Exceptional catalytic efficiency in mineralization of the reactive textile azo dye (RB5) by a combination of ultrasound and core–shell nanoparticles (CdS/TiO$_2$)

Narjes Ghows, Mohammad H. Entezari*

Department of Chemistry, Ferdowsi University of Mashhad, 91775, Mashhad, Iran

ARTICLE INFO

ABSTRACT

A novel composite with a core–shell structure (CdS/TiO$_2$) was prepared through the combination of microemulsion and ultrasound (20 kHz). The degradation of reactive black 5 (RB5) was carried out in aqueous solution in a series of experiments by CdS/TiO$_2$ nanoparticles. This composite with mole ratio of 1/6 has shown an exceptional sonocatalytic activity in comparison to the pure nanoparticles of TiO$_2$ and CdS. A significant decrease in the concentration of RB5 ($\approx$94%) was observed in 3 min sonication of the solution containing the core–shell nanocomposite. While at the same time, the concentration was reduced to 4% under sonication without nanocomposite and 50% under UV light with nanocomposite. The increased catalytic activity of nanocomposite in the presence of ultrasound is due to the enhancement of mass transfer, cleaning and sweeping the surface of catalyst, and preventing the aggregation of particles. In addition, the presence of CdS nanoparticles in the composite acts as photosensitizer which not only extends the spectral response to the visible region but also reduces the charge recombination. The selected combined method (sonocatalysis) was able to decolorize and oxidize simultaneously the organic dye with a complete mineralization into SO$_4{}^{2-}$ and NO$_3{}^-$ ions.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide as a heterogeneous photocatalyst has received extensive attention for the degradation and mineralization of organic pollutants from water in recent 10 years [1–4]. One of the major disadvantage of TiO$_2$ as a photocatalyst is due to its relatively large band gap (E_g = 3.2 eV for anatase phase) that can only be excited by UV radiation with wavelength less than 380 nm. This strongly causes a limited use of the solar spectra as a source for the photoreaction. Another major limiting factor is the high rate of recombination of the photogenerated electron/hole pairs. Due to these limitations, a coupling of a large band gap semiconductor with a smaller one which contains suitable potential energies for activating in the visible range [5] is of great interest for the degradation of organic pollutants by the solar radiation.

In particular, CdS with ideal band gap energy (2.4 eV) is very unstable against photocorrosion in aqueous solutions. Hence, it has been combined with other materials such as ZnO, and TiO$_2$ [6–8]. These composite materials improve the photo-efficiency, photostability, and maximize the interfacial areas between the two compounds [5,9,10] to enhance their catalytic properties. In addition to the flat band potential of the components,

the photocatalytic performance of the coupled semiconductors is also related to the crystallinity of the particles, the particle size, and the geometry [9,11,12]. These parameters strongly depend on the manner that the couples are prepared. A few examples concerning the combination of CdS and TiO$_2$ have been reported for the photoelectrochemistry [13], water splitting [14], and degradation of pollutants [9,11]. But, it requires a post-thermal treatment for obtaining a coupled nanocomposite and a long time for their photocatalytic performance. Furthermore, the UV light is screened by catalyst particles itself and therefore the region exhibiting the catalytic power is spatially limited in the reactor [15]. Hence, it seems that these limitations can be eliminated by ultrasonic irradiation as an energy source. This is attributed to the synergetic effect of ultrasonic/nanocomposite. Since, the presence of solid particles in a liquid increases the nucleation sites for cavity formation, resulting in the generation of more free radicals [15,16]. In fact, the particle size and its amount could affect the production of OH radical [3,17–22]. However, the large particles which are close to the ultrasonic transducer can block the energy input into the solution [3]. In addition, acoustic cavitation produced by ultrasonic waves profoundly increases the surface area and mass transfer between the two phases. Both of them enhance the diffusion at the interface mixing better than the conventional agitation [2,23]. Moreover, it seems that ultrasound under the mild conditions can improve the contact of the two components in the nanocomposite, crystallinity, and the uniform deposition of the nanosized inorganic particles

* Corresponding author. Tel.:+98 511 8797022x306; fax: +98 511 8795457.
E-mail address: moh_entezari@yahoo.com (M.H. Entezari).

onto another surface or template with the removal of surface contamination [24–28]. Our recent works confirmed that the synthesis of crystalline nanomaterials without any post-thermal treatment is easier with ultrasound than the other methods [29–31]. Ultrasound is able to cause a thin and homogeneous coating [32]. This is due to the high temperatures produced during the cavitation which facilitates the crystallization of the semiconductors [30,33–35].

In this study, CdS/TiO$_2$ couples have been prepared by a combination of ultrasound and microemulsion in order to: (i) exploit the maximum optical absorption in the visible range, (ii) increase the surface contact between CdS and TiO$_2$ nanoparticles, (iii) facilitate the crystallization of the semiconductors. As a result, the prepared composite has high sonocatalytic efficiency for the degradation of the selected dye. This is attributed to the synergetic effect of ultrasound and CdS/TiO$_2$, where the former annihilates any mass-transfer limitations with unblocking catalyst active sites and the latter provides increased nucleation sites for the cavity formation. The sono-catalytic efficiency of the CdS/TiO$_2$ coupling is highly dependent on the proportion ratio of the components. They exhibited a faster degradation rate of reactive black 5 than the individual components. In addition, easier workup, higher degradation efficiency, shorter reaction time, better control in preparation of core–shell with uniform shape can be considered as advantageous of this study.

2. Experimental

2.1. Materials

Ethylenediamine, sulfur, p-xylen, titanium tetra-isopropoxide (TTIP), CTAB (cetyl trimethyl ammonium bromide) and 1-butanol from Merck, CdCl$_2$·2H$_2$O from Fluka, and RB5 from Germany (Dystar Company) have been used without further purification. De-ionized water was used for the sample preparation.

2.2. Procedure

2.2.1. Synthesis of core–shell nanocomposite
The synthesis of core–shell nanocomposite and the structure and morphology of the final products has been reported in our recent work [32].

