Fast sonochemically-assisted synthesis of pure and doped zinc sulfide quantum dots and their applicability in organic dye removal from aqueous media

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ARTICLE INFO

Keywords:
Sonochemically synthesis
Quantum dots
Victoria blue R
Nanophotocatalysts
Salt effect

ABSTRACT

In this research, a sono-assisted chemical precipitation method was developed for a quick and efficient water-based synthesis of zinc sulfide (ZnS) quantum dots (QDs), in room temperature. ZnS QDs as pure and doped with some transition metal ions (such as Cu2+, Mn2+, Ag+) were prepared in the presence of L-cysteine, as capping agent. In comparison with the previous conventional methods, applying the ultrasonic irradiation provides a significant decrease in the reaction time. In comparison with previous reported conventional chemical QD synthesis methods, the required time for a complete synthesis in the presence of ultrasonic irradiations was significantly reduced to a period as short as 15 min, in a temperature of 40 °C. The sono-synthesized QDs were characterized with various techniques such as colorimetry, UV–Vis absorption spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). A broad absorption band between 270 and 290 nm was observed for colloidal ZnS QDs with the optical band gap larger than 3.68 eV. From the XRD and TEM results, the average particle size below 5 nm was estimated for the prepared QDs. After characterization, the samples were employed as nanophotocatalysts during a UV-derivate photocatalytic process for the degradation of Victoria blue R (VBR), as a pollutant dye. To obtain the optimal operating conditions, the influence of the affecting parameters such as the initial pH of the dye solution, irradiation time, initial dye concentration, type, electrolyte salt concentration and dosage of the nanophotocatalyst samples on the degradation efficiency (DE %) was comprehensively studied, all in batch mode. Taking the optimum conditions into account, the maximum removal of VBR dye (> 95%) can be obtained by spectrophotometric measurements at alkaline pH of 10.5, in the presence of low amounts of QDs (3 mg) and after 30 min of being exposed to UV irradiations. The results demonstrate that despite the removal of VBR, the QDs prepared by sonochemically method can be reused for at least six more times; without a significant decrease in their photocatalytic properties.

1. Introduction

Quantum dots (QDs) have received considerable attentions in various research groups, in the recent years; due to several unique properties of this class of nanomaterials [1,2]. These luminescent and zero-dimensional nanocrystals with physical dimensions smaller than excitonic Bohr radius are known for their tunable sizes, narrow emission spectra, broad absorption spectra, strong signal intensity and high photo-stability [3,4]. Among the many types of QDs, zinc sulfide (ZnS) QDs with limited dimensions of 1–10 nm, have become a remarkably important type of semiconductor nanoparticles, in a wide range of applications [5]. According to the literature, they could be used in solar cells [6,7], luminescent detection [8,9], electronics [10], biomedical imaging [11], drug delivery [12], diagnostic [13], cytotoxicity [14], and photocatalytic applications [15,16]. Moreover, due to the absence of toxic elements in zinc-based QDs, higher surface area of ZnS QDs compared to their bulky counterparts, and also the wider gap energy in ZnS QDs, they are considered as ideal hosts for doping a large variety of metal impurities [17,18].

Today, numerous methods are available for synthesis of QDs [19], however; among conventional methods, the chemical precipitation method has become one of the most effective and economical method for synthesis of ZnS QDs. This synthetic method has several advantages including simplicity, low-cost, availability of the equipment, and...
capability of producing the nanoparticles with high purities and yields [20].

In recent years, due to unique characteristics of the ultrasonic assisted method, it has emerged as a potential alternative for synthesis of ultra-small particles such as QDs [21–23]. As found, by using the ultrasonic irradiation through the chemical synthesis provide a combined route with more beneficial and favorable method; considering the required synthetic time, used temperature and the uniformity of the resulted particles in this approach [24]. In sono-chemical methods, the acoustic cavitations in an irradiated liquid is takes place in exposure to ultrasound radiation (20 kHz–10 MHz); the process which can produce a temperature of 5000° in Kelvin over a nanosecond, large cooling rates (1011 Ks⁻¹) and pressures > 1800 kPa. During the cavitations, the formed bubbles implode and cause shock-waves; which structurally modify the ultrasound-irradiated items [25]. Moreover, by ultrasonic methods, the morphology, shape, size, and the surface defects of QDs can be controlled [26]. However, still little comprehensive researches have been performed on sonochemically ly synthesis and characterization of colloidal ZnS QDs; as well as their applications as nanophotocatalysts for UV-driven degradation of pollutant dyes.

