



Role of quantum dots nanoparticles in the chemical treatment of colored wastewater: Catalysts or additional pollutants

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Abstract

The objective of the study was to investigate the presence and the activity of quantum dots nanoparticles in colored wastewaters. The special interest is devoted to the investigation of their role in the typical treatment of water or wastewater, studying their influence on the effectiveness of applied treatments methods. The standard chemical processes for water treatment and disinfection (direct UV photolysis and direct ozonation) were applied for the degradation of colored organic pollutant, reactive azo dye, in the presence/absence of CdSe/ZnS core-shells quantum dots. The obtained results indicated that investigated nanoparticles inhibit the overall efficiency of applied processes, especially in the case of direct UV photolysis, although catalytic effect might be expected in part due to the semiconductor nature of quantum dots. Such results lead to a conclusion that CdSe/ZnS nanoparticles behave as additional pollutants in the system. They should be removed from the system prior the treatment, because their presence could decrease the efficiency, i.e., prolong the time of treatment and correspondingly increase the costs of the treatment process.

Key words: wastewater treatment; CdSe/ZnS core-shells; reactive azo dye; UV irradiation, ozone

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Introduction

In the vast array of contaminants of anthropogenic origin which could reach our water supplies, the sizable fraction pertains to synthetic dyes. Synthetic dyes are present in many spheres of our everyday life with the continuously growing application. Among all dye types, those of reactive type are the most common used textile dyes due to their numerous advantages; providing of bright colors, excellent colorfastness and ease application (Zollinger, 1987; Hunger, 2002). However, reactive dyes hydrolyze easily, resulting in a high portion of unfixed (or hydrolyzed) dye which has to be washed off during the dyeing process. As much as 50% of the initial dye load is present in the dye bath effluent (Hunger, 2002) being a major threat to the surrounding ecosystems due to documented health hazards caused by the toxicity and potentially carcinogenic nature of such organic pollutants (Nillson et al., 1993). Therefore, the necessity for effective dye wastewater treatment prior to the discharge into natural effluents is highly demanded. Nowadays, many technologies are available, but the degradation methods (either biological or chemical) drawn interest due to avoidance of secondary

waste generation (Sincero and Sincero, 2003; Viessman and Hammer, 2005). The innovative water/wastewater treatment methods with the promising potential include the applications of nanomaterials, whether used as adsorbents, catalysts or ion exchangers (Savage and Diallo, 2005). However, the unknown behavior of nanomaterials in the environment and possible negative influence arise many questions related to their application. Thus, their integration in water/wastewater treatment process should be investigated (Wiesner and Bottero, 2005; Kumar, 2006). Simultaneously with increasing dye production and application, presumably the fastest-growing field in nowadays science, but industry as well, is related with the development, production, and application of variety of nanoparticles. Generally, nanomaterials can significantly differ in their properties comparing to either corresponding components in the pure form, or with materials/composites where both of the phases have macroscopic dimensions (Kenneth, 2001; Bhushan, 2007). Due to increasing interest for nanomaterials, it could be expected that their production and application in different fields and industries will constantly grow. As a consequence, it can be predicted that the presence of nanoparticles in the environment is going to be increased in the near future. Thus, the potential

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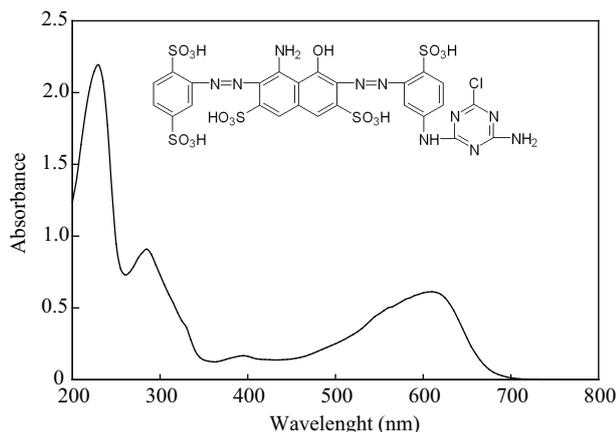


Fig. 1 UV/Vis spectra and molecular structure of C.I. Reactive Blue 137.

interactions with pollutants, as well as the possible application in integrated treatment methods should be also investigated.

