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Photocatalytic degradation of Congo Red by hydrothermally synthesized nanocrystalline TiO₂ and identification of degradation products by LC–MS

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Abstract

Degradation of Congo Red (CR) dye in aqueous solutions was investigated by means of photocatalysis of TiO₂ which was hydrothermally synthesized at 200 °C in 2 h, in anatase phase with 8 nm crystallite size. Efficiency of TiO₂ in photocatalytic degradation under visible irradiation was studied by investigating the effects of amount of TiO₂, irradiation time, initial CR concentration and pH. It was found that complete decolorization is achieved within 30 min of irradiation. Effects of nitrate and sulphate ions and humic acid on the degradation were also tested. The results were compared with Degussa P-25 TiO₂ at the same degradation conditions. Degradation products were detected using LC–MS technique. The probable pathways for the formation of degradation products were proposed.
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1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. Waste waters generated by the textile industries contain considerable amounts of non-fixed dyes, especially of azo dyes, and huge amount of inorganic salts. Azo dyes with aromatic moieties linked together by azo (–N=N–) chromophores, represent the largest class of dyes used in textile processing and other industries. Of all the dyes available, approximately 50–70% are aromatic azo compounds [1,2]. More than 60% of commercial dyes based on ca. 8000 with different chemical structures are used in textile, food, pharmaceutical, paper and ink industries, and usually they are discharged in waste water.

About 1–20% of the total world production of dyes is lost during the dyeing process and released in the textile effluents [3]. It is well known that some azo dyes and their degrada-

tion products such as aromatic amines are highly carcinogenic [4]. Physical methods such as adsorption, biological methods (biodegradation) and chemical methods such as chlorination and ozonation are the most frequently used methods for removal of the textile dyes from waste water. Others are flocculation, reverse osmosis and adsorption onto activated carbon. Since they are not destructive but only transfer the contamination from one phase to another, a different kind of pollution is faced and further treatments are required. Namely, advanced oxidation processes have been extensively investigated [5–8]. Among these processes, heterogeneous photocatalysis is found as an emerging destructive technology leading to total mineralization of most of organic pollutants. In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated TiO₂. Among various semiconducting materials most attention has been given to TiO₂ because of its high photocatalytic activity, resistance to photocorrosion, low cost, non-toxicity and favorable band-gap energy. That is why TiO₂ has real advantage in the photocatalytic activity [9–12].

For TiO₂ synthesis, the hydrothermal process is more attractive since hydrothermally synthesized TiO₂ has several advantages, such as being fully anatase phase with nanocrys-

talline size, fine particle size with more uniform distribution and high dispersion either in polar or non-polar solvents, stronger interfacial adsorption and easy coating on different supporting material [13,14]. Additionally, aqueous solvents used in the hydrothermal process are environmentally acceptable [15].

In this present study, it was aimed to investigate the photocatalytic degradation of Congo Red (CR) and examine the effectiveness of hydrothermally synthesized TiO₂. Identification of degradation products using LC–MS technique was also performed.

2. Experimental

2.1. Materials

Titanium-*iso*-propoxide (Ti(OPr^i)₄, Alpha, 97%) was used as titanium source for TiO₂ synthesis. Hydrochloric acid (Merck, 37%) was used as catalyst for alkoxide hydrolysis. *n*-Propanol (Riedel de Haen, 99%) stored over molecular sieve (Fluka, 3 Å XL8) was used as solvent. Commercial Degussa P-25 TiO₂ (Aldrich) was used for comparison. 1000 mg L^{-1} Congo Red (C₃₂H₂₄N₆O₆S₂) stock solution was prepared by dissolving Congo Red powder (BDH Chemical Ltd., Poole, England) in de-ionized water. Other chemical like NaNO₃, Na₂SO₄, NaOH, humic acid and various solvents used during the synthesis were purchased either from Aldrich or Merck. Double distilled water was supplied from Millipore waters Milli Q distillation unit.

Dye concentration was measured by Carry 50 Model UV–vis spectrophotometer (Varian, USA). Photodegradation studies were performed in a Suntest CPS (Heraeus GmbH, Hanau, Germany). The Suntest was equipped with a 1 kW Xenon lamp with an effect of 675 W m^{-2}. During the studies whole spectrum of the Xe lamp (310–800 nm, λ_{max} = 460 nm) was utilized. Liquid chromatography–mass spectrometry (LC–MS) measurements were performed using Agilent 1100 series (Waldbronn, Germany) with electrospray ionization mass spectrometry.

2.2. Methods

Experimental procedure followed the order: (1) hydrothermally synthesis of Nano-TiO₂, (2) examination of photocatalytic efficiency of TiO₂ for degradation of CR by investigating the effects of amount of the TiO₂, irradiation time, initial CR concentration and pH, (3) comparison of the results with commercial available Degussa P-25 TiO₂ under the same catalysis conditions, (4) examination of effects of NO₃$^-$ and SO₄$^{2-}$ and humic acid on photocatalytic activity and (5) identification of degradation products by means of liquid chromatography–mass spectrometry technique.