In this research, a facile, fast and efficient sonochemically precipitation method was performed for synthesis of pure and Cu²⁺, Mn²⁺, Ag⁺ ions doped ZnS QDs, in the presence of l-cysteine as an efficient capping agent, in aqueous media. After characterization, the photocatalytic properties of the sonically modified QDs were investigated based on their photodegradation efficiency in removal of Victoria blue R (VBR) dye; as a representative pollutant. The impacts of experimental conditions on efficiency of the photocatalyst were evaluated and optimized in photodegradation studies. Reusability, kinetic model and the probable mechanism of QDs-based photocatalytic process were investigated and discussed in optimum conditions.

2. Experimental

2.1. Materials and Apparatus

Sodium sulfide (Na₂S·9H₂O; 98%; w/w) nitrate salts of zinc (Zn(NO₃)₂·4H₂O), copper (Cu(NO₃)₂·4H₂O), silver (AgNO₃) manganese (Mn(NO₃)₂·5H₂O), and l-cysteine (C₆H₇NO₂S) used in this research had analytical grades and have been purchased from Merck Company (Darmstadt, Germany). The VBR dye (C₂₇H₃₀O₅S), purchased from Sigma-Aldrich Company, had laboratory reagent grade. The pH of solutions was adjusted by aqueous solution of hydrochloric acid (HCl) and sodium hydroxide (NaOH). Also, VBR solutions with desired concentrations was adjusted by aqueous solution of hydrochloric acid (HCl) and sodium hydroxide (NaOH) also. All UV–Vis absorbance spectra were obtained by a Perkin-Elmer UV–Visible spectrophotometer LAMBDA-25 (USA). Transmission electron microscopic (TEM) images of the prepared QDs were recorded using a Philips CM120 (Philips Electronics Ltd., Amsterdam, Netherlands). Moreover, the X-ray diffraction (XRD) pattern was obtained using German Bruker D8Advanced Diffractometer with Cu Kα source (λ = 1.5406 Å). An ultrasonic bath with a heating system (KMH1-120W6501 model Pulse, Italy) at a frequency of 40 kHz and power of 120 W was used for the ultrasound-assisted extraction procedure. The pH of sample solutions was measured with a Metrohm 692 pH-meter. In photocatalyst process, UV irradiation was carried out with a 36 W/m² mercury lamp (Philips).

2.2. Sonochemically Ly Synthesis of Pure and Doped ZnS QDs

Sonochemically synthesis of ZnS QDs as pure and metal ion doped samples was carried out via the chemical precipitation method similar to the one reported in the literature, in an ultrasonic batch [27]. In the first step which took about five minutes long, 250 mL of zinc nitrate solution (0.1 mol·L⁻¹) was added to a three necked flask and was placed in the ultrasonic batch (40 °C). Then, 250 mL of capping agent solution (i.e. l-cysteine) with the same concentration was drop-wisely added to zinc solution by a dropping funnel; in a nitrogen atmosphere. In the next step, the sodium sulfide solution with a concentration and volume equal to that of zinc solution was drop-wisely added to the flask; under continual ultrasonic irradiation. The formation of white colloids of ZnS QDs was quite clear after adding an initial volume of sulfide solution to the zinc solution. The resulted suspension was then collected, centrifuged, washed with distilled water and finally dried for about 18 h at 50 °C. The preparation of Cu²⁺, Mn²⁺ and Ag⁺ ions doped ZnS QDs (i.e. Zn₁₋ₓMₓS) with different weight percentage (x = 0.005, 0.01 and 0.03) were carried out in the similar way; taking the desired weight percentage in the initial aqueous solution of Zn²⁺ and the dopants.