2.2.2. Sonication of dye solution with core–shell nanocomposite
A total of 50 mL of RB5 solution (100 mg/L) containing nanocomposite (0.05 g) as a catalyst was sonicated (20 kHz Sonifier W-450, output acoustic power 41 W, horn with 1.9 cm diameter) for 10 min in a Rosset cell at initial pH of 6.5. The temperature was controlled by the circulating bath at 38 °C. Then the sample was centrifuged at 8000 rpm for 3 min to separate the suspended catalyst particles from aqueous solution. Some other experiments were carried out with the same conditions under UV lamp (30 W, λ = 360 nm, distance from liquid surface = 20 cm) and some under sunlight with clear sky in August 1990 (GPS coordinates: N = 36°18′41.6″, E = 59°31′54.2″).

2.3. Sample analysis

The absorbance of the sample was measured by spectrophotometer (model Unico 2800) at 599 nm which corresponds to the maximum absorbance of RB5. The absorption was converted to concentration through the standard curve of reactive black 5.

The total organic carbon (TOC) of the samples was determined by a TOC-V CPH (model Shimadzu) analyzer after separation of solid phase by centrifuge.
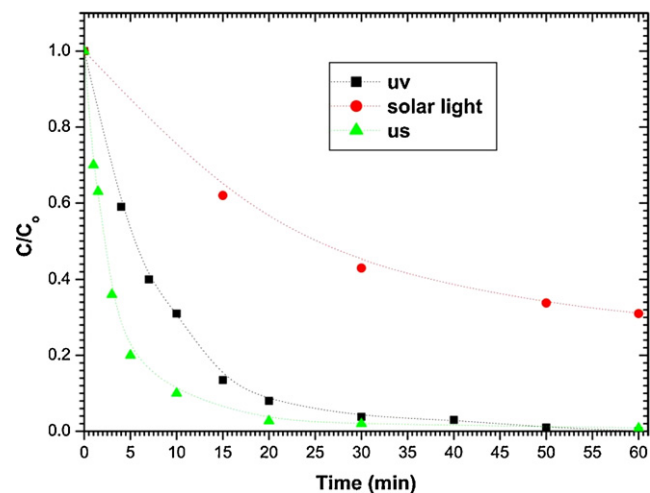

Fig. 1. Effect of irradiation source on the dye removal (50 mL solution 200 ppm, temperature 38 °C, power of ultrasound 66%, stirring 600 rpm).

The formation of inorganic ions was detected with IC 761 ion-chromatograph (model Metrohm).

3. Results and discussion

3.1. Irradiation source

Fig. 1 compares the rate of dye removal from aqueous solution with different combinations. The combination of ultrasound and nanocomposite (sonocatalyst) shows the highest activity with respect to the combination of nanocomposite with UV light and nanocomposite with sunlight. This is attributed to the synergetic effect of ultrasound and semiconductor. The solid particles increase the nucleation sites for cavity formation, resulting in the generation of more free radicals [16]. Moreover, ultrasonic shockwave prevents blocking of catalyst active site (in contrast to UV light, that the light is screened by catalyst particles itself), increases the availability of the effective sites, and reduces any mass-transfer limitations.

3.2. Adsorption isotherm

Adsorption isotherm of RB5 on nanocomposite surface was determined by mixing 50 mL aqueous solution of dye at various initial concentrations at pH 6.5 for 30 min in a dark place. Data obtained from the adsorption experiments was fitted to the Langmuir equation (Supporting Fig. S1):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}$$

where C_e is the equilibrium concentration of RB5 after 30 min, q_e is the adsorbed dye concentration on the catalyst surface, and b and Q_m are Langmuir adsorption constants which were calculated as 64 mg g^{-1} and 0.50 L mg^{-1}, respectively.

3.3. Effect of pH

The pH has a great effect on the sonocatalytic degradation of dye (Fig. 2). The surface charge of TiO$_2$ particles and the adsorption of dye on the surface vary by changing the pH. The interpretation of pH effects on the efficiency of dye removal is a very difficult task. This is due to the multiple roles of pH on the ionization state of the surface, hydroxyl radical formation, agglomeration of
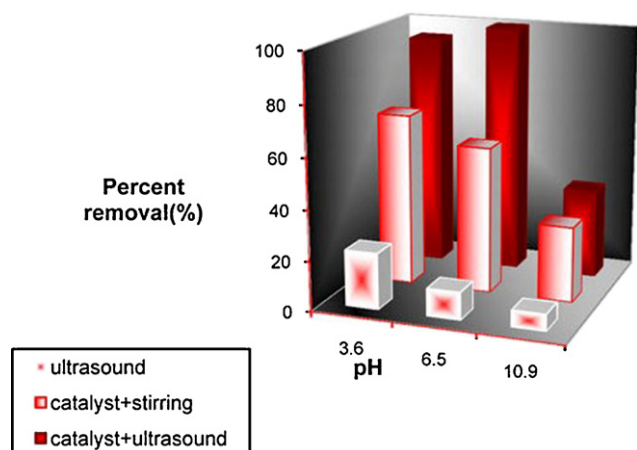
Fig. 2. The effect of pH on the removal of pollutant (50 mL solution 100 ppm, 0.05 g catalyst, temperature 38 °C, time 10 min, stirring 600 rpm).

Fig. 3. The effect of concentration on the removal of pollutant in the presence of ultrasound (50–400 ppm solution, 0.05 gr catalyst, temperature 38 °C, power of ultrasound 66%, time 10 min).

particles, and the specification of dye and products [36]. The pH can affect the adsorption and agglomeration which are important factors on sonocatalytic degradation of RB5. The literature indicated that pH_{zpc} of TiO_2 for anatase is 6.8 [37,38]. Therefore, when the solution pH is less or more than pH_{zpc}, the surface hydroxyl groups of TiO_2 would undergo a proton association or dissociation reaction and lead to a positive or negative charge on TiO_2 surface. Repulsion between charged surfaces prevents the agglomeration of the catalyst particles in the medium.