Typical representative of such new materials are quantum dots (QDs), nanomaterials made from a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons in all three spatial directions. They can vary in nanoparticle size up to 10 nm (Alivisatos, 1996a). QDs are lately applied in different fields and industries, such as electronics, medicine, optical science. Their superior transport and optical properties giving them advantages to be used as diode lasers, amplifiers and biological sensors (Alivisatos, 1996a, 1996b; Masumoto and Takagahara, 2002). Since QDs are made from semiconductor materials, they are appropriate representatives of nanomaterials for our study. Nanomaterials with the increasing presence in the environment and theoretical potential to be used in water/wastewater treatment technologies.

The main objective of this study was to investigate the role of QDs nanoparticles presence in colored wastewaters. The special interest is devoted to the investigation of their role in the typical treatment of water or wastewater, studying their influence on the effectiveness of applied treatment methods. We performed standard chemical processes for the water treatment and disinfection; direct UV photolysis and direct ozonation, for the degradation of colored organic pollutant, reactive azo dye, in the presence/absence of CdSe/ZnS core-shells QDs.

1 Experimental

As a model organic colored pollutant a synthetic reactive azo dye, C.I. Reactive Blue 137 (RB137) (CIBA-Geigy, Switzerland) was used. RB137 is commercial dye used mostly for dyeing cotton fibers. The chemical structure and dye absorbance UV/Visible spectra are presented in Fig. 1. The initial concentration of RB137 in all experiments was 40 mg/L, resulting with the initial total organic content (TOC) of 12.92 mgC/L. The used QDs nanoparticles, CdSe/ZnS core-shells (Evident Technologies, USA) (Fig. 2) are used without any pretreatment. Their physical properties are listed in Table 1.

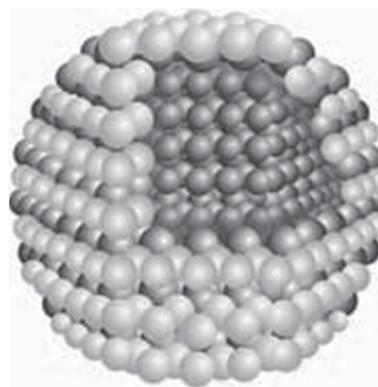


Fig. 2 Typical quantum dot CdSe/ZnS core-shell nanoparticle (so called nanocrystal).

It has to be emphasized that QDs are purchased as toluene suspension. Hence, toluene was introduced in the reaction mixture along with QDs. In order to estimate the influence of added QDs, the experiments including the addition of only toluene to RB137 model solution were performed as the background. For that purpose toluene, GC grade (99.8 %) (Fisher Scientific, USA) was used. All solutions were prepared with deionized water with conductivity less than 1 μ S/cm.

All experiments were performed in the glass water-jacketed batch reactor. The middle of the reactor was occupied with the quartz tube in which a mercury lamp emitting UV-C irradiation at 254 nm with the typical intensity on 2 cm \approx 4.4 mW/cm² (UVP-Ultra Violet Products, Cambridge, UK) placed vertically. The value of incident photon flux at 254 nm, 2.34×10^{-6} Einstein/sec, was calculated on the basis of hydrogen peroxide actinometry experiments (Nicole et al., 1990). In the experiments where UV irradiation was required, the UV lamp was switched on. In the experiments involving ozone, ozone was introduced into the reactor. Ozone was generated from pure oxygen (> 99.9%), introducing it into the ozone generator (OL80W/FM, OzoneLab, Canada). The outlet gas mixture from the ozonizer, i.e., mixture of ozone and oxygen, was fed into the reactor through a sintered glass plate diffuser located in the bottom half of the reactor. The rate of ozone generation in reactor inlet stream was 8×10^{-3} g/min. The total volume of the treated solution was 0.5 L in all cases, while the mixing of the solution was provided by magnetic stirring bar. Experiments were carried out at $24.2 \pm 0.2^\circ\text{C}$, while initial pH of the treated solution was 5.9. The added volume of QDs/toluene suspension or only toluene was 0.2 mL, giving the mass concentrations of 346.7 and 10