2.2.1. Preperation of TiO₂

Ti(OPr^i)₄ was dissolved in *n*-propanol. After stirring for 5 min at ambient temperature, *n*-propanol–hydrochloric acid mixture was added into the former alkoxide solution. After stirring, a mixture of water and *n*-propanol was added into the last solution. The mixture was stirred at ambient temperature for a while. The mole ratio of H₂O/Ti(OPr^i)₄ and HCl/Ti(OPr^i)₄

Table 1
Some characteristic properties of Nano-TiO₂ and Degussa P-25

Property	Nano-TiO₂	Degussa P-25
Crystalline type	Anatase	Anatase (80%) + Rutile (20%)
Crystallite size (nm)	8	30
TiO₂ content (%)	90	
BET surface area (m² g^{-1})	114	50
Average pore diameter (nm)	2.12	30
Micropore volume (cm³ g^{-1})	0.023	
Adsorption average pore diameter (Å)	21.3	
Size of micropores (Å)	15	
Size of mesopores (Å)	22–33	

were 2 and 0.2, respectively. The final solution was then transferred into a Teflon-lined stainless steel autoclave cell. The cell was heated at 200 °C for 2 h. After cooling down the cell, separation of the solids from the solvents by centrifuging and drying the solid phase in a vacuum sterilizer at 30 °C for 4 h, TiO₂ was finally obtained. Hereafter, it was called as Nano-TiO₂. Crystalline phase of Nano-TiO₂ was analyzed by XRD, SEM and BET analysis. Detailed spectroscopic and morphological characterization of Nano-TiO₂ has been reported elsewhere [13,15]. Various properties of Nano-TiO₂ are listed in Table 1.

2.2.2. Photodegradation of Congo Red

Prior to examination of photocatalytic activity of Nano-TiO₂, it was ultrasonically dispersed in water which is not including dispersant. The product was a self-dispersed and transparent TiO₂ sol. For photocatalytic degradation experiments, desired volume of the dye solution was added into Nano-TiO₂ sol. Before irradiation in the suntest, mixture of Nano-TiO₂ and CR was soaked in the dark for 30 min at room temperature to maintain adsorption of CR onto Nano-TiO₂. Then, Nano-TiO₂/CR sol was poured into glass reaction cell. The cell was immediately placed in the suntest operated at 675 W m^{-2}.

Color removal in the samples was determined by the technique using absorbance value at the maximum of the absorption spectrum which is λ = 502 nm for CR. Degradation was quantified by detecting final dye concentration in the samples before, during and after visible irradiation. Before UV–vis spectrophotometric analysis of the dye, no filtration was needed for the samples including Nano-TiO₂, since they are already dispersed and transparent, whereas the samples containing Degussa P-25 needed to be removed from it's suspension by filtration.

To determine an optimum working condition for CR degradation, amount of Nano-TiO₂ to be contained in the dye solution, irradiation time, initial CR concentration and pH were varied. Degradation ratio was calculated using the equation,

$$\text{Degradation ratio}\,(\%) = \frac{C_0 - C_t}{C_t} \times 100$$

where C_0 is the initial concentration of CR and C_t is the instant concentration in the sample. The relation of $\ln C_0/C_t$ with irradiation time (t) was used to predict degradation kinetics.

Table 2
Conditions employed during LC–MS measurement

Parameter	Condition
Column	Agilent SB-C$_{18}$
Eluent types	Acetonitrile/10 mM ammonium acetate (24/76%, v/v) at pH 5.9
Flow rate (mL min^{-1})	0.3
Injection volume (μL)	10
Nebulizer pressure (psi)	60
Column temperature (°C)	25
Dry gas flow rate (L min^{-1})	5
Dry temperature (°C)	350
Vaporize temperature (°C)	400
LC–MSD ion trap and atmospheric pressure chemical ionization (APCI ion source)	

Concentrations of some selected contaminant in the sample were adjusted to be 20 mg L^{-1} NO$_3^-$, 300 mg L^{-1} SO$_4^{2-}$ or 160 mg L^{-1} humic acid.

Degradation products were monitored by LC–MS. Measurement conditions are listed in Table 2. LC–MS analysis was performed after addition of one drop of NaOH to the sample and filtration by Hydropinilic PVDF Millipore Millex HV filter.