The acidic solution favors adsorption of the dye molecules onto TiO_2 surface due to the change in the specification of the dye. The pK_a values for the dye are almost close to 3.8 and 6.9 [39]. Then, the dye molecules are in the molecular form in acidic medium. But, the sulfonate group cannot be protonated under the applied pH and it can be existed in the anionic form. Therefore, there is an attraction between the surface of the nanocomposite and the dye molecule through the sulfonate group at acidic pH. This results to the adsorption of dye molecules onto the surface and consequently its degradation with hydroxyl radicals produced by catalyst [2]. But, a small decrease of degradation was observed in acidic medium in comparison to the neutral conditions in sonocatalytic degradation. This should be due to the adding of inorganic acid (HCl) to the solution which led to an increase amount of Cl^- in the solution. The Cl^- ions can react with hydroxyl radicals and produce inorganic radical anions with lower activity than hydroxyl radical in the degradation of dye [40].

In alkaline medium, the dye molecules are mostly in their anionic forms. In this situation, the columbic repulsion is appeared between the negative charged surface of the catalyst at high pH and the negative charge of anionic groups. Therefore, the removal was lower in basic pH medium (pH 10.9).

The results clearly demonstrate that the combination of catalyst and sonication in near neutral pH causes an additive effect on the degradation rates of the pollutant which is due to the more efficient generation of hydroxyl radicals by nanocomposite.

The rate of degradation was very slow by sonication alone. Since, RB5 is a non-volatile compound and the place of degradation would be mostly at the exterior of the cavitation bubbles [41–43]. A little increase of degradation rate in acidic conditions might be due to the more hydrophobic character of the resulting dye molecule with respect to the basic conditions which the dye molecule has more hydrophilic character. As the hydrophobic character of the molecule increases, the chance of presence of the molecule near the cavitation is higher and this leads to more degradation [44].
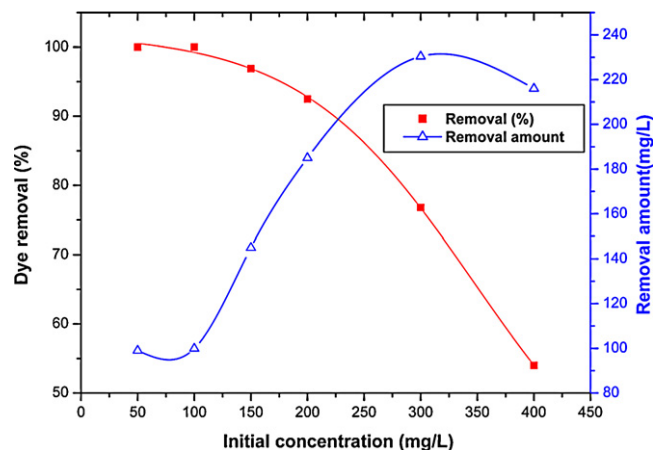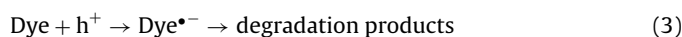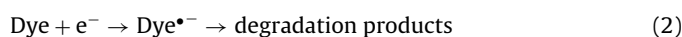
3.4. Effect of initial concentration

Fig. 3 shows the influence of initial concentration of RB5 in the range of 50–400 mg/L on its sonocatalytic degradation using the synthesized nanocomposite (TiO_2/CdS) as a catalyst. The amount of dye removal increased by increasing the dye concentration and then decreased. But, the percent removal of RB5 decreased with increasing the initial concentration. For instance at the concentration of 100 mg/L, a complete removal (100%) was achieved after about 10 min while at the concentration of 300 mg/L, it decreased to 76.8% after 10 min. As the amount of composite is fixed, the number of adsorption sites is constant. By increasing the dye concentration, the chance of trapping the dye molecule at higher concentrations is less than lower concentrations. At higher concentrations, most of the composite sites are occupied and the chance of finding sites for the adsorption is low. This is the reason for the lower removal percentage at higher concentrations. In addition, for the highest removal under sonication there is an optimum concentration for the pollutant in the mixture. The concentration below and above the optimum concentration can cause a lower effect of cavitation.

The dye degradation happens in different ways. Some dye molecules degrade by hydroxyl radical through oxidation (Eq. (1)) [4]. In addition, several authors have proposed the dye removal occurs through direct electron (e^-) transfer from the semiconductor surface to the dye molecule [36,45,46], as shown by Eq. (2). Direct oxidation by reaction with holes (h^+) has also been reported [36,47], as shown by Eq. (3). Thus, with increasing the dye concentration, it is not possible to degrade 100% of the pollutant as the available species responsible for degradation is approximately constant under the applied conditions.

$$Dye + OH^\bullet \rightarrow Dye^{\bullet-} + H_2O \rightarrow \text{degradation products} \tag{1}$$

$$Dye + e^- \rightarrow Dye^{\bullet-} \rightarrow \text{degradation products} \tag{2}$$

$$Dye + h^+ \rightarrow Dye^{\bullet-} \rightarrow \text{degradation products} \tag{3}$$