Table 1 Physical property of used CdSe/ZnS core-shells

Property ^a	Value
λ_E (emission peak)	520 nm
d (crystal diameter)	3.3 nm
ϵ (molar extinction coefficient)	5.0×10^4 ((mol/L) \cdot cm) ⁻¹
M_r (molecular weight)	94 μ g/nmol
Φ (quantum yield)	> 50%
Coloration of QD suspension in toluene	Green

^a Data adopted from Evident Technologies, USA (www.evidenttech.com).

mg/L of toluene and QDs, respectively. The duration of each experiment was 120 min. In the first 60 min of the treatment the reaction mixture containing RB137 and QDs and/or toluene was stirred in the dark, while in next 60 min direct UV photolysis or ozonation was applied. The initial period of 60 min of only stirring the solution in the dark was performed due to the fact that applied CdSe/ZnS core-shells are semiconductors and it is well known from the semiconductor photochemistry (photocatalysis with TiO₂, ZnO, etc.) that suspensions should be mixed in the dark to allow the equilibrium. In such manner the possible loss of the target organic compound due to the possible adsorption should be taken into account (Pichat, 2003). Samples were taken periodically from the reactor (-60, -40, -20, 0, 5, 10, 15, 20, 30, 40, 50 and 60 min) and thereafter immediately analyzed. The time -60 indicates addition of CdSe/ZnS and/or toluene, while time 0 indicates start of treatment process. All experiments were performed in triplicates and averages are reported, while the reproducibility of experiments was > 95%.

The degradation of RB137 was monitored by UV/Vis spectrophotometer (Lambda EZ 201, PerkinElmer, USA) scanning UV and visible spectra in the range of 200–800 nm. Degradation of RB137 was determined on the basis of absorbance measurements at $\lambda_{\max 1} = 610$ nm, pick corresponding to dye chromophore (decolorization), and $\lambda_{\max 2} = 280$ nm, pick corresponding to aromatic structures in dye molecule (aromaticity removal). The third pronounced pick in the dye spectra with the maximum at 230 nm corresponds mostly to triazine structures in dye molecule. The degradation or dissolving of added toluene was monitored on $\lambda_{\max 3} = 260$ nm. The organic content of RB137 model solution was established on the basis of TOC measurements, performed by total organic carbon analyzer (TOC-V_{CPN}, Shimadzu, Japan). Handylab pH/LF portable pH-meter (Schott Instruments GmbH, Mainz, Germany) was used for pH measurements.

2 Results and discussion

The study is directed to explore the influence of CdSe/ZnS core-shells on the treatment of RB137, whether used QDs are able to serve as potential catalysts in applied chemical treatment methods. In the first step of the study the role of QDs in direct UV photolysis as a treatment of RB137 model wastewater was investigated. The changes in UV/Vis spectra during the direct UV photolysis of RB137 model wastewater in the absence and presence of QDs are shown in Fig. 3.

A decrease in spectral bands with the maximum at 610 nm (corresponding to the chromophore of RB137), and at 260 nm (corresponding to toluene) can be observed. On the other hand, a slight increase of spectral band absorbing in UV region at 280 nm, characteristic for aromatic structures, is also recorded regardless the presence of QDs (Fig. 3). The decrease of the spectral bands in visible region indicates the decolorization of model wastewater (cleavage of RB137 chromophores), while a decrease of spectral band at 260 nm is a result of toluene degradation.