3. Results and discussion

3.1. Effects of parameters on the degradation of CR

3.1.1. Effect of amount of Nano-TiO$_2$

For examining the effect of amount of catalyst in the degradation medium (Congo Red solution together with Nano-TiO$_2$ sol), several amounts of Nano-TiO$_2$ (between 0.031 and 0.250 g) were ultrasonically dispersed in 20 mL of distilled water and calculated amount of CR solution from 1000 mg L^{-1} of CR stock solution was added into the sol, and then initial solution was completed to 25 mL to obtain a Nano-TiO$_2$/CR medium containing 20 mg L^{-1} of CR. After soaking in the dark, the samples containing various amounts of Nano-TiO$_2$ irradiated for 20 min. Fig. 1 shows that degradation increased from 85 to 93.9% by increasing the amount of Nano-TiO$_2$ from 0.125 to 0.25 wt%. However, degradation drastically decreased after the ratio of 0.25%. A solid to liquid ratio of 0.25 wt% seems adequate for photooxidation of 94% of 20 mg L^{-1} CR just in 20 min. Higher amounts showed no positive effect on the degradation. The reason for this is supposed with increased opacity of the suspension, brought as a result of excess of TiO$_2$ particles. This can be explained in terms of availability of active sites on TiO$_2$ surface and the light penetration of photoactivating light into the sol. The availability of active sites increases with the suspension of catalyst, but the light penetration and hence, photoactivated volume of the sol shrink. Moreover, the decrease in the percentage of degradation at higher catalyst loading may be also due to deactivation of activated molecules by collision with ground state molecules. Most of the studies have reported enhanced degradation rates for catalyst loading up to 400–500 mg L^{-1}. Agglomeration and sedimentation of the TiO$_2$ particles have also been reported [3,16]. In this condition, some parts of the
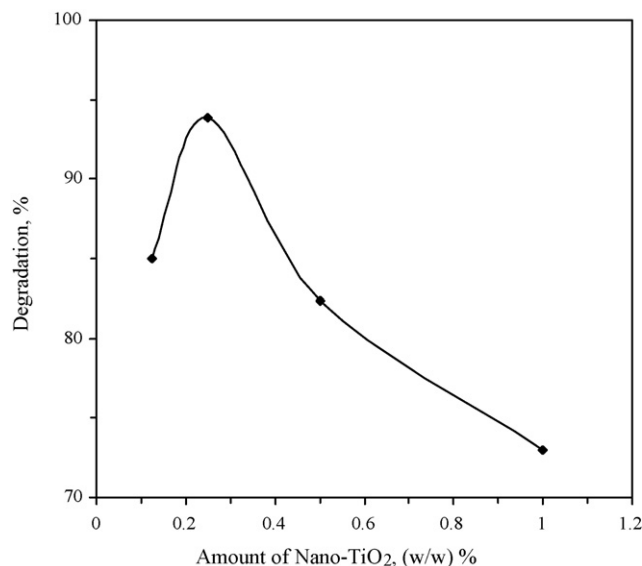

Fig. 1. Effect of amount of Nano-TiO$_2$ on photodegradation of Congo Red. Volume = 25 mL; initial concentration of CR = 20 mg L^{-1}; irradiation time = 20 min; pH of the medium = 2.

catalyst surface become unavailable for photon absorption, and dye absorption thus bringing little stimulation to the catalytic reaction.

3.1.2. Effect of irradiation time

Shown in Fig. 2 is the effect of irradiation time on CR degradation. Color of the sample changed to colorless with increasing irradiation time. The experiments showed that absorbance value corresponding to 502 nm increases as irradiation time was increased from 5 to 30 min, concluding that degradation was completed nearly within 30 min. It was observed that decolorization and photodegradation increased with increase in the
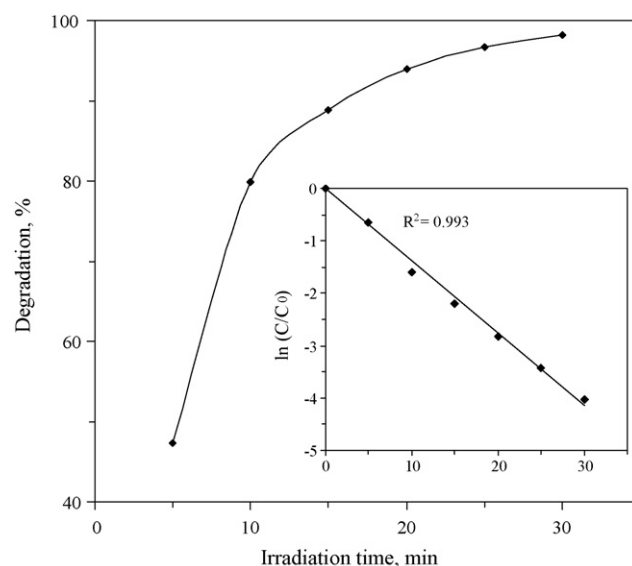

Fig. 2. Effect of irradiation time on photodegradation of CR. Inset presents the degradation kinetics of CR by means of plotting ln(C/C_0) vs. time. Volume = 25 mL; initial concentration of CR = 20 mg L^{-1}; amount of Nano-TiO$_2$ = 0.25% (w/w); pH of the medium = 2.

irradiation time. In order to determine the kinetics of photodegradation, the relationship between $\ln C_0/C_t$ and irradiation time was plotted (as inset in Fig. 2). It was found that the degradation reaction of CR under the catalysis of Nano-TiO$_2$ basically obeys to the first order reaction kinetics. However, Konstantinou and Triantafyllos [3] and Bandara et al. [17] have reported that the reaction rate decreases with irradiation time, since it follows apparent first order kinetics and additionally a competition for degradation may occur between the reactant and the intermediate products. The slow kinetics of dyes degradation after certain time limit is due to: (a) difficulty in converting the N-atoms of dye into oxidized nitrogen compounds, (b) the slow reaction of short chain aliphatics with $^\bullet$OH radicals and (c) the short life time of photocatalyst because of deactivation of active sites by deposition of degradation products.