3.5. Effect of sonication time

The removal of RB5 from aqueous solution was shown by three different methods: sonication of solution with nanocomposite (Fig. 4a), sonication alone (Fig. 4b), and comparison of the mentioned methods with mixing of solution by nanocomposite under UV (Fig. 4c). It was found that, all absorption peaks decayed more or less with respect to the original dye solution spectrum. The largest reduction (more than 95%) was achieved in the
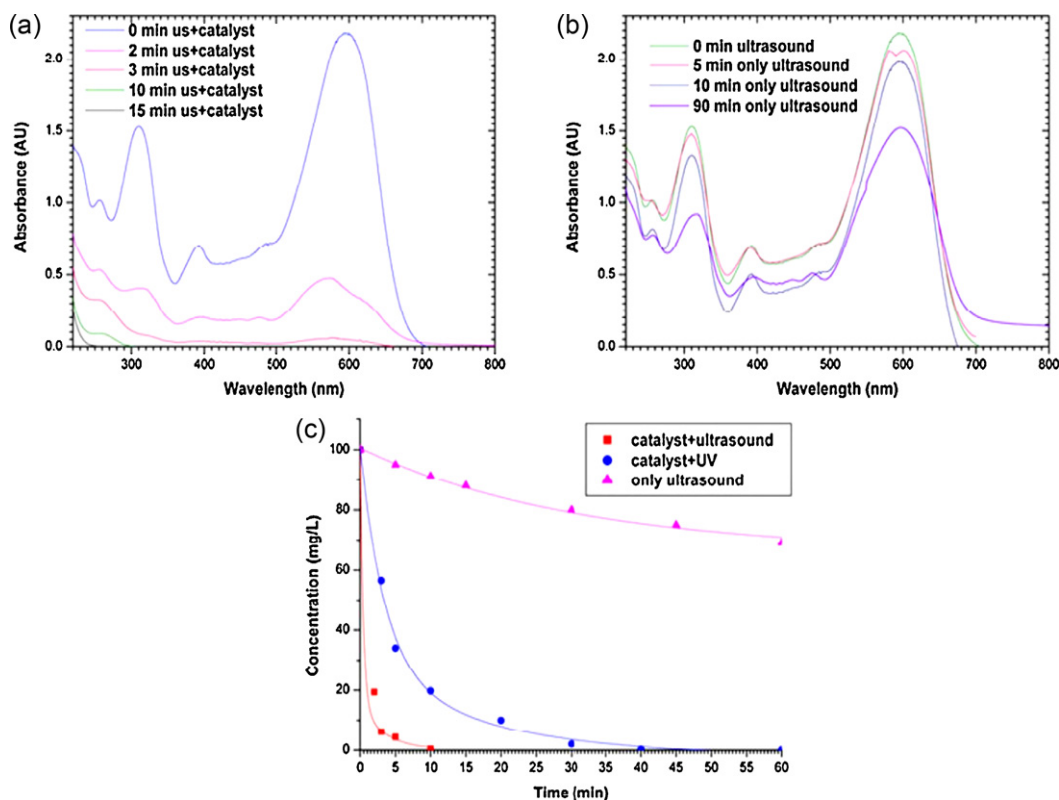
Fig. 4. The effect of contact time on the removal of dye. (a) Catalyst with ultrasound (sonocatalyst), (b) sonication alone, (c) the change of concentration with time (50 mL solution 100 ppm, 0.05 g catalyst, temperature 38 °C, intensity of ultrasound 66%).

presence of nanocomposite powder with ultrasound (sonocatalyst) in less than 3 min. These results indicate that the removal of RB5 by nanocomposite CdS/TiO$_2$ combined with ultrasonic irradiation was more effective than those by UV method and sonication alone.

Ultrasonic irradiation of semiconductor nanocomposite as well as light in the environment may promote •OH formation or superoxide radicals (•O$_2$) on the surfaces of the catalyst. Formation of these reactive oxygen species initiates a series of chemical reactions that promotes the power of oxidation. The reactive species might be formed by the absorption of light from the environment by the nanocomposite and hot energies from ultrasonic cavitation which leads to the excitement of semiconductor and production of electron and hole. Finally, the reactive species can be formed by the redox reactions of electron and hole with adsorbed species on the surface of nanocomposite. In addition, the pyrolysis of H$_2$O molecules and direct formation of hydroxyl radical through the cavitation is another source of production. They are capable of undergoing further reaction with solutes adsorbed at the bubble–solution interface [41,42,48] or with solutes in bulk solution [49]. Moreover, ultrasonic shockwave prevents blocking of catalyst active site. But, the efficiency of ultraviolet light was lower which is due to the UV-screening of the catalysts.

Sonication alone can degrade the dye molecule by the radicals produced through the cavitation. It is assumed that a local high concentration of hydroxyl radicals exist at the interface region of the collapsing bubbles [42,50] and some of them escape to the bulk of solution [44]. RB5 is a non-volatile compound and the region of degradation would be at the exterior of the cavitation bubbles.

3.6. IR spectrum

The IR study was done for understanding the adsorbed species on the catalyst and also their degradation through appearance and disappearance of different peaks. Supporting Fig. S2 shows the IR spectrum of the samples. For sonocatalytic reactions, the adsorbed species are significant. They will react with sonoexcited products on the catalyst surface and produce reactive radicals which are powerful oxidants in degrading organics in water. The band at 1625 cm^{-1} corresponds to the bending mode of adsorbed water. The intense band at 1504–1514 cm^{-1} has been attributed to the –N=N– bond vibrations or to the aromatic ring vibrations sensitive to the interaction with the azo bond [46]. The bands at 1599, 1572, and 1452 cm^{-1} are linked to C=C aromatic skeletal vibrations [51]. Finally, the peaks at 1122, 1226, 1130, and 1047 cm^{-1} are respectively assigned to the stretching of the SO$_4$ group and sulfoxide [52]. A slight shift of the bands toward lower wave numbers and a major decrease of the band intensities are observed. The most important shift is observed for the band associated with the chromophore part of the dye, which is shifted from 1514 to 1504 cm^{-1}. While the bands of associated to the sulfonate group are almost disappeared. The changes observed show that degradation of the adsorbed species is taking place. This is particularly true for the band at 1504 cm^{-1}, which reflects the destruction of the chromophore part of the azo dye.