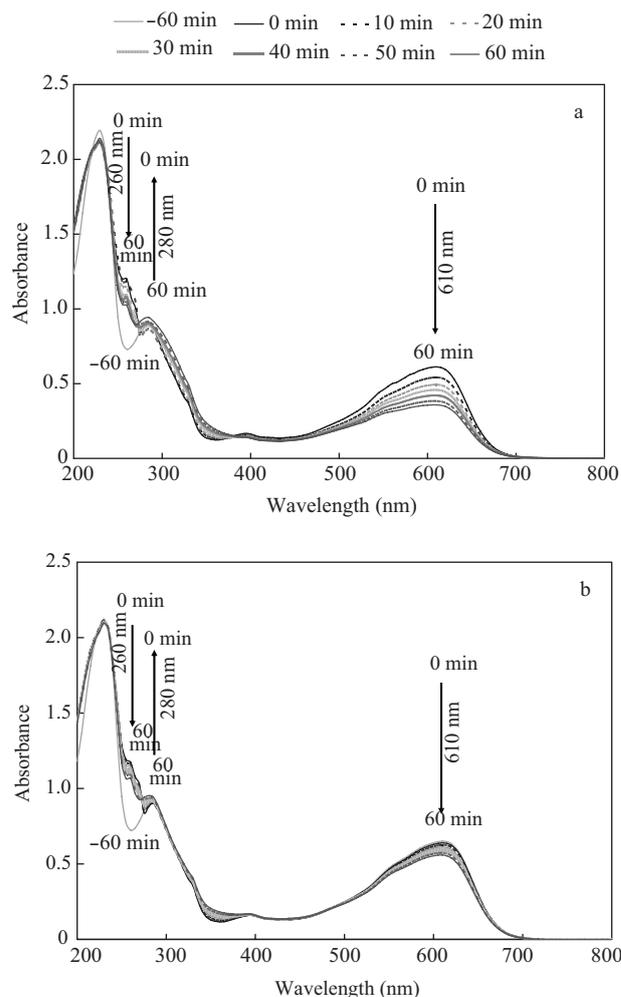


Fig. 3 Changes of RB137/toluene spectra during the treatment by UV process in the absence (a) and presence (b) of CdSe/ZnS core-shells.

The plausible explanation for the slight increase of the peaks absorbing at 280 nm could be found in the fact that toluene is degraded to aromatic compounds absorbing in UV region at the wavelength 280 nm as well (e.g., *o*-, *m*- and *p*-cresols, benzaldehyde) (Van Durme et al., 2005). Although the trends of increase or decrease of these three characteristics peaks are not in direct correlation with the presence or absence of QDs, it can be observed that the rates of changes are. This fact clearly indicates that QDs influenced RB137 degradation efficiency. In order to better estimate such influence the following comparison was made.

In Fig. 4 the decrease/increase of above mentioned absorbance peaks A_{610} , A_{280} and A_{260} presenting decolorization, toluene degradation and changes in content of aromatic compounds (aromaticity), respectively, are compared. The changes in organic content of studied wastewater are presented as well. The results are expressed as normalized values related to the initial ones of RB137 model wastewater without toluene and QDs (dashed line in Fig. 4). It is worth of noting that presented normalized values of organic content did not include the remained toluene in the system; only non-volatile compounds formed by its degradation are recorded by the used method (results are marked as TOC*). The influence of QDs on the process

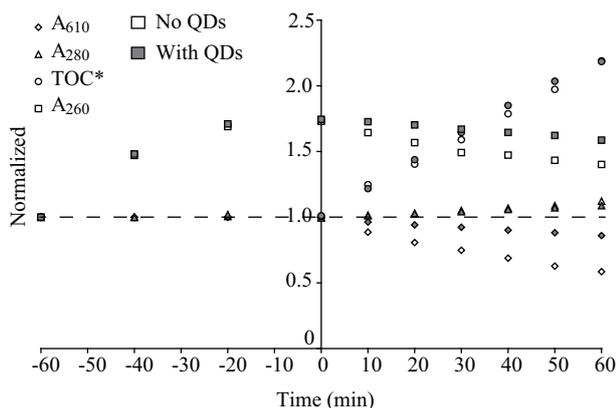


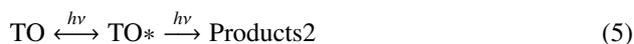
Fig. 4 Comparison between decolorization, toluene degradation, changes in aromaticity and organic content of RB137/toluene model wastewater during the UV degradation in the absence and presence of QDs.