3.1.3. Effect of initial CR concentration

A series of CR solutions with different concentrations were used to observe the effect of initial dye concentration on degradation. As shown in Fig. 3, 98% of 20 mg L^{-1} CR degradation was maintained. But it decreased gradually with increasing CR concentration. It is generally noted that increase in dye concentration leads to decrease in the degradation rate. The ratio of degradation relates to the probability of $^\bullet$OH radicals formation on the catalyst surface and to the probability of $^\bullet$OH radicals reacting with dye molecules. As initial concentration of the dye increases, the probability of reaction between dye molecules and oxidizing species also increases. On the contrary, the degradation efficiency decreases with further increase in the dye concentration. The reason is that the generation of $^\bullet$OH radicals on the surface of catalyst is reduced at high dye concentrations, since the active sites are covered by dye molecules. Another possible reason is the UV-screening effect of the dye. At high dye concentrations, a significant amount of UV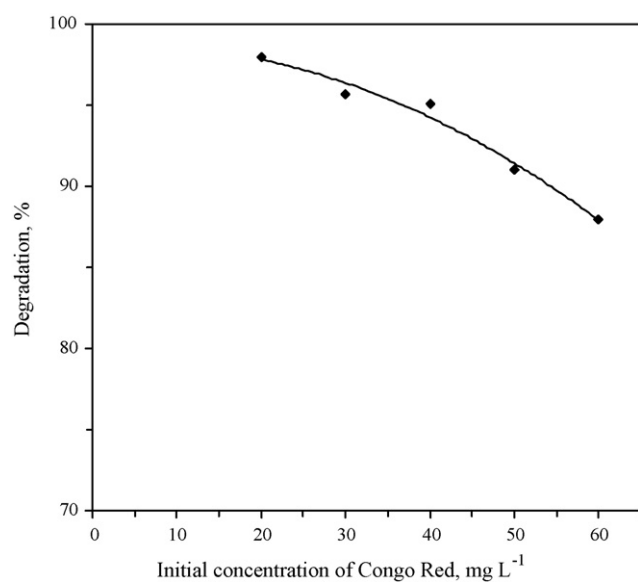 may be absorbed by dye molecules, instead of TiO$_2$ particles. This can reduce the efficiency of catalytic reaction, since concentrations of $^\bullet$OH and O$_2{}^{\bullet-}$ decrease [3,5]. The major portion of degradation occurs in the region near to the irradiated side (termed as reaction zone) where the irradiation intensity is much higher than in the other side. Thus, at higher dye concentrations, degradation decreases at sufficiently long distances from the light source or the reaction zone due to the radiation in the penetration of light. Hence, as Li et al. [11] have stated that as initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases.

3.1.4. Effect of pH

Several tests were performed to observe the effect of pH on photodegradation. Natural pH of 20 mg L^{-1} CR is 5. But pH of the medium decreased by the presence of Nano-TiO$_2$, so that pH of the samples containing 0.25% (w/w) Nano-TiO$_2$ and 20 mg L^{-1} CR was nearly 2. pH of the medium was varied between 2 and 10 by addition of NaOH. It was found that degradation considerably decreases in alkaline pH region (Fig. 4). Additionally, during the experiments, it was realized that at higher pH values, a noticeable gel formation was observed in the sample. This phenomenon caused low CR concentrations which are not due to photodegradation, since CR removed from the medium by filtration as adsorbate on the surface of precipitating Nano-TiO$_2$. Therefore, further experiments were carried out at the original pH of the Nano-TiO$_2$ and CR medium.