3.7. Effect of catalyst composition

The rate of dye removal was examined by different catalysts from pure components to different composites. Fig. 5 shows the rate of dye removal by TiO$_2$, CdS and CdS/TiO$_2$ with two different ratios (1/2.5, 1/6.0). The degradation rate of RB5 in the presence of CdS/TiO$_2$ with ratio equal to 1/6 shows a significant difference with respect to the other samples. The high activity of the composite photocatalyst is due to the fast charge separation and transportation throughout the particles [5,9,53] as well as the contact between TiO$_2$ and solution which is sufficient for the creation of active
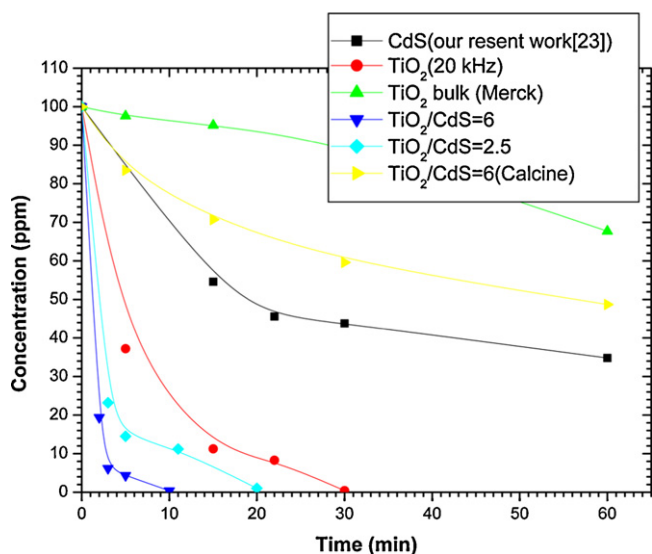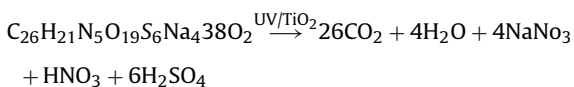
Fig. 5. Comparison of different catalysts for the dye removal in the presence of ultrasound (50 mL solution 100 ppm, 0.05 gr catalyst, temperature 38 °C, power of ultrasound 66%).

radicals [11]. The possible role of TiO_2 nanoparticles is to provide sites for collecting the electrons generated from CdS, enabling thereby an efficient electron–hole separation as depicted. The charge separated state can be followed by the emission decay of the sample. In nanocomposite a decrease in the intensity of the luminescence emission was observed for CdS. This means the significant quenching in emission measurements can be attributed to the electron transfer between excited CdS and TiO_2. This quenching behavior represents the deactivation of the excited CdS via electron transfer to TiO_2 particles [53]. The sonocatalytic performance of coupled semiconductors is related to the charge separation, the surface contact between nanoparticles, the crystallinity, and sizes in the coupled particles.

3.8. Mineralization of the dye

A complete photocatalytic mineralization reaction of reactive black 5 has been suggested as follows [54,55]:

$$C_{26}H_{21}N_5O_{19}S_6Na_4 38O_2 \xrightarrow{UV/TiO_2} 26CO_2 + 4H_2O + 4NaNo_3$$

$$+ HNO_3 + 6H_2SO_4$$

The formation of CO_2, NO_3^-, and SO_4^{2-} has been extensively studied by Poulios and Tsachpinis [55]. They reported that after the decolorization, the intermediates were present in the medium.

The sonocatalytic mineralization of RB5 was followed by measuring the TOC during the process. Fig. 6 shows the TOC and its variation with time during the sonocatalytic degradation. The TOC was abated to about 50% of the initial value in less than 10 min of irradiation, and then decreased slowly. This is might be due to a detrimental effect of the adsorbed SO_4^{2-} ions on the catalyst surface [56]. It is another fact that the intermediates such as carboxylic acids are difficult to oxidize than their parent compound (azo dye in this case). Therefore, a complete oxidation may proceed with slower rate [36]. But, the degree of mineralization in UV method was very low. The results obtained from the absorbance and TOC measurements indicate that the decay of the chromophore in the dye molecule is a relatively fast process (disappearance of chromophore peak in the visible spectra) but overall degradation requires more time. Some intermediates are in the form of organic
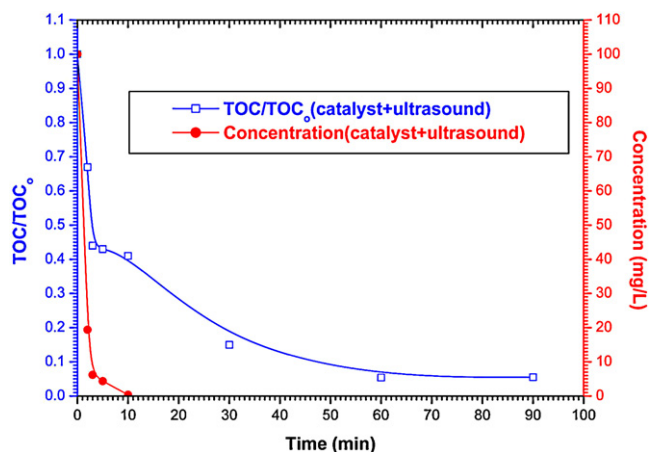

Fig. 6. Concentration and TOC of the RB5 solution versus time.

acids which could be the reason for the decrease of pH from neutral to slightly acidic (from 6.5 to 5) [57].

Evolution of sulfate ions in the solution confirmed the results of TOC. The concentration of this ion was 16 mg/L and 19 mg/L in the solution after 10 min and 60 min sonication, respectively. Sulfate ions are primary products from the initial attack on the sulfonyl group of dye by a direct reaction with positive holes or hydroxyl radicals. Between both oxidative agents ($OH^\bullet$ and h^+), it is suggested that the reaction with holes could be preferential since the adsorbed molecule is in contact with the surface of titania via one of its sulfonate groups [58]. Surprisingly, Only 40% of the sulfate was present in the solution (less than the expected stoichiometric quantity). This behavior could be described as a partially irreversible adsorption of SO_4^{2-} ions. The strong adsorption of SO_4^{2-} could partially inhibit the reaction rate which, however, remains acceptable [56,59]. The concentration of nitrate ions was 17 mg/L and 19 mg/L in the solution after 10 min and 60 min sonication, respectively. On the other hand, substantial increase in the conductivity from 101 μS/cm to 121 μS/cm suggests the formation of ions such as nitrate or sulfate.

3.9. Proposed mechanism of sonocatalytic degradation

A few mechanism and satisfying explanation can be found about the sonocatalytic degradation of organic pollutants in the presence of various semiconductor materials [2,4,9,26]. It is obvious that further studies are necessary to determine the mechanism in greater details.

Kamat and Patrick [60] have demonstrated the simultaneous migration of both electrons and holes in coupled semiconductor photocatalysts. An increase in the lifetime of the photo-generated pairs due to the hole and electron transfers between the two semiconductors in nanocomposite, was invoked in many cases as the key factor for the improvement of the photoactivity.

