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# Ultraviolet/ultrasound-activated persulfate for degradation of drug by zinc selenide quantum dots: Catalysis and microbiology study

Ali Fakhri[a,b,*], Mahsa Naji[c], Shiva Tahami[d]

[a] Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[b] Young Researchers and Elites Club, Science and Research Branch, Islamic Azad University, Tehran, Iran
[c] Department of Materials Engineering, Karaj Branch, Islamic Azad University, Karaj, Iran
[d] Department of Biology, Karaj Branch, Islamic Azad University, Karaj, Iran

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ABSTRACT

In this study, wet chemical method used for ZnSe quantum dots (QDs) and characterized by, UV–vis, photoluminescence spectroscopy, X-ray diffraction and transmission electron microscopy. The crystallites size of ZnSe QDs was 4.0 nm. The average diameters of ZnSe QDs were 3.0–5.3 nm. Ritalin was degraded using the UV/ZnSe QDs/persulfate process. The several parameters investigated for the influence of Rtialin degradation were the temperature, the persulfate concentration, and the initial Ritalin concentration. The values of optimum parameters ware room temperature, concentration persulfate 5 mmol/L and initial Ritalin concentration 0.09 mmol/L. Comparative analyses showed the maximum degradation of Ritalin was found for ZnSe/persulfate under ultra-visible and ultra-sonic irradiation process. Comparative analysis showed the maximum degradation of Ritalin was found for ZnSe/persulfate under ultra-visible and ultra-sonic irradiation process. The values of first-order rate constants from degradation of Ritalin at 25 °C were $0.96 \times 10^{-2}$, $1.09 \times 10^{-2}$, $1.59 \times 10^{-2}$ and $2.19 \times 10^{-2}$ for US/PS, UV/PS, ZnSe/US/PS and ZnSe/UV/PS system, respectively. The antibacterial activity evaluation against two bacterials, including Gram-positive bacteria *Staphylococcus aureus* (ATCC 43300), *Bacillus megaterium* (ATCC 14581) and Gram-negative bacteria *Pseudomonas aeruginosa* (ATCC 27853), *Micrococcus luteus* (ATCC 4698) was considered. It was found that the MIC values for the antibacterial assay in the presence of ZnSe QDs were around 0.30 mM with 64.0, 66.0, 79.2, and 83.5% inhibition for the *S. aureus*, *B. megaterium*, *P. aeruginosa and M. luteus* bacterial strains, respectively. Then, results show that the ZnSe QDs have antibacterial activity.

## 1. Introduction

In recent decades, residuals of pharmaceutical compound in aquatic environments have received worldwide attention due to the enormous amounts involved and the incomplete metabolic transformation in organisms [1–3]. As a class of prevalent drugs used for both human and veterinary medicines, Ritalin are the most identified in surface water and wastewater [1]. Serious concern has been expressed for the migration potential into the environment and the long-term chronic effects of low concentrations in water [4]. The residuals of drug were demonstrated to induce the development of pathogens, posing potential threats to humans and other organisms by gene transformation [5] Similar to other pharmaceutically active compounds, drug have poor biodegradability in the water, making conventional waste water treatment plants (WWTPs) unsuitable for the reduction of drug [6]. Therefore, an alternative treatment process with cost-effective ability in the purification of drug-contaminated water is urgently needed. Then, removal or decompose of Ritalin is very important. The novelty of this work is synthesis of nanosample for degradation this pollution.

Radical-based advanced oxidation processes (AOPs) have gained much attention for Ritalin degradation, and previous studies have demonstrated that pharmaceutical compounds can be effectively degraded by conventional AOPs based on hydroxyl radicals (HR-AOPs), including UV and UV/$H_2O_2$ [7] photocatalysis [8], ozonolysis [9], sonolysis [10], Fenton and Fenton-like reaction [11]. Despite the tremendous advantages, HR-AOPs exhibit unselective characteristics for the oxidation of organic compounds resulting in low efficiency in complex environmental matrices. Recently, sulfate radical based AOPs (SR-AOP) has been proved as novel AOPs for decontamination in aqueous medium by the persulfate, peroxymonosulfate, potassium persulfate and ammonium persulfate activation [12]. The methods adapted for sulfate radical generation include heat [13], electromag-

* Corresponding author at: Department of Chemistry, CTBIAU, Tehran, Iran.
*E-mail address:* ali.fakhri88@yahoo.com (A. Fakhri).

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netic waves, ultrasound and UV [14], transition metal ions and oxides [15], bases [16], quinones [17], phenols [17] and carbon materials [18]. Among these processes, activation based UV is a promising method for high degradation efficiency, gentle reaction conditions and no metal ions leakage. Nowadays, the photo-chemical process plays an important role in pharmaceutical compound degradation [19–54].

In recent years, preparation of semiconductor QDs has much interest due to their optical properties, photo and chemical stability. QDs can be synthesized both in organic or as aqueous solutions due to a light emitting wide range of these materials [55–57]. ZnSe an n-type semiconductor has attracted considerable attention due to several applications such as, photo-detectors full color display and light-emitting diodes [58,59].

Thus, ZnSe QDs were applied for degrading Ritalin under UV + US/persulfate and the antibacterial activity was studied toward *Staphylococcus aureus*, *Bacillus megaterium*, *Pseudomonas aeruginosa*, *and Micrococcus luteus.*

## 2. Experimental

### 2.1. Materials and Characteristic Apparatus

Raw materials used in the present study were procured from Sigma-Aldrich, Ltd. Table 1 indicate the properties of Ritalin. The X-ray diffractometer (XRD) Philips X'Pert were used to examine the morphology. The particle size of the QDs was measured using Transmission Electron Microscope (TEM, JEM-2100F HR, 200 kV). Photoluminescence and UV–Vis spectroscopy were carried out using TEC Avaspec 2048 Spectrophotometer (excitation source = Xenon arc lamp 450 W).