The decrease in the degradation after a certain pH value can also be explained by both the surface chemical state of TiO$_2$ and the ionization state of ionizable organic molecules at this pH. It is very well-known that for pH values higher than the point of zero charge (pzc) which is pH 6.5 [18] for TiO$_2$, the surface becomes negatively charged and it is the opposite for pH < pH$_{pzc}$. CR molecule with two sulfonic groups ionizes easily even in strong acidic media and becomes a soluble CR anion. Therefore, in the
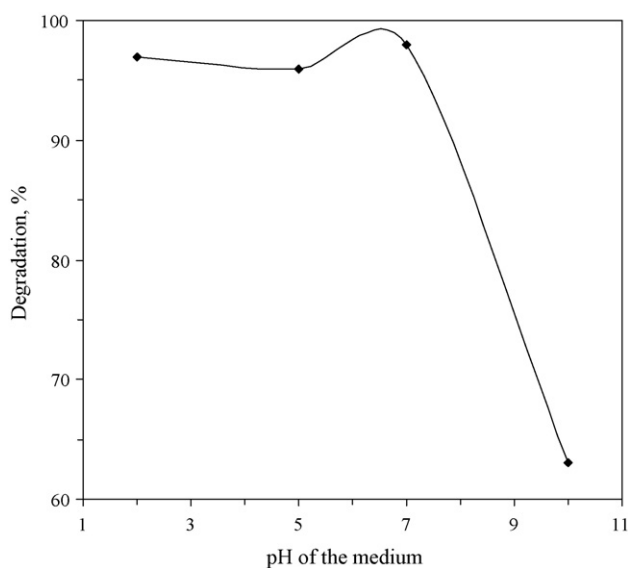

Fig. 3. Effect of initial concentration of CR on photodegradation of CR. Volume = 25 mL; amount of Nano-TiO$_2$ = 0.25% (w/w); irradiation time = 30 min; pH of the medium = 2.

Fig. 4. Effect of medium pH on photodegradation of CR. Volume = 25 mL; amount of Nano-TiO$_2$ = 0.25% (w/w); initial concentration of CR = 20 mg L^{-1}; irradiation time = 30 min.
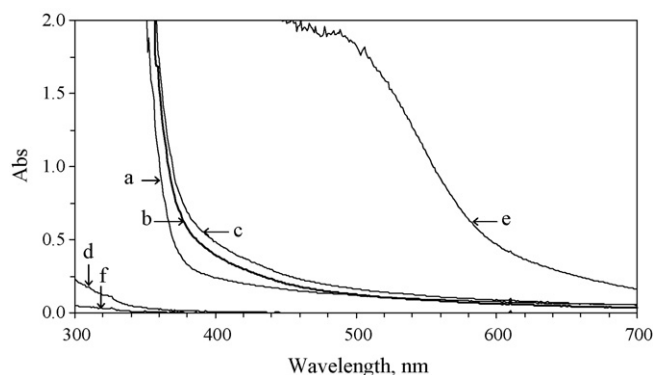
Fig. 5. UV–visible monitoring of various media containing 0.25% (w/w) Nano-TiO$_2$ after irradiation for 30 min. (a) Nano-TiO$_2$ sol, (b) Nano-TiO$_2$ together with 20 mg L^{-1} CR, (c) Nano-TiO$_2$ together with 20 mg L^{-1} CR and 20 mg L^{-1} NO$_3^-$, (d) Nano-TiO$_2$ together with 20 mg L^{-1} CR and 300 mg L^{-1} SO$_4^{2-}$, (e) 160 mg L^{-1} humic acid and 20 mg L^{-1} CR before irradiation and (f) Nano-TiO$_2$ together with 20 mg L^{-1} CR and 160 mg L^{-1} humic acid.

acidic and neutral solutions, CR anions are easily adsorbed to TiO$_2$ particles with positive surface charge. These CR anions can be oxidized directly by oxygen under visible radiation. That is why high degradation ratios were achieved in acidic and neutral pH regions. However, at higher pH values, CR anions are generally excluded away from the negatively charged surface of TiO$_2$ particles, so degradation ratio decreases. The reason for slight increase in degradation ratio in alkaline medium may be occurrence of partial radical oxidation degradation [3,5,16]. Higher degradation rate at acidic pH has also been reported for Vis/TiO$_2$ experiments due to the efficient electron transfer process due to strong surface complex bond formation. This effect is less marked in neutral/basic pH solutions [19].

3.2. Effects of nitrate, sulphate and humic acid

Waste water may contain various pollutants, organic solvents, acidic or basic species, as well as dissolved organic matter and humic substances, when mixed with other waste streams. NO$_3^-$, SO$_4^{2-}$ and humic acid are also present in real waste water produced by textile industry.

20 mg L^{-1} NO$_3^-$, 300 mg L^{-1} SO$_4^{2-}$ and 160 mg L^{-1} humic acid were separately added into the samples and then irradiated under predetermined conditions. It was observed that when SO$_4^{2-}$ and humic acid are added to the sample, a gel forms. Therefore, it was removed from the system before spectrophotometric measurements. Shown in Fig. 5 is the effects of some ions on the degradation of CR. As seen in Table 3 which presents data obtained from Fig. 5, presence of NO$_3^-$,

Table 3
Degradation of 20 mg L^{-1} CR in different media containing Nano-TiO$_2$

Medium	Degradation ratio (%)
CR only	98
CR and 20 mg L^{-1} NO$_3^-$	95
CR and 300 mg L^{-1} SO$_4^{2-}$	99
CR and 160 mg L^{-1} humic acid	99

SO$_4^{2-}$ and humic acid do not affect the degradation rates significantly. Addition of 20 mg L^{-1} NO$_3^-$ changed the degradation ratio from 98 to 95.6%, whereas addition of either 300 mg L^{-1} SO$_4^{2-}$ or 160 mg L^{-1} humic acid caused insignificant shifting in the degradation ratio.