efficiency is the most evident from the decolorization extents (Fig. 4). Significantly lower color removal was achieved after 60 min treatment in the presence of QDs (only 16.0%) in comparison to the case without QDs (41.5%). Furthermore, toluene degradation profile was rather different regarding the presence of QDs (Fig. 4), while other two parameters do not differ significantly. Such results indicate the inhibitory effect of QDs toward RB137, but toluene as well. This observation is in a contrast with our expectations based on the facts that QDs are made from semiconductor materials. Several studies using semiconductor nanoparticles involving constitution components of used QDs in this study (Cd, Zn), or with composites where both of the phases have microscopic dimensions, are found in the literature. In these studies used semiconductor micro/nano-particles containing either Cd or Zn showed catalytic effect in organic pollutants degradation when illuminated by UV or even sunlight (Hoffmann et al., 1995; Pichat, 2003; Bessekhouad et al., 2004; Lo et al., 2004). According to the semiconductor photochemistry, the illumination of semiconductor (nano)particle by UV or even visible light causes that electrons from valence band cross the gap and are transferred into the conduction band, creating the electron-hole (e^- , h^+) pair at the semiconductor (nano)particle surface. Photogenerated electrons are able to react with adsorbed electron acceptor species, i.e., dissolved oxygen, resulting with superoxide radical formation or its protonated form, HO_2 (Reaction (1)). The holes react with electron donor species, i.e. either water (or hydroxyl ion) (Reaction (2)) or pollutant molecule itself (usually organic specie which can be marked as R-H) (Reaction (3)), resulting with the formation of hydroxyl radicals (HO) capable to degrade organics and pollutant radical which initiates further degradation mechanism, respectively (Hoffmann et al., 1995; Pichat, 2003).



However, according to the above presented results obtained in our study (Fig. 4), it seems that semiconductor

nanoparticles did not cause the catalytic effect although one can expect it due to the above presented theory and their nature. Moreover, it seems that semiconductor nanoparticles CdSe/ZnS core-shells caused inhibitory effect under illumination by UV-C irradiation. According to the literature, the plausible explanations for such system behavior could be that: (1) either transparency of the solution was decreased due to the addition of (nano)particles, (2) or that active sites at the semiconductor (nano)particle surface were blocked/contaminated (Pichat, 2003), (3) or due to the “photon shielding effect”. Since the concentration of QDs in our case was rather low (10 mg/L) it is more likely that solution transparency was not significantly influenced by QDs addition. Hence, the observed system behavior could be attributed to the contaminated active sites at the QDs surface, either by inorganic or organic species, and/or mentioned “photon shielding effect”. If the active sites on the semiconductor surface of QDs were contaminated, resulting with the non- or low HO and $O_2^{\cdot-}$ radicals generation according to the above presented mechanism (Reactions (1)–(3)), the degradation of present pollutants would occur through direct photolysis (Reactions (4) and (5)):



Hence, the “photon shielding effect” between the pollutants can be expected, i.e. species in the system (RB137 and toluene, but QDs as well) would compete each other for absorbing UV irradiation energy. It should be emphasized that initial concentrations of present pollutants were significantly different ($[RB137]_0 \ll [toluene]_0$), as well as their physical properties ($\varepsilon(RB137)_{254\text{ nm}} = 18124 \text{ ((mol/L}\cdot\text{cm)}^{-1}) \gg \varepsilon(toluene)_{254\text{ nm}} = 2073 \text{ ((mol/L}\cdot\text{cm)}^{-1}$ and $\Phi(RB137)_{254\text{ nm}} = 0.0042 \text{ mol/Einstein} \ll \Phi(toluene)_{254\text{ nm}} = 0.025 \text{ mol/Einstein}$). The extinction molar coefficients are calculated from Eq. (6) by measuring absorbance of RB137 or toluene solution at 254 nm. Absorbance A , can be expressed as a:

$$A = \varepsilon \times c \times l \quad (6)$$

where, ε is the molar absorption coefficient with dimensions $(\text{concentration} \times \text{length})^{-1}$, and l is the cell path length (Atkins, 1994). The values of quantum yields of RB137 and toluene were calculated using so-called “LL model”, a semi-empirical model based on the Lambert’s law (Beltran, 2003):

$$r_{UV} = -\frac{dc_i}{dt} = \Phi_i \times F_i \times I_0 \times \left[1 - \exp\left(-2.303 \times L \times \sum \varepsilon_j \times c_j\right) \right] \quad (7)$$

being $F_i = \frac{\varepsilon_i \times c_i}{\sum \varepsilon_j \times c_j}$ where, Φ_i , $\varepsilon_{i(j)}$, I_0 and L state for quantum yield, extinction coefficients, intensity of incident photon flux

and effective path of radiation, respectively. Taking into account the physical properties of QDs listed in Table 1, it can be clearly seen that used QDs possess much higher molar extinction coefficient and especially quantum yield than both organic pollutants ($\Phi_{\text{QDs}} > 50\%$ in comparison to 0.42% and 2.5% of RB137 and toluene, respectively). Hence, their involvement in the “photon shielding effect” can be expected as well, resulting in the decreased efficiency of direct UV photolysis in RB137 and toluene degradation, as observed in our experiments (Fig. 4). Furthermore, besides these two assumed negative effects (blocking/contamination of active sites and “photon shielding effect”) there are evidences in the literature that nanoparticles differ significantly in properties comparing with materials in micro-dimensions (Kenneth, 2001; Nowack and Bucheli, 2005; Bhushan, 2007; Tao et al., 2009). For instance, Nowack and Bucheli (2005) stated that the physical properties (e.g., melting point, electrical conductivity) and reactivity (e.g., catalytical activity, sorption capacity) of nanoparticles vary dramatically as a function of size and can be very different from the bulk material. Furthermore, Tao et al. (2009) studied the activity of two mesoporous silica nanopartileces which showed diametrically different influence on the oxidation of epinephrine. However, we would not speculate about the changes in the possible properties of used QDs because we did not perform the comparative analysis running the experiments with corresponding materials/composites having micro-dimensions.

To better estimate the observed inhibitory effect, the comparison of the degradation rates of model wastewater by direct UV photolysis process in the absence and presence of QDs was performed (Table 2). The reaction rate order was firstly determined, and then the degradation rate constants were calculated. Using the different functional dependences of concentration on time (Connors, 1990), it was determined that all of them obey the first order reaction kinetics. The values of first order rate constants for all monitored parameters (color and toluene removal, TOC* and aromaticity increase) were calculated using linear regression.

It can be seen that the difference between the cases, i.e. the observed inhibitory effect, resulted with significantly lower degradation rate constants in the case of color and toluene removal (A_{610} and A_{260} , respectively); even three times higher rates are calculated for the case without QDs (Table 2), speaking in favor of above mentioned “photon shielding effect” caused by QDs presence. On the other hand, the rate constants calculated for the increase in aromaticity and total non-volatile organic content of RB137/toluene wastewater (TOC*) differ only slightly,

indicating the close correlation of these two parameters. Interestingly, although toluene was more degraded in the case without QDs, the TOC* and aromaticity are very similar in both cases. Taking into account the fact that dye degradation in the absence of QDs was a faster process, and considering that $[\text{RB137}]_0 \ll [\text{toluene}]_0$, it can be assumed that measured A_{280} and TOC* would not be compensated by both lower A_{610} and A_{260} as obtained. The decrease of A_{610} means that dye chromophore was degraded, i.e. TOC* should decrease, while the decrease of A_{260} means that toluene was degraded resulting with increased A_{280} and TOC*. However, due to the much higher $[\text{toluene}] \gg [\text{RB137}]$ it seems that both values of A_{280} and TOC* should increase more in the absence of QDs, which was not the case. The plausible explanation could be that QDs rerouted typical degradation mechanism; favoring the formation of more non-volatile aromatic compounds absorbing at 280 nm than it was obtained in the absence of QDs. In such manner, similar values of both aromaticity and TOC* parameters were obtained, although significantly lower $[\text{toluene}]$ was recorded in the absence of QDs (Fig. 4).