In this work a novel composite of core–shell CdS/TiO_2 with a high sonocatalytic activity and appropriate adsorbability were obtained through the combination of nano-sized CdS and TiO_2 particles. The possible process of sonocatalytic degradation and reactions are proposed in Fig. 7 based on the following statements:

(i) Based on the cavitation in our experiments, the ultrasonic irradiation can result in the formation of high temperatures as a spot (hot spot theory). The high temperatures produced by ultrasound brings many holes and electrons which are changed to reactive radicals on the surface of semiconductor catalyst [3,4,9]. Under these conditions, a series of reactions can take place on the surface of nanocomposite. In addition,
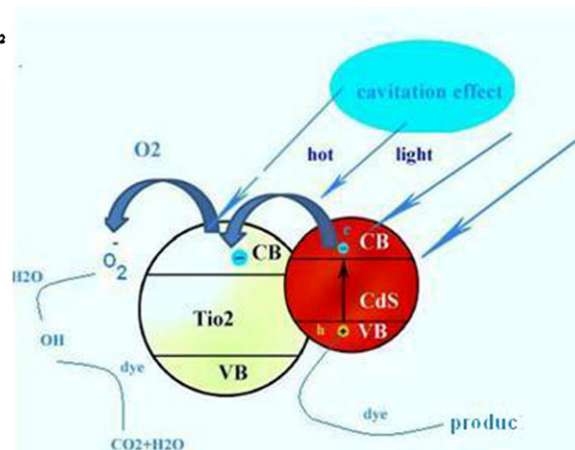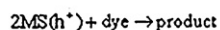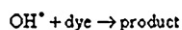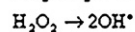
$$MS - TiO_2 + h\nu (> 400nm) \rightarrow MS(h^+ + \bar{e})/TiO_2$$

$$MS(h^+ + \bar{e})/TiO_2 \rightarrow MS(h^+)/Tio_2(\bar{e})$$

$$TiO_2(\bar{e}) + O_2 \rightarrow O_2^-$$

$$O_2^- + H_2O \rightarrow HO_2^\bullet + OH^-$$

$$HO_2^\bullet + H_2O \rightarrow H_2O_2 + OH^\bullet$$

$$H_2O_2 \rightarrow 2OH^\bullet$$

$$OH^\bullet + dye \rightarrow product$$
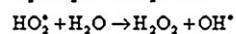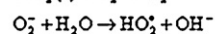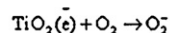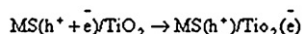
$$2MS(h^+) + dye \rightarrow product$$

Fig. 7. Proposed mechanism for RB5 removal.

the cavitation promotes the electron transfer from CdS to TiO$_2$ through the crystal interphase between TiO$_2$ and CdS, which effectively results in the separation of electron–hole pairs. This separation enhances the sonocatalytic activity.

(ii) Enhancing the mass transfer of organic materials such as dye molecule between the liquid phase and the catalyst surface which is due to the shockwave propagation of the cavitation process.

(iii) Increasing the catalytic activity by de-aggregation of the catalyst particles which tend to aggregate due to its high potential surface energy.

(iv) Cleaning and sweeping the catalyst surface due to acoustic micro-streaming which allows more active catalyst sites to be available.

The contribution of the mentioned effects is difficult to be differentiated and the overall net effect is an enhancement in the rate of dye degradation.

4. Conclusion

In this study, the sonocatalytic activities of nano-sized TiO$_2$, nano-sized CdS and its composite CdS/TiO$_2$ with two different ratios were compared by the degradation of RB5. The experimental results showed that the prepared nanocomposite of TiO$_2$/CdS exhibited a high sonocatalytic activity in comparison with pure nano-sized TiO$_2$ and CdS. The presence of catalyst enhanced the rate of RB5 removal. The extent of removal depends on the operating conditions employed such as the type and concentration of catalyst, initial dye concentration and solution pH. The removal of dye increases with the increase of ultrasonic irradiation time, while the removal percentage was decreased with the increase of initial concentration. A significant decrease in the concentration of RB5 was observed at initial times of sonication in sonocatalytic method for the higher mole ratio of the nanocomposite. In addition to the decolorization, sonocatalytic method was able to mineralize the organic compound into SO$_4^{2-}$ and NO$_3^-$ ions completely. The increased catalytic activity was due to the improvement of charge separation by the nanocomposite and de-aggregation of the nanocatalyst by ultrasound which allows more active sites to be available for the reaction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.08.049.

References

[1] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO$_2$ for hydrogen production, Renew. Sust. Energy Rev. 11 (2007) 401–425.

[2] D.E. Kritikos, N.P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Photocatalytic degradation of reactive black 5 in aqueous solutions: effect of operating conditions and coupling with ultrasound irradiation, Water Res 41 (2007) 2236–2246.

[3] N. Shimizu, C. Ogino, M. Farshbaf Dadjour, T. Murata, Sonocatalytic degradation of methylene blue with TiO$_2$ pellets in water, Ultrason. Sonochem. 14 (2007) 184–190.

[4] J. Wang, W. Sun, Z. Zhang, Z. Xing, R. Xu, R. Li, Y. Li, X. Zhang, Treatment of nano-sized rutile phase TiO$_2$ powder under ultrasonic irradiation in hydrogen peroxide solution and investigation of its sonocatalytic activity, Ultrason. Sonochem. 15 (2008) 301–307.

[5] P.V. Kamat, Quantum dot solar cells. Semiconductor nanocrystals as light harvesters, J. Phys. Chem. C 112 (2008) 18737.

[6] L. Spanhel, H. Weller, A. Henglein, Photochemistry of semiconductor colloids. 22. Electron injection from illuminated CdS into attached TiO$_2$ and ZnO particles, J. Am. Chem. Soc. 109 (1987) 6632–6635.

[7] S.J. Jum, G.K. Hyun, A.J. Upendra, W.J. Ji, S.L. Jae, Fabrication of CdS nanowires decorated with TiO$_2$ nanoparticles for photocatalytic hydrogen production under visible light irradiation, Int. J. Hydrogen Energy 33 (2008) 5975–5980.