These species may compete for the active sites on the TiO$_2$ surface or deactive the photocatalyst and subsequently decrease the degradation rate. Alternatively, they may act as light screens, thus reducing the photon receiving efficiency. Daneshaver et al. [16] and Epling and Lin [20] studied the effects of anionic species on degradation of dyes. Of the anionic species they have studied (NaCl, HCl, NaNO$_3$, H$_3$PO$_4$ and NaHCO$_3$), HCl exhibited the strongest inhibition effect followed by H$_3$PO$_4$. Inhibition effects of anions can be explained by the reaction of positive holes and hydroxyl radical with anions that behaved as h$^+$ and •OH scavengers, resulting prolonged color removal. Probably the adsorbed anions compete with dye for the photooxidizing species on the surface and preventing the photocatalytic degradation of the dyes. Formation of inorganic radical anions (e.g. Cl$^-$, NO$_3^-$) under these circumstances is possible occur. Although the reactivity of these radicals may be considered they are not as reactive h$^+$ and •OH and thus the observed retardation effect still thought to be the strong adsorption of the anions on the TiO$_2$ surface. The dyes containing sulfur atoms are mineralized into sulphate ions. Release of sulphate ions dye degradation was a little slower than decolorization. Generally it is found that nitrate ions have little effect on the kinetics of reaction whereas sulphate, chloride and phosphate ions especially at concentrations of greater than 10^{-3} mol L^{-1} can reduce the rate by 20–70% due to the competitive adsorption at the photoactivated rate.

Mechanistically and physically, the presence of humic acid in a reaction mixture could significantly reduce light transmittal, and therefore the photooxidation rate. Humic acid might also compete with organic dyes for the active sites on the surface. In the natural environment, humic acids are highly oxidized substances. For humic substances to be completely oxidized a lot of energy is required. Once absorbed onto the TiO$_2$ surface, humic substances might be more resistant to being oxidized than organic dyes and would thus stay longer on the TiO$_2$ surface. In this manner, photobleaching rates of dyes would be significantly reduced [20,21].

3.3. Comparison of Nano-TiO$_2$ with Degussa P-25

Effectiveness of Nano-TiO$_2$ and Degussa P-25 was compared under identical experimental conditions (Fig. 6). Degussa P-25 adsorbs more dye than Nano-TiO$_2$, resulting with a decrease in degradation rate. As the amount of dye adsorbed on the surface of the catalyst increases, thereby the active sites are covered with dye ions, formation of •OH radicals decreases. It is shown in Fig. 6 that degradation does not show a significant variation. Additionally, Nano-TiO$_2$ cannot easily remove from the medium, since it is well dispersed. This seems like a disadvantage, but reuse of the same medium remained after the first photodegradation could be considered. In previous studies investigating repetitive usage of Nano-TiO$_2$, it was revealed that it shows
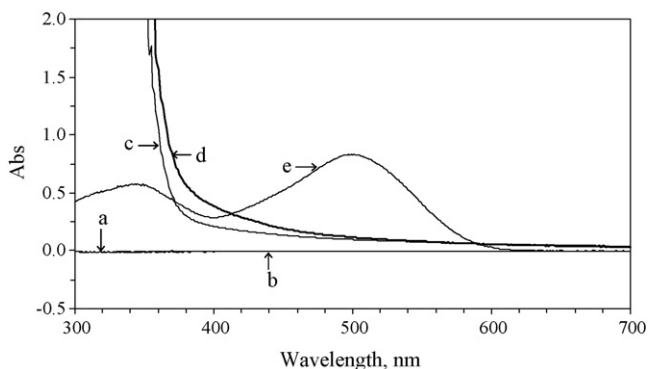
Fig. 6. Comparison of UV–visible spectrum of Degussa P-25 and Nano-TiO$_2$ for photodegradation of CR after irradiation. Volume = 25 mL; concentration of CR = 20 mg L^{-1}; amount of each Degussa P-25 and Nano-TiO$_2$ = 0.25% (w/w); irradiation time = 30 min. (a) Degussa P-25, (b) Degussa P-25 together with CR, (c) Nano-TiO$_2$, (d) Nano-TiO$_2$ together with CR and (e) CR before irradiation.

higher photocatalytic activity than Degussa P-25, even after the fourth use for degradation of Rhodamine B and Methylene Blue [13,15].