Since the inhibitory effect of QDs on RB137 dye degradation when was treated by UV irradiation was observed, our intention was to investigate whether QDs influence in the same manner the other chemical treatment methods, e.g., ozonation. The results of changes in UV/Vis spectra of RB137/TO model wastewater obtained during the treatment by ozonation in the absence and presence of QDs are presented in Fig. 5.

One can observe that the leveling off of characteristic absorbance peaks corresponding to dye chromophore and toluene (A_{610} and A_{260} respectively) (Fig. 5) is significantly faster than that obtained in the case of direct UV photolysis (Fig. 3). Moreover, the peak absorbing in UV region with the maximum at 280 nm which corresponds to aromatic structures leveled off as well, which was not the case when direct UV photolysis was applied. This clearly implies that ozonation is more powerful treatment method for studied model wastewater than direct UV photolysis. Furthermore, one can observe that both presented spectrograms in Fig. 5 are very similar to each other without clear indications on QDs influence to monitored parameters used for process efficiency estimation. In order to estimate the changes between the cases, monitored parameters and TOC* are plotted at the same graph (Fig. 6), including the comparison of calculated first order rate constants corresponding to monitored parameters (Table 2). According to the calculated values of rate constants, it can be concluded that the influence of QDs is minor; very close values are obtained in all cases, although somewhat faster decolorization and toluene degradation can be noticed in the absence of QDs (Fig. 6).

However, very interesting results are obtained for aromaticity and TOC*. In certain point of treatment, when complete color removal was achieved and at approximately $t_{1/2}$ of $[\text{toluene}]$, a leveling off in trend of toluene degradation curve can be observed. The same phenomenon can be observed for the aromaticity monitoring (A_{280}) in the

Table 2 Calculated pseudo-first order rate constants (k_{obs})

Process	Presence of QDs	Rate constant ($k_{\text{obs}} \times 10^{-4} \text{ sec}^{-1}$)			
		A_{610}	A_{280}	TOC*	A_{260}
Direct UV photolysis	–	1.55	0.29	2.33	0.65
	+	0.43	0.23	2.40	0.25
Direct ozonation	–	47.4	4.00	–	3.82
	+	42.2	4.83	–	3.25

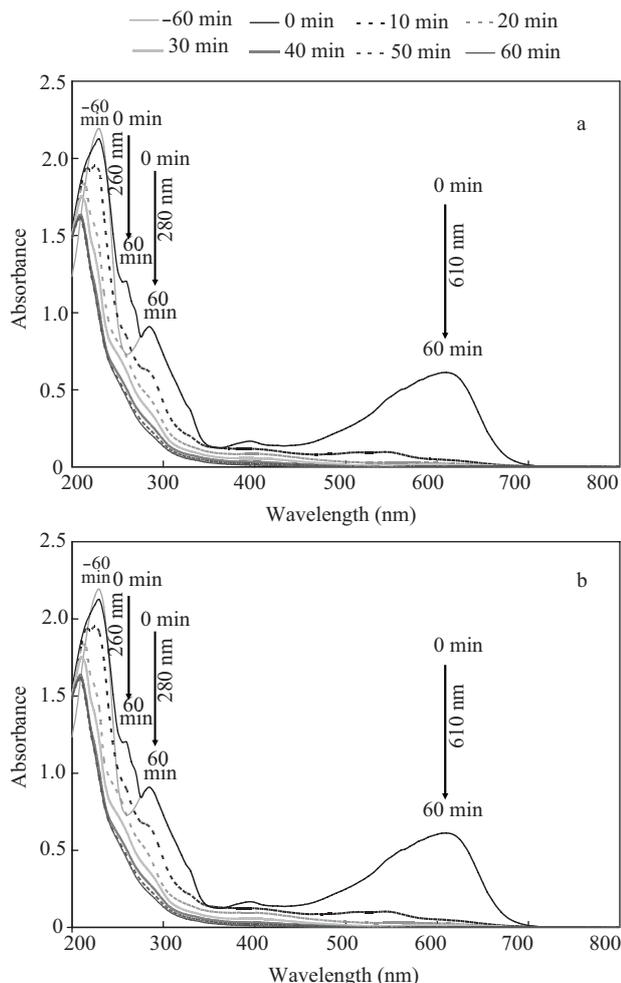


Fig. 5 Changes of RB137/toluene spectra during the treatment by ozone process in the absence (a) and presence (b) of CdSe/ZnS core-shells.