[8] J.C. Kim, J. Choi, Y.B. Lee, J.H. Hong, J.I. Lee, J.W. Yang, et al., Enhanced photocatalytic activity in composites of TiO$_2$ nanotubes and CdS nanoparticles, Chem. Commun. 502 (2006) 4–6.

[9] J. Wang, Z. Jiang, L. Zhang, P. Kang, Y. Xie, Y. Lv, R. Xu, X. Zhang, Sonocatalytic degradation of some dyestuffs and comparison of catalytic activities of nano-sized TiO$_2$, nano-sized ZnO and composite TiO$_2$/ZnO powders under ultrasonic irradiation, Ultrason. Sonochem. 16 (2009) 225–231.

[10] P.A. Sant, P.V. Kamat, Inter-particle electron transfer between size-quantized CdS and TiO$_2$ semiconductor nanoclusters, Phys. Chem. Chem. Phys. 4 (2002) 198–203.

[11] Y. Bessekhouad, N. Chaoui, M. Trzpit, N. Ghazzal, D. Robert, J.V. Weber, UV–vis versus visible degradation of Acid Orange II in a coupled CdS/TiO$_2$ semiconductors suspension, J. Photochem. Photobiol. A: Chem. 183 (2006) 218–224.

[12] P.R. Yu, J.M. Nedeljkovic, P.A. Ahrenkiel, R.J. Ellingson, A.J. Nozik, Size dependent femtosecond electron cooling dynamics in CdSe quantum rods, Nano Lett. 4 (2004) 1089–1092.

[13] S. Chen, M. Paulose, C. Ruan, G.K. Mor, O.K. Varghese, D. Kouzoudis, et al., Electrochemically synthesized CdS nanoparticle-modified TiO$_2$ nanotube-array photoelectrodes: preparation, characterization, and application to photoelectrochemical cells, J. Photochem. Photobiol. A: Chem. 177 (2006) 77–184.

[14] J.S. Jang, W. Li, S.H. Oh, J.S. Lee, Fabrication of CdS/TiO$_2$ nano-bulk composite photocatalysts for hydrogen production from aqueous H$_2$S solution under visible light, Chem. Phys. Lett. 425 (2006) 278–282.

[15] M. Kubo, K. Matsuoka, A. Takahashi, N. Shibasaki-Kitakawa, T. Yonemoto, Kinetics of ultrasonic degradation of phenol in the presence of TiO_2 particles, Ultrason. Sonochem. 12 (2005) 263.

[16] C. Sauter, M.A. Emin, H.P. Schuchmann, S. Tavman, Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and de-agglomeration of nanoparticles, Ultrason. Sonochem. 15 (2008) 517–523.

[17] A. Keck, E. Gilbert, R. Köster, Influence of particles on sonochemical reactions in aqueous solutions, Ultrasonics 40 (2002) 661–665.

[18] H.B. Marschall, K.A. Mørch, A.P. Keller, M. Kjeldsen, Cavitation inception by almost spherical solid particles in water, Phys. Fluids 15 (2003) 545–553.

[19] T. Tuziuti, K. Yasui, M. Sivakumar, Y. Iida, Correlation between acoustic cavitation noise and yield enhancement of sonochemical reaction by particle addition, J. Phys. Chem. A 109 (2005) 4869–4872.

[20] E. Cho, B. Park, M. Lim, J. Khim, Sonochemical degradation in presence of particle, Proc. Symp. Ultrason. Electron. 31 (2010) 89–90.

[21] T. Tuziuti, K. Yasui, T. Kozuka, A. Towata, (AIST), influence of particle addition on sonochemiluminescence intensity under pulsed ultrasound, Proc. Symp. Ultrason. Electron. 31 (2010) 355–356.

[22] T. Tuziuti, K. Yasui, T. Kozuka, A. Towata, Influence of liquid-surface vibration on sonochemiluminescence intensity, J. Phys. Chem. A 114 (2010) 7321–7325.

[23] M.H. Entezari, N. Ghows, M. Chamsaz, Combination of ultrasound and discarded tire rubber: removal of Cr(III) from aqueous solution, J. Phys. Chem. A 109 (2005) 4638.

[24] N.A. Dhas, K.S. Suslick, Sonochemical preparation of hollow nanospheres and hollow nanocrystals, J. Am. Chem. Soc. 127 (2005) 2368–2369.

[25] S. Anandan, F. Grieser, M. Ashokkumar, Sonochemical synthesis of Au–Ag core–shell bimetallic nanoparticles, J. Phys. Chem. C 112 (2008) 15102–15105.

[26] W. Ho, J.C. Yu, Sonochemical synthesis and visible light photocatalytic behavior of CdSe and $CdSe/TiO_2$ nanoparticles, J. Mol. Catal. A: Chem. 247 (2006) 268–274.

[27] A. Tiehm, S. Krabnitzer, Y. Koltypin, A. Gedanken, Chloroethene dehalogenation with ultrasonically produced air-stable nano iron, Ultrason. Sonochem. 16 (2009) 617.

[28] A.L. Morel, S.I. Nikitenko, K. Gionnet, A. Wattiaux, J. Lai-Kee-Him, C. Labrugere, B. Chevalier, G. Deleris, C. Petibois, A. Brisson, M. Simonoff, Sonochemical approach to the synthesis of $Fe_3O_4@SiO_2$ core–shell nanoparticles with tunable properties, ACS Nano 2 (2008) 847.

[29] M.H. Entezari, N. Ghows, Micro-emulsion under ultrasound facilitates the fast synthesis of quantum dots of CdS at low temperature, Ultrason. Sonochem. 18 (2011) 127–134.

[30] N. Ghows, M.H. Entezari, Ultrasound with low intensity assisted the synthesis of nanocrystalline TiO_2 without calcinations, Ultrason. Sonochem. 17 (2010) 878–883.

[31] N. Ghows, M.H. Entezari, A novel method for the synthesis of CdS nano-particles without surfactant, Ultrason. Sonochem. 18 (2011) 269–275.

[32] N. Ghows, M.H. Entezari, Fast and easy synthesis of core–shell nanocrystal (CdS/TiO_2) at low temperature by micro-emulsion under ultrasound, Ultrason. Sonochem. 18 (2011) 629–634.