3.4. Degradation products

Degradation products formed at the end of irradiation process were analyzed by LC–MS and identified by interpretation of their mass spectra data presenting their molecule ion peaks with respect to m/z (where m is molecular weight of the intermediates in the mass spectra). Main species detected in the solutions are presented in Fig. 7 including LC–MS spectra for the aqueous solution of 20 mg L^{-1} CR (Fig. 7a), for CR (20 mg L^{-1})/TiO$_2$ (0.25%, w/w) sol which was only soaked for 30 min (Fig. 7b), and for the latter after soaking for 30 min and then irradiation for 30 min (Fig. 7c). However, the certified references are not available for the degradation products occurred in the spectra, the species given in Scheme 2 was considered as possible degradation products of CR during irradiation.

The spectrum of CR in Fig. 7a is different from that of CR in the irradiated sample containing Nano-TiO$_2$ shown in Fig. 7b. The difference can be explained by decomposition of the species
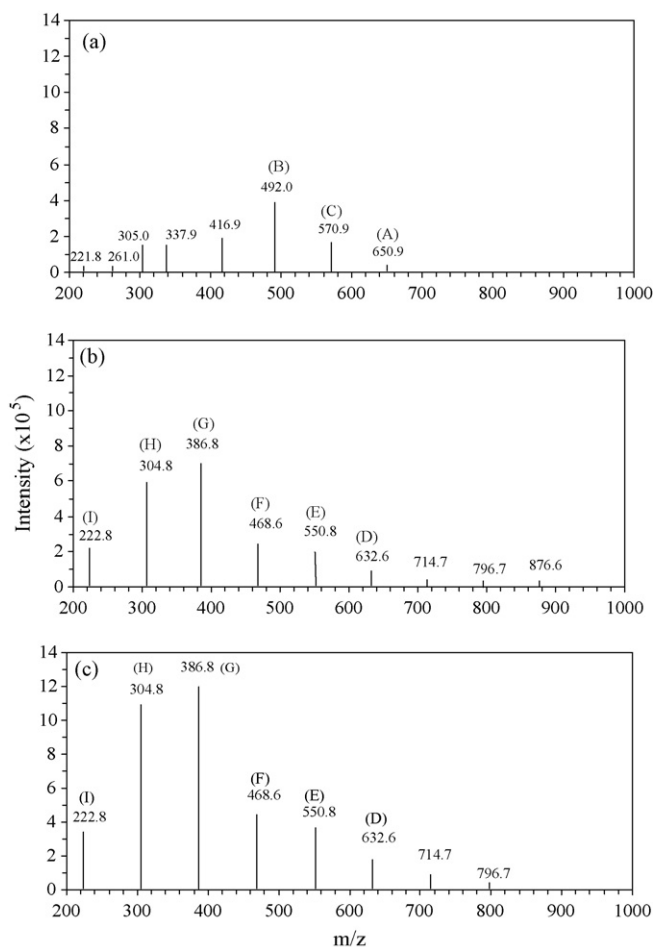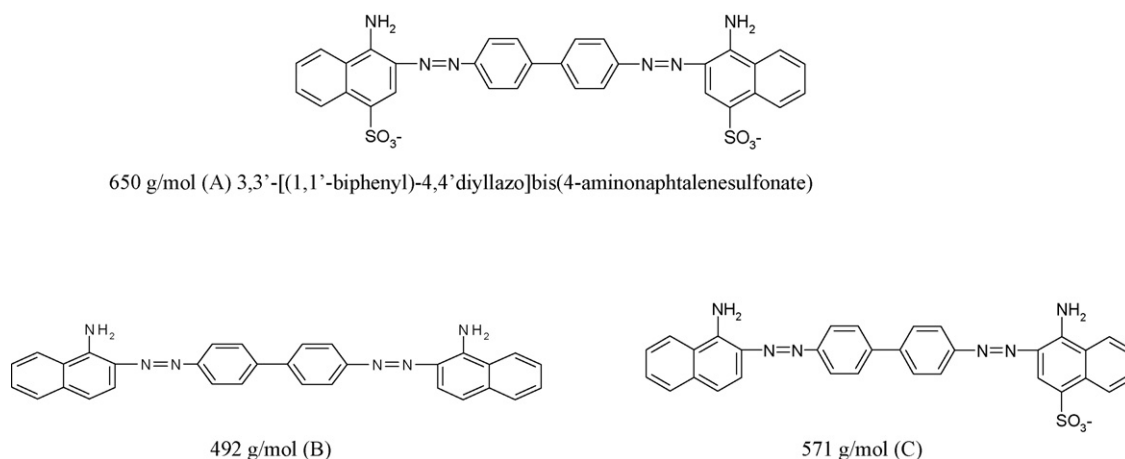

Fig. 7. Spectra of CR before irradiation (a), CR and Nano-TiO$_2$ before irradiation (b) and CR and Nano-TiO$_2$ after irradiation (c), according to LC–MS. Amount of Nano-TiO$_2$ = 0.25% (w/w); irradiation time = 30 min; CR = 20 mg L^{-1}; pH 2.