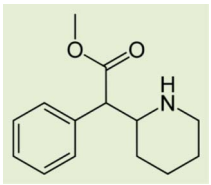
### 2.2. Preparation of ZnSe QDs

For synthesis it, $Zn(O_2CCH_3)_2$ (0.6 g) and $SeCl_4$ (0.409 g) Was considered with deionized water, hydrazine hydrate and ethylene glycol (9:6:3), respectively in a 200 mL flask and simultaneously 2 mL of 0.1 M PVP was added. Then the mixture was refluxed under stirring at 700 °C for 8 h. Then, the precipitates were washed several times with methanol and distilled water, and final calcined at 400 °C for 6 h.

### 2.3. Procedure of Degradation Performance

The bath method was conducted in an open glass cylinder (Diameter = 10.0 cm, Height = 30 cm) with the temperature controlled at 20 ± 0.5 °C using a water bath. An 11 W low-pressure mercury lamp emitting at 254 nm was used in the apparatus and preheated for 45 min until fixed dosages of Ritalin and persulfate were spiked into 2000 mL solutions to activate the reactions. The sonoreaction was performed with an ultrasonic bath (XUB6; Grant Co., Ltd., England; 35 kHz; 200 W). A magnetic stirrer under the reactor was adopted to ensure homogeneous exposure, and 0.1 M HCl and NaOH were used for the pH adjustment. 20 min of nitrogen aeration was conducted before the degradation reaction started to remove dissolved oxygen in the solutions. Using the two dimensional Gas Chromatogharphy (GC∗GC) (Kimia Shangarf Pars Research CO., Iran) for determination of Ritalin concentration.

**Table 1**
Physico-chemical properties of Ritalin.

| Characteristics | Ritalin |
|---|---|
| Chemical structure |  |
| Molecular formula | $C_{14}H_{19}NO_2$ |
| Molecular weight (g/mol) | 233.31 |
| Water solubility (mg/mL) | 1.25 |
| Boiling Point (°C) | 136 |

### 2.4. Antibacterial Activity Assay

The ZnSe QDs antibacterial activity was tested using a microdilution method and the minimum inhibitory concentration (MIC) values were measured toward Gram-positive *Bacillus megaterium* (ATCC 14581), *Staphylococcus aureus* (ATCC 43300), and Gram-negative *Pseudomonas aeruginosa* (ATCC 27853), *Micrococcus luteus* (ATCC 4698) bacteria were revived with brain heart infusion (BHI, Sigma-Aldrich) agar at 37 °C for 24 h. For the antibacterial activity assay, a modified resazurin method was used [60,61]. In a typical experiment, aliquots of 100 µL of (ZnSe QDs) stock solutions were each diluted with 100 µL of BHI and 20 µL of the bacteria suspension ($1.5 \times 10^8$ cfu/mL). Thus, the MIC value is the lowest concentration at which a color change occurred and, consequently, no visible bacterial growth was observed.

## 3. Results and Discussion

### 3.1. Characterization of ZnSe QDs Prepared

X-ray diffraction pattern for ZnSe sample prepared is shown in Fig. 1. The Wurtzite (hexagonal) structure (JCPDS card no.15-0105) of ZnSe QDs can be seen in all diffraction peaks of pattern. The several peaks with diffraction form (002), (101), (110), (103), (112), (202), (203), and (210) planes show ZnSe hexagonal phase. The crystallites size values have been found with the Scherrer formula:

$$D = 0.9\lambda/\beta Cos\theta \quad (1)$$

where β is the full-widths-at-half-maximum (FWHM) of the diffraction peaks. The crystallites size of ZnSe QDs was 4.0 nm.

Transmission electron microscopy (TEM) used for morphology characterization of the as-prepared ZnSe QDs. Fig. 2 shows the TEM images and the corresponding size distributions indicate that the average diameters of ZnSe QDs were 3.0–5.3 nm, respectively.

UV–Vis absorption applied for the optical properties of ZnSe QDs (Fig. 3). There is an obvious shoulder peaks in the UV–Vis absorption spectrum, which can be assigned to the band gap and the second excited state within each crystallite, respectively. The absorption spectra of

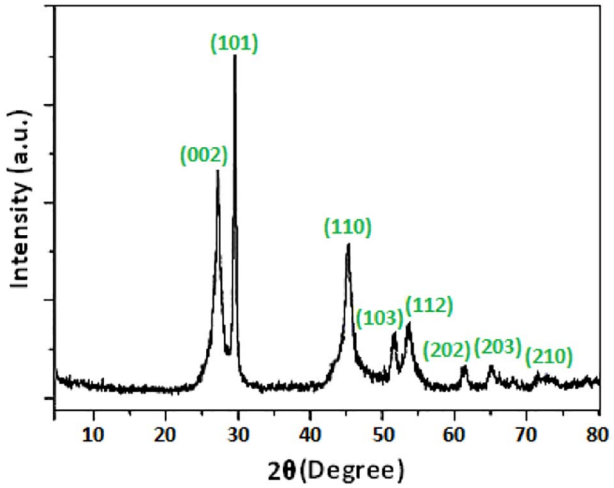



**Fig. 1.** X-ray diffraction patterns of ZnSe QDs.