %	Optimum % of doping	reference
Rhodamine B	0 -1	0.06	[15]
Ethanoic acid	1 (only one %)	Negative effect for any %	[23]
4-Nitrophenol	0.3 – 5.0	Negative effect for any %	[28]
Acid orange 7	1 (only one %)	Negligible effect	[24]
E 131 VF dye	0.2 -1.2	Negative effect for any %	This work

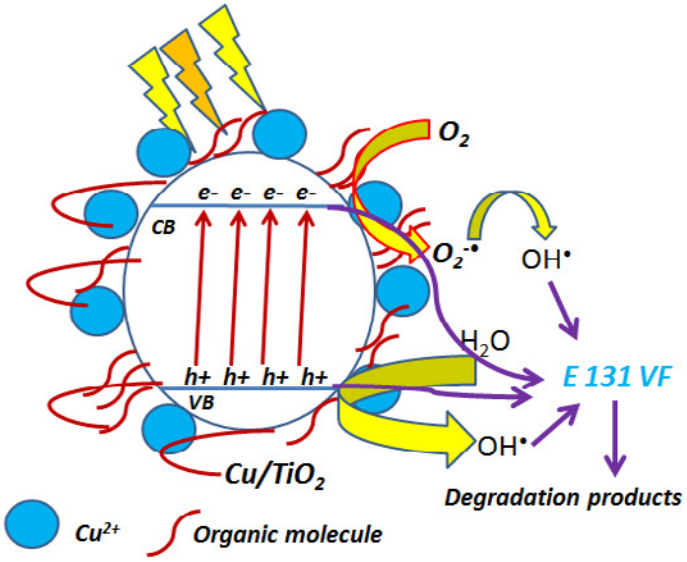

Fig.10. Our proposed mechanism for photocatalytic degradation of E 131 VF dye over Cu/TiO_2 photocatalyst under UV irradiation.

3) The increase in the recombination of photogenerated electrons and holes which is a function of the amount of Cu added. Paola et al. showed that the rate constants of e^--h^+ recombination increases when metal loading increases [22].

Proposed mechanism for E 131 VF dye degradation

Fig. 10 shows the surface of TiO_2 after doping by Cu^{2+} in organic media and proposed mechanism for the photocatalytic degradation of E 131 VF dye over Cu/TiO_2 sample. High-energy electrons are formed on Cu/TiO_2 surface under UV irradiation. These electrons are excited from valance band to conduction band of TiO_2 and the holes remain on the valance band of TiO_2. The oxygen molecules adsorbed on the surface of photocatalyst trap the electron from the TiO_2 and thus a number of

active species including $OH^{\bullet}$ and $O_2^{\bullet-}$ radicals are produced. These species attack to E 131 VF dye molecules and decompose them. The photoinduced holes (h^+) can react with H_2O oxidizing them to $OH^{\bullet}$ radicals or oxidize the dye molecules. The reactions at the surface of photocatalyst initiating the degradation of E 131 VF dye can be expressed as follows:

$Cu/TiO_2 + h\nu \rightarrow e^-$ (CB) + h^+ (VB)
$O_2 + e^-$ (CB) $\rightarrow O_2^{\bullet-}$
$H_2O + h^+$ (VB) $\rightarrow OH^{\bullet} + H^+$
$O_2^{\bullet-} + H^+ \rightarrow HOO^{\bullet} \rightarrow OH^{\bullet}$
E 131 VF + $OH^{\bullet}$ → degradation of the dye
E 131 VF + h^+(VB) → oxidation products
E 131 VF + e^-(CB) → reduction products.

CONCLUSION

In this work, we prepared Cu doped TiO_2 samples containing different amounts of Cu (0.2-1.2 % mole ratio) in two different media by impregnation method. The XRD, Raman and FTIR techniques which are bulk techniques were unable to prove the presence of small amounts of copper on the surface of TiO_2, but the EDX analysis confirmed 0.5 At% of Cu. The crystal dimension of TiO_2 increased in the range of 26-35nm but the rutile /anatase ratio decreased from 16% to 9% after Cu doping in two different media compared to P25. We used the prepared samples for kinetics study of the photocatalytic degradation of food colorant E 131 VF. Our obtained results showed that the doping TiO_2 with Cu(II) had a detrimental effect on the photocatalytic activity of TiO_2 whatever the solvent used due to agglomeration of the nanoparticles and presence of some organic molecules on TiO_2 surface. The photocatalytic degradation rate constant of TiO_2 (P25) was 0.24 (au) but it decreased to 0.015 (au) in the presence of the sample containing 0.6% Cu. We suggest studying the effect of doping to add the metal salt during the sol gel preparation of TiO_2 in order to prevent the agglomeration of the nanoparticles.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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