[33] S. Avivi (Levi), O. Palchik, V. Palchik, M.A. Slifkin, A.M. Weiss, A. Gedanken, Sonochemical synthesis of nanophase indium sulfide, Chem. Mater. 13 (2001) 2195–2200.

[34] W.P. Huang, X.H. Tang, Y.Q. Wang, Y. Koltypin, A. Gedanken, Selective synthesis of anatase and rutile via ultrasound irradiation, Chem. Commun. 141 (2000) 5–1416.

[35] S.S. Lee, K.W. Seo, S.H. Yoon, I.-W. Shim, K.-T. Byun, H.-Y. Kwak, CdS coating on TiO_2 nanoparticles under multibubble sonoluminescence condition, Bull. Korean Chem. Soc. 26 (2005) 1579.

[36] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[37] J. Wang, Z. Pan, Z. Zhang, X. Zhang, F. Wen, T. Ma, et al., Sonocatalytic degradation of methyl parathion in the presence of nanometer and ordinary anatase titanium dioxide catalysts and comparison of their sonocatalytic abilities, Ultrason. Sonochem. 13 (2006) 493–500.

[38] J. Zhao, K. Wu, T. Wu, H. Hidaka, N. Serpone, Photodegradation of dyes with poor solubility in an aqueous surfactant/TiO_2 dispersion under visible light irradiation, J. Chem. Soc., Faraday Trans. 94 (1998) 673–676.

[39] D. Lucio, D. Laurent, G. Roger, Adsorption of remazol black B dye on activated carbon felt, Carbon-Sci. Technol. 1 (2) (2008) 66–71.

[40] M.A. Rauf, S.B. Bukallah, A. Hammadi, A. Soliman, F. Hammadi, The effect of operational parameters on the photoinduced decoloration of dyes using a hybrid catalyst V_2O_5/TiO_2, Chem. Eng. J. 129 (2007) 167–172.

[41] A. Tauber, G. Mark, H.-P. Schuchmann, C. von Sonntag, Sonolysis of tert-butyl alcohol in aqueous solution, J. Chem. Soc., Perkin Trans. 2 (1999) 1129–1135.

[42] K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura, Y. Maeda, Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes, Ultrason. Sonochem. 12 (2005) 255–262.

[43] R. Vijayakumar, Yu. Koltypin, I. Felner, A. Gedanken, Sonochemical synthesis and characterization of pure nanometer-sized Fe_3O_4 part, Mater. Sci. Eng. A 286 (2000) 101–105.

[44] S. Vajnhandl, A.M.L. Marechal, Case study of the sonochemical decolouration of textile azo dye reactive black 5, J. Hazard. Mater. 141 (2007) 329–335.

[45] W.Z. Tang, H. An, UV/TiO_2 photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 31 (1995) 4157–4170.

[46] K. Vinodgopal, D.E. Wynkoop, P.V. Kamat, Environmental photochemistry on semiconductor surfaces: photosensitized degradation of a textile azo dye, acid orange 7, on TiO_2 particles using visible light, Environ. Sci. Technol. 30 (1996) 1660–1666.

[47] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B Environ. 31 (2001) 145–157.

[48] A. Henglein, Adv. Sonochem. 3 (1993) 17.

[49] R.A. Caruso, M. Ashokkumar, F. Grieser, Sonochemical formation of gold sols, Langmuir 18 (2002) 7831.

[50] B. Yim, H. Okuno, Y. Nagata, R. Nishimura, Y. Maeda, Sonolysis of surfactants in aqueous solutions: an accumulation of solute in the interfacial region of the cavitation bubbles, Ultrason. Sonochem. 9 (2002) 209.

[51] R. Silverstein, T. Clayton, T. Morril, Spectrophotometric Identification of Organic Compounds, Wiley, New York, 1991.

[52] C. Bradua, L. Frunzab, N. Mihalchea, S.-M. Avramescua, M. Neata, I. Udreaa, Removal of reactive black 5 azo dye from aqueous solutions by catalytic oxidation using CuO/Al_2O_3 and NiO/Al_2O_3, Appl. Catal. B: Environ. 96 (2010) 548–556.

[53] A. Kongkanand, K. Tvrdy, K. Takechi, M. Kuno, P.V. Kamat, Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe–TiO_2 architecture, J. Am. Chem. Soc. 130 (2008) 4007–4015.

[54] A. Mills, R. Davies, The photomineralization of reactive black 5 sensitized by titanium oxide: a study of the initial kinetics of dye photobleaching, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Amsterdam, The Netherlands, 1993, pp. 595–600.

[55] I. Poulios, I. Tsachpinis, Photodegradation of the textile dye reactive black 5 in the presence of semiconducting oxides, J. Chem. Technol. Biotechnol. 74 (1999) 349–357.

[56] C. Gomes da Silva, J.L. Faria, Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation, J. Photochem. Photobiol. A: Chem. 155 (2003) 133.

[57] K. Sahel, N. Perol, H. Chermette, C. Bordes, Z. Derriche, C. Guillard, Photocatalytic decolorization of Remazol Black 5 (RB5) and Procion Red MX-5B—isotherm of adsorption, kinetic of decolorization and mineralization, Appl. Catal. B: Environ. 77 (2007) 100–109.

[58] M. Karkmaz, E. Puzenat, C. Guillard, J.M. Herrmann, Photocatalytic degradation of the alimentary azo dye amaranth. Mineralization of the azo group to nitrogen, Appl. Catal. B: Environ. 51 (2004) 183–194.

[59] M. Kerzhentsev, C. Guillard, J.M. Herrmann, P. Pichat, Photocatalytic pollutant removal in water at room temperature: case study of the total degradation of the insecticide fenitrothion (phosphorothioic acid O,O-dimethyl-O-(3-methyl-4-nitro-phenyl) ester), Catal. Today 27 (1996) 215.

[60] P.V. Kamat, B. Patrick, Photophysics and photochemistry of quantized zinc oxide colloids, J. Phys. Chem. 96 (1992) 6829–6834.