2.3. Investigation of Photocatalytic Properties of Sonochemically Prepared QDs

Photocatalytic activities of the prepared QDs were evaluated by examining the degradation of VBR solution, in the presence of nanophotocatalysts; in exposure to UV light irradiation. For this purpose, in each experiment, a certain amount of nanophotocatalyst was added to a typical VBR dye solution with the desired concentration and adjusted pH. It is worth noting that, before the irradiation, the colloidal solution was magnetically stirred in the darkness for almost 1 h to achieve the adsorption equilibrium after adsorption of the dye molecules onto the surface of the QDs powders [28]. The solution was then transferred to the photoreactor and was exposed to UV-irradiation; while continuously being stirred. The mercury lamp was put above a laboratory-made photoreactor and the distance between the test suspension and the UV lamp was constantly kept 15 cm, in order to avoid heating effects. At certain time intervals, 2 mL of suspension was taken by a syringe and was separated from the nanophotocatalysts by a filter membrane; and then the remaining dyes were analyzed by using UV–Vis spectrophotometer, during the photodegradation process. The degradation efficiency percentage (DE%) in each time was calculated from the well-known equation: DE% = [(C₀ − Cₜ)/C₀] × 100; where C₀ is the initial concentration and Cₜ is the VBR dye concentration at time t [29].

3. Results and Discussion

Fig. 1 shows the absorption spectra of the pure and metal ions doped ZnS QDs with their corresponding photographic images. The absorption band of the colloidal ZnS QDs has occurred between 270 and 290 nm whereas that of the macro-crystalline ZnS is reportedly around 350 nm [30]. The direct optical band gap (Eg) values of the pure and doped QDs were determined by Tauc’s relation [31], as: 

\[ a \nu h = \alpha_0 (h \nu - E_g)^{n/2} \]

where \( \nu \) is the photon energy, \( \alpha_0 \) and \( E_g \) are photon energy, a constant and optical band gap of the nanoparticles, respectively. The obtained \( E_g \) for the samples including ZnS, ZnS:Cu, ZnS:Mn and ZnS:Ag QDs was found to be larger than 3.68 eV (Table 1). The observed increase in \( E_g \) values of ZnS has been found out to be a result of decrease of the particles’ sizes to values lower than 10 nm [32]. The observed blue shift in the absorbance spectra of the QD samples as well as the enhancement in their \( E_g \) values may be related to a decrease in the particles’ sizes; which is resulted from the quantum size confinement effect [33].

Moreover, the structural properties of the sonochemically prepared ZnS QDs were thoroughly studied by X-Ray Diffraction technique. The
typical XRD patterns of pure and doped ZnS with 1% of dopant are illustrated in Fig. 2; where several relatively strong reflection peaks in the 2θ region of 10°–80° are displayed. The three distinguished peaks for ZnS QDs (in 2θ = 28.65°, 47.77° and 56.33°) were observed for all samples. The peak positions at the corresponding 2θ values were indexed as (1 1 1), (2 2 0) and (3 1 1), respectively; with a close compatibility with the database for crystalline ZnS with a cubic zinc blend structure (JCPDS Card: 5-566) [34]. The slight shift in the diffraction peak positions was related to the successful doping of metal ion impurities in the crystal structure [35,36]. According to Scherer equation [37], the particle size of the QD samples was calculated to be in the nanometer range, with an average particle size of 1.27 nm. Fig. 2 also depicts that the sonochemically synthesized QDs capped by l-cysteine are almost spherical in shape with nano-scaled sizes below 3 nm.

3.2. Photodegradation of VBR by the Sonochemically Prepared ZnS QDs

In this section, to investigate the photocatalytic activities of as-prepared ZnS QDs, the degradation of VBR dye was examined in exposure of a UV light irradiation and the efficiency of reaction was measured by detection of the changes in the maximum absorption intensity of VBR dye at its maximum wavelength of 591 nm. As shown in Fig. 3, pure ZnS QDs exhibit high photocatalytic activities in different concentrations of VBR dye. The pH of dye solutions was adjusted at 10.5 by aqueous solution of HCl and NaOH. This can be attributed to the small size of sonochemically prepared ZnS QDs, as well as their high surface areas; enabling the nanophotocatalysts to be active in exposure to UV light and to exhibit an excellent performance in removal of VBR dye. Besides, the decrease in the decolorization efficiency (DE %) with an increase in VBR concentration; resulting in the active sites of nanophotocatalysts to be occupied; which in turn leads to a decrease in the number of active sites, may be due to the high adsorption of dye molecules on the surfaces of QDs. Meanwhile; at high dye concentrations, light photons passages to the solution were prevented; thus, the required energy for activation of all sites will not be supplied [38].