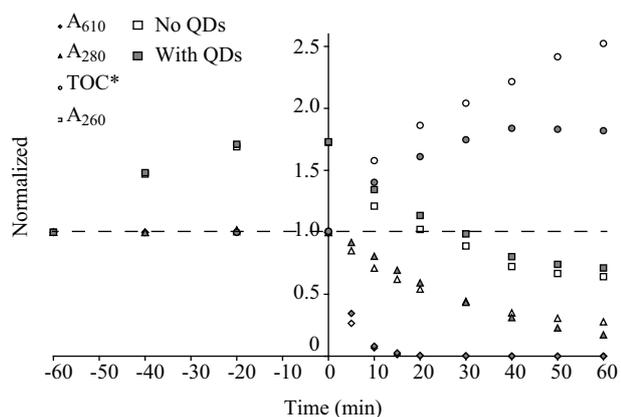


Fig. 6 Comparison between decolorization, toluene degradation, changes in aromaticity and organic content of RB137/toluene model wastewater during the ozonation in the absence and presence of QDs.

absence of QDs and TOC* in the presence of QDs (Fig. 6). This effect indicates that decrease in the rate of toluene degradation resulted in the formation of more aromatic compounds absorbing at 280 nm in the absence of QDs and that more non-volatile organics were mineralized in the presence of QDs. The observed effects imply on more complex behavior of QDs presence during the ozonation process than in the case of direct UV photolysis. However, it could also indicate on rerouted pathways of RB137 (or at

least its degradation by-products) and/or toluene. From all presented results, we concluded that neither catalytic nor inhibitory behavior of QDs could be claimed with the high certainty; in the case of direct UV photolysis an inhibitory effect was observed presumably due to the contamination of QDs active sites and/or “photon shielding effect”. On the other hand, in the case of ozonation it seems that QDs promoted degradation reactions in certain treatment time point. However, the results might indicate that QDs could reroute the degradation mechanism of RB137 and/or toluene, but more investigations are needed to confirm this assumption.

3 Conclusions

The study was focused on the investigation of the presence of quantum dots nanoparticles in colored wastewaters, devoting the special interest to their role in the typical treatment of water or wastewater by studying their influence on the effectiveness of applied treatment methods. In that purpose we applied standard chemical processes for the water treatment and disinfection; direct UV photolysis and direct ozonation, for the degradation of colored organic pollutant, reactive azo dye RB137, in the presence/absence of CdSe/ZnS core-shells quantum dots.

The obtained results indicated that investigated nanoparticles showed rather inhibitory effect on the overall efficiency of degradation process, especially in the case of direct UV photolysis, although catalytic effect could be expected in part due to their semiconductor nature. Furthermore, it seems that QDs rerouted typical degradation mechanism of either toluene or RB137 or both; favoring the formation of more aromatic compounds absorbing at 280 which are non-volatile. In such manner a similar values of aromaticity and TOC* were achieved regardless QDs presence, although more toluene was degraded in the absence of QDs. In the case of ozonation, an inhibitory effect was almost negligible. It seems that after the complete decolorization and toluene degradation up to the certain point QDs acted as catalysts promoting the mineralization and aromaticity removal in comparison to the case without QDs.

However, the obtained results lead to conclusion that CdSe/ZnS nanoparticles could rather behave as additional pollutants than catalysts, and consequently they should be removed from the system prior the treatment. Otherwise, their presence could decrease the process efficiency, i.e. prolong the time of treatment and correspondingly increase the costs of the treatment process, especially in the case of UV-based treatment technologies.

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