at different m/z ratios in the ion trap and atmospheric pressure chemical ionization source of the instrument, i.e., presence of Nano-TiO$_2$ changes the decomposition of CR. The peaks in the spectrum of CR observed at 416.9, 492.0 and 570.9 m/z ratios (Fig. 7a) are not observed in the spectrum of CR/Nano-TiO$_2$ sol

650 g/mol (A) 3,3'-[(1,1'-biphenyl)-4,4'diyllazo]bis(4-aminonaphtalenesulfonate)

492 g/mol (B)

571 g/mol (C)

Scheme 1. Species for CR in water before irradiation, determined according to LC–MS spectrum. Letter in parenthesis is the possible species cited in Fig. 7a.
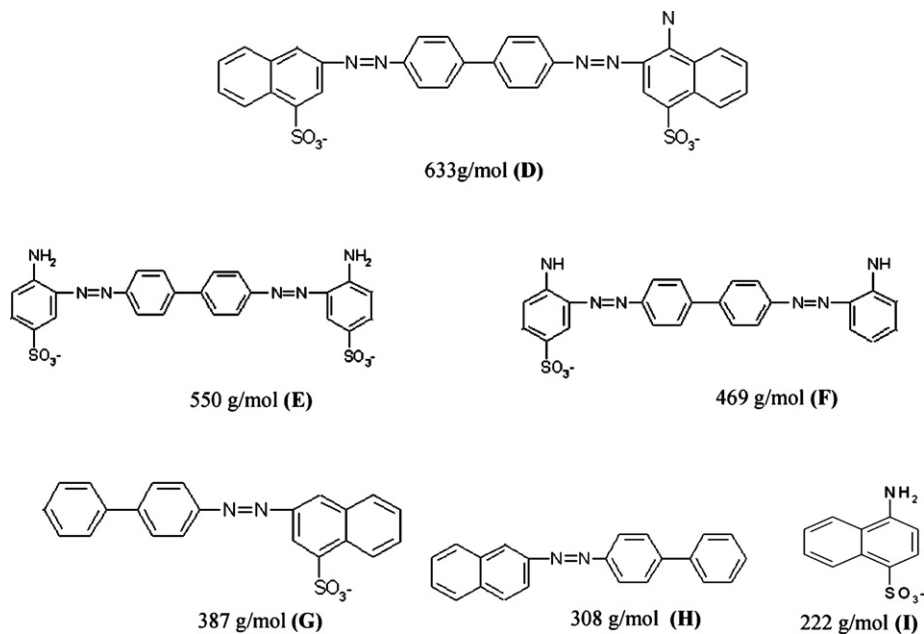
Scheme 2. Possible degradation products of CR after irradiation, as determined by LC–MS spectrum given in Fig. 7c. Letter in parenthesis is the possible species cited in Fig. 7c.

(Fig. 7b). Therefore, the data obtained from Fig. 7b and c is found more useful for identification of the degradation products formed after the irradiation process. Degradation of CR may occur via the following steps, (i) cleavage of benzene ring (specifically, benzene rings on the sides decompose), (ii) cleavage of C-S bond between the aromatic ring and the sulfonate groups by OH$^\bullet$ radicals attack, (iii) cleavage of various C–N and C–C bonds of the chromophore group and (iv)–N=N– double bond cleavage. According to the results, degradation pathway for CR was suggested as given in Scheme 2. Shown in Scheme 1 are the species detected for the aqueous CR solution, occurred after LC–MS ionization source of the instrument. Shown in Scheme 2 are possible species formed after irradiation of the CR/Nano-TiO$_2$ solution. When data in Fig. 7b and c are compared, the intermediates with the same m/z ratios are observed together with higher peak intensities in Fig. 7c, suggesting that CR degradates to the species in Scheme 2, together with remarkable decolorization and insignificant mineralization to give CO$_2$ and H$_2$O during the irradiation.

4. Conclusions

Photodegradation of Congo Red in aqueous solutions with the catalysis of hydrothermally synthesized anatase TiO$_2$ with nanocrystalline size (8 nm) was studied. The effects of amount of Nano-TiO$_2$, irradiation time, initial CR concentration and pH on the degradation of CR were examined. It was observed that 0.25 wt% Nano-TiO$_2$ can easily degrade 20 mg L^{-1} CR dye after visible irradiation for 30 min. The degradation reaction of CR basically followed the first order reaction kinetics. Effects of sulphate and nitrate ions, and humic acid on the degradation was examined and it was found that nitrate is not more effective, even slightly decreases the degradation ratio, whereas sulphate and

humic acid have no significant effect. Comparison of the relevant results with Degussa P-25 TiO$_2$ showed that degradation does not show a significant variation. Moreover, than that Degussa P-25 needs filtration after being used for further purposes, whereas Nano-TiO$_2$ can be repetitively used for supplementary degradation stages. CR degradates to the other aromatic species together with complete decolorisation, whereas mineralization to carbon dioxide and water is not significant within the irradiation periods employed in this study.

Acknowledgements

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