In addition, effect of the pH solution, as a significant factor, on the
The efficiency of photodegradation reactions was studied over the pH range of 5–12, 90 min UV irradiation. Moreover, solubility of capped ZnS QDs shown to be quite possible in strong alkaline solutions; hence the above-mentioned range for pH (5–12) was selected [39]. As it can be seen from Fig. 4, the degradation of VBR was improved by increasing the pH of the initial solution and reached to its maximum value in alkaline pH of 10.5 and then significantly decreased in strong alkaline solutions. In acidic media, the positively charged surface of the particles may decrease the desired interactions between the dye molecules and the surface of QDs. Meanwhile, at the pH values lower than the isoelectric point of ZnS (7.0–7.5), the repulsive forces between the cationic dye species and the positively charged surface of QDs prevent the diffusion of the dye species and subsequently; their adsorption on the nanophotocatalysts surface [40]. Moreover; in the free radical-assisted process in low pH values; the formation of hydroxyl radicals was limited [41]. Based on the above discussions the observed decrease in the DE% is reasonable. However; at stronger alkaline solutions (pH > 11), the probable competition of hydroxyl ions with dye species for occupying the active sites may be lead to a decrease in photocatalytic activities of the sites, in environments with pH values greater than 11 [42]. Therefore, in this work, pH = 10.5 was selected as the suitable value for the experiments.

In the next studies, the effect of QDs dosages on the degradation of VBR dye was evaluated, too. According to the obtained results (Fig. 5), DE% was independent from the nanophotocatalyst dosage over the range of 3–12 mg and low amounts of QDs are needed for a high photocatalytic activity (> 98%); even at high concentrations of VBR dye. Based on the observations presented in Fig. 5A, it can be concluded that the synthetic method (i.e. sonochemically-assisted precipitation method) produced the photocatalyst particles with high surface areas and considerable active sites.

In order to study the effect of doping on photocatalytic activity of ZnS QDs, photodegradation experiments were performed in the presence of doped ZnS QDs (Cu²⁺, Mn²⁺, Ag⁺); with different dopant percentage (0.5,1.0, 3.0%; w/w), under optimum conditions. As obtained, the photodegradation efficiencies were improved by increasing

<table>
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<tr>
<th>Type of QDs</th>
<th>E_g (eV)</th>
<th>Photographical images of the samples</th>
</tr>
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<tr>
<td>Undoped ZnS</td>
<td>4.15</td>
<td><img src="image" alt="Pure ZnS" /></td>
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<td>ZnS:Cu (0.5%)</td>
<td>3.88</td>
<td>![ZnS:Cu (0.5%)]</td>
</tr>
<tr>
<td>ZnS:Cu (1%)</td>
<td>3.91</td>
<td>![ZnS:Cu (1%)]</td>
</tr>
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<td>ZnS:Cu (3%)</td>
<td>4.05</td>
<td>![ZnS:Cu (3%)]</td>
</tr>
<tr>
<td>ZnS:Ag (0.5%)</td>
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<td>![ZnS:Ag (0.5%)]</td>
</tr>
<tr>
<td>ZnS:Ag (1%)</td>
<td>3.92</td>
<td>![ZnS:Ag (1%)]</td>
</tr>
<tr>
<td>ZnS:Ag (3%)</td>
<td>3.95</td>
<td>![ZnS:Ag (3%)]</td>
</tr>
<tr>
<td>ZnS:Mn (0.5%)</td>
<td>3.81</td>
<td>![ZnS:Mn (0.5%)]</td>
</tr>
<tr>
<td>ZnS:Mn (1%)</td>
<td>3.90</td>
<td>![ZnS:Mn (1%)]</td>
</tr>
<tr>
<td>ZnS:Mn (3%)</td>
<td>3.95</td>
<td>![ZnS:Mn (3%)]</td>
</tr>
</tbody>
</table>

Fig. 2. XRD patterns of the sonochemically prepared pure and doped ZnS QDs, enclosed with a typical TEM image.
the percentage of dopant slightly from 0.0% to 1.0% of Ag\(^+\) dopant (Fig. 5B). The similar pattern was observed for other dopants (Fig. S1). However; a negative effect on photocatalytic activity of ZnS QDs was observed at high dopant percentages. The observed change in the photodegradation efficiencies may be due to the change in the number and the lifetime of free carriers (electrons/holes); as a function of type and percentage of the dopants [43]. Moreover; the change in the crystalline size of the doped samples upon doping process may affect the photocatalytic performance of the resulted samples [44]. As reported; the various amounts of dopant may provide the shallow or strong trapping sites for charge carriers in the semiconductor structure; subsequently; the number of charge carriers as well as their recombination rates may be varied [45].

In the study of salt effect on the photodegradation efficiency of as-prepared nanophotocatalyst samples; the effect of various salts with different concentrations was examined. In the salt concentration effect,
the different dye solutions with different ionic strength were prepared using 0.001, 0.01 and 0.1 mol·L⁻¹ of NaCl aqueous solution. In addition, in order to study the effect of electrolyte type, several experiments was performed in the presence of various possible co-existing salts, in optimum conditions. For this happen, a sample containing 50 mL of 50 mg·L⁻¹ VBR solution with adjusted at a pH of 10.5 was prepared in the presence of 0.1 mol·L⁻¹ of NaNO₃, Na₂SO₄, and Na₂CO₃ and the results were compared with the typical tested solution in the absence of any salt. The results were presented in Fig. 6. As seen in Fig. 6(A), the presence of electrolyte at high concentrations provided a negative effect on the photocatalytic activity of QDs; and DE% was decreased continuously by increasing the salt concentration; so that it reached to ~75% in 0.1 mol·L⁻¹ of NaCl solution. Furthermore, from Fig. 6(B), all of the used electrolytes show the masking effect on photocatalytic activity of as-prepared ZnS QDs. As reported, all of the anions can act as the radical scavenger with different strengths and react with the hydroxyl radicals in a similar pathway as: Xⁿ⁻ + ·OH → Xⁿ⁻ + OH⁻ [18]. Moreover, some anions can provide an ionic shield around the catalyst surface and reduce the electrostatic attractions between QDs surface and the dye molecules [46].

In order to examine the reusability of as-prepared ZnS QDs, six cycles experiments were performed, in optimum conditions entailing 20.0 mg·L⁻¹ of VBR dye, 3 mg of QDs, pH of 10.5, and irradiation time of 75 min. After each cycle, the concentration of the test solution was adjusted to its initial concentration, by addition of certain amounts of VBR dye. As shown in Fig. 7, no significant loss in photocatalytic activity of pure and doped ZnS QDs is observed after at-least six cycles; therefore, the sonochemically prepared QDs may be considered as photosetable and reusable nanophotocatalysts during the photo-degradation process.

3.3. Kinetic Model and Probable Mechanism

From the obtained results in the kinetic study; considering the observed changes in the absorbance intensity over the under-study reaction time period, clearly lead to the fact the kinetic of the present heterogeneous photocatalytic reactions can be expressed by the Langmuir-Hinshelwood model [47]:

\[
\ln \left( \frac{C_0}{C_t} \right) = k_{dye} t = K_{dye} t
\]

where \( C_0 \) and \( C_t \) are concentration of dye at time 0 and t (in mg/L), respectively. Also, \( k \) is the reaction rate constant (min⁻¹), \( K_{dye} \) is the
adsorption coefficient of dye onto the photocatalyst particle (L/mg), and \( k_{app} \) is the apparent rate constant calculated from the curves (min\(^{-1}\)). A typical result of the fitted kinetic model in the presence of pure ZnS QDs was shown in Fig. 8. As it can be seen in the figure, a linear relationship between \( \ln \left(\frac{C_0}{C_t}\right) \) and the time with the acceptable correlation coefficients (\( R^2 \)) implies that the photodegradation of VBR catalyzed by the sonochemically synthesized ZnS QDs follows the pseudo first-order kinetics. The kinetic data obtained by the pseudo first-order model were given in Table 2.

The probable mechanism of QDs-based photodegradation progress was already confirmed by the photo-generated electrons assisted pathway [48]. The main active species of electrons (\( e^- \)), holes (\( h^+ \)), hydroxyl radicals (OH\( \cdot \)) and superoxide radicals are commonly formed after UV irradiations inducing nanophotocatalysts' activation; assisted by the formation of charge carriers (i.e. e\(^-\)/h\(^+\)) which is resulted from electron transfers from valence-band to conduction-band. It is hypothesized that photo-generated electrons in QDs might react with the dissolved oxygen molecules; thus producing various radicals [15]. As expected, dye molecules could be oxidized or degraded by active radicals. Subsequently, the pollutant dye will dissociated to smaller or less toxic species. The probable mechanism is briefly presented in (8):

\[
\begin{align*}
QDs + UV \text{light} &\rightarrow QDs \left( e^- + h^+ + \text{VBR} \right) \quad (1) \\
QDs (e^- + h^+) &\rightarrow QDs + \left( O_2 \right)_{ads} \quad (2) \\
QDs (h^+) + (H_2O)_{ads} &\rightarrow QDs + \left( HO \right)_{ads} + \left( H^+ \right)_{ads} \quad (3) \\
QDs (h^+) + \left( HO \right)_{ads} &\rightarrow QDs + \left( HO \right)_{ads} \quad (4) \\
\left( O_2 \right)_{ads} + H^+ &\rightarrow +HOO^- \quad (5) \\
2HO^- &\rightarrow H_2O_2 + O_2 \quad (6) \\
H_2O_2 + e^- &\rightarrow OH^- + OH^- \quad (7) \\
\text{(Active radicals) + VBR dye molecules} &\rightarrow \text{Degradation of the dye} \quad (8)
\end{align*}
\]

4. Conclusion

In this research a simple, fast and efficient chemical precipitation method assisted by ultrasonic irradiation was introduced for a water-based synthesis of pure and doped ZnS QDs. The ultra-small QDs and with a uniform cubic structure was prepared in an aqueous media by applying the sonochemical approach. Moreover, the sonochemically prepared samples provided more stability and reusability in the photocatalytic experiments. The thorough study on the doping effects revealed that at low percentages of dopants, photocatalytic activity leads to enhancement of photodegradation properties. By performing a comparison between characteristics of the present photodegradation method (based on sonochemically-prepared QDs) with those of other reports (Table 3 [16,17,49–55]), it was clearly distinguished that the present method can be considered as a promising one for removal of cationic dyes with high performance degradation and reasonable re-action time.

### Table 2

<table>
<thead>
<tr>
<th>C\text{VBR} (ppm)</th>
<th>( k_{app}(2zS) ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( k_{app}(2zS_0.99C_{Cu0.01}S) ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( k_{app}(2zS_0.99Mn0.01S) ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( k_{app}(2zS_0.99Ag0.01S) ) (min(^{-1}))</th>
<th>( R^2 )</th>
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<td>10</td>
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<td>0.9973</td>
<td>3.72 \times 10^{-2}</td>
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<td>3.37 \times 10^{-2}</td>
<td>0.983</td>
<td>3.67 \times 10^{-2}</td>
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<td>15</td>
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<td>0.9990</td>
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<td>25</td>
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<td>2.86 \times 10^{-2}</td>
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<td>2.58 \times 10^{-2}</td>
<td>0.987</td>
<td>2.70 \times 10^{-2}</td>
<td>0.9990</td>
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### Table 3

<table>
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<tr>
<th>Process</th>
<th>Type of sorbent/catalyst</th>
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<th>pH of sample solution</th>
<th>Equilibrium/degradation Time (min)</th>
<th>Ref</th>
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<tr>
<td>Adsorption</td>
<td>Perlite</td>
<td>0.5 g/50 cm(^3)</td>
<td>6.0</td>
<td>60</td>
<td>[49]</td>
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<tr>
<td>Adsorption</td>
<td>Fly ash</td>
<td>1.0 g/50 mL</td>
<td>8.0</td>
<td>80</td>
<td>[50]</td>
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<td>Adsorption</td>
<td>SDS modified Fe(_3)O(_4) magnetic nanoparticles</td>
<td>10 mg/50 mL</td>
<td>7.5</td>
<td>45</td>
<td>[16]</td>
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<td>Adsorption</td>
<td>Prosopis juliflora-Modified Carbon/Zn/Alginate Polymer Composite</td>
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<td>5.0</td>
<td>40</td>
<td>[51]</td>
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<td>Adsorption</td>
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<td>270</td>
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<tr>
<td>Adsorption</td>
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<td>120</td>
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<td>Photodegradation</td>
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<td>10.0</td>
<td>120, 90</td>
<td>[17]</td>
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<tr>
<td>Photodegradation</td>
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<td>3 mg/50 mL</td>
<td>10.5</td>
<td>75</td>
<td>This work</td>
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Supplementary data to this article can be found online at https://doi.org/10.1016/j.jphotobiol.2018.02.016.

Acknowledgements

The authors gratefully acknowledge the support of this work by the University of Yasouj Research Council (Gryu-89131306) for financial support.

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