Visible light assisted photocatalytic degradation of Rhodamine B dye on CdSe-ZnO nanocomposite: Characterization and kinetic studies

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ABSTRACT:

The paper involves the heterogeneous photocatalytic degradation of Rhodamine B dye (RhB) employing ZnO and ZnO/CdSe nanocomposites as photocatalysts which was synthesized via chemical bath deposition (CBD) method. Nanocomposite CdSe-ZnO powders have been synthesized by varying CdSe/ZnO molar ratios. The structural, optical, morphological, and topological characteristics of as synthesized materials were investigated using the appropriate characterization instrument such as X-ray diffractometer (XRD), diffuse reflectance spectrophotometer (DRS), atomic force microscope (AFM) and field emission scanning electron microscope (FE-SEM). It seems that the growth of CdSe particles onto ZnO particles in a core-shell like structure. The photocatalytic performance of ZnO/CdSe nanocomposite has been investigated under affecting factors such as catalyst dosage, RhB concentration and initial pH of RhB solution. The photocatalytic degradation reactions were carried out by exposing the aqueous suspension of the dye and ZnO/CdSe system with visible light. The residual concentration of RhB dye was measured using a UV-visible spectrophotometer at maximum wavelength of dye ($\lambda_{\text{max}}$ 554 nm). The decolorization process was found to follow pseudo first-order kinetics which is well expressed by the represented by the Langmuir-Hinshelwood (L-H) kinetic model. The maximum decolonization efficiency of 99% was achieved within 180 min at optimum conditions, dye conc. 10 mg/L, pH 10, CdSe (10%)-ZnO dose 1.5 g/L. The ROS studies indicate that hydroxyl radicals and holes are the predominant reactive species within the same step. Furthermore, CdSe (10%)-ZnO shows a good stability after reuse for 15 successive cycles and hence it expected to be promising in polluted water treatment.

Keywords: nanocomposite, photocatalytic degradation, Rhodamine B, visible light, CdSe-ZnO, COD
1. Introduction

In recent decades, lack of clean water has become one of the most urgent problems facing the world. The lack or scarcity of freshwater is associated with climate change like increasing greenhouse gas concentrations or with the steadily increasing pollution of pure water resources which is relates with increasing water consumption as a result of the increase in population growth beside the increase in agricultural and industrial activities [1]. The pollution issue is a complex problem due to existence of many pollutants in water such as dyes, paints, detergents, fertilizers, pesticides, heavy metals, pharmaceuticals, herbicides, microorganisms, etc [2]. Several techniques have been used to treatment and recycling of polluted waters such as adsorption[3],[4], ozone oxidation [5], coagulation and flotation [6] and membrane separation [7]. Besides, the photocatalysis process has become one of the most widely applicable and more efficient technology to remove toxic pollutants in water and wastewaters due to advantages such as better performance, quick reaction rate, toxic free property, low cost and high chemical stability of photocatalysts and high efficiency. Photocatalytic degradation using nano-semiconductors demonstrate improved photocatalytic activity because they have large (surface/volume) ratio, narrow band gap energy and more active cites compared to bulk materials[8]. Recently, nano-semiconductors such as Fe₂O₃[9], ZnO[10], SiO₂ [11] and SnO₂[12] have been receiving significant attention due to their excellent photocatalytic activities. Among above photocatalysts, ZnO has been the most commonly studied material for photocatalysis due to its advantage of excellent photocatalytic efficiency, high carrier mobility, appropriate band gap, good chemical and optical stability, suitable coast, and optimal environmental and biological compatibility [13, 14]. In spite of its high photocatalytic activities and stabilities, ZnO photocatalyst is not suitable for visible light assisted photocatalytic performance due to its wide band gap energy (3.2 eV) [10]. The combination of two or more constituent materials with different properties to formation new material composite with improved properties or even with new properties, for this goal, many researches have made great to improve the photocatalytic properties of nano-semiconductors utilizing various methods and technologies. In many applications, controlling of size and the shape of synthesized nanoparticles play a significant role in improving nanoparticles applications [15]. The narrow band gap CdSe semiconductor (1.74 eV) has become interest in the recent years because it has useful properties for photocatalysis applications[16]. CdSe matches with the visible light region and explore ultimate optical properties with visible light response. There is a significant growth in researches to achieve regular deposition of CdSe nanoparticles onto surfaces of p-type semiconductor nanoparticles (ZnO, TiO₂, SnO₂) via different techniques such as thermal decomposition [17], electrodeposition technique [18], Combined CBD-CVD [19] and sol-gel[20]. Among the above techniques, chemical solution deposition or chemical bath deposition (CBD) is a facile and relatively inexpensive process to produce various nanomaterials. For many years, researchers have been trying to sensitize ZnO nanostructure with narrow band gap materials for photocatalysis application [21, 22]. Heterogeneous
photocatalytic treatment of different wastewater contaminations originated from different types of wastewaters has been carried out in the presence ZnO or TiO₂ under UV light irradiation. ZnO and TiO₂ are the essential UV photocatalysts because they are a wide bandgap semiconductors and their bandgaps are in UV region, so they can't sense visible light [23, 24]. The UV range activity restricts the utilization of ZnO and TiO₂ as a visible-light-driven photocatalysts. For this reason, much interest in photocatalysis field has focused on the use of ZnO or TiO₂ nanocomposites to extend the optical response of these materials into the visible light range. Various modification methods and techniques have been obtained to make wide-bandgap semiconductors sense light at higher wavelengths as well. Such methods include sensitization of semiconductor surfaces with organic dyes[25] and polymerd [26], coupling of semiconductors [27, 28] and metal doping of semiconductors. In the current study, we have adopted a facile route for synthesis of ZnO/CdSe nanocomposites using chemical bath deposition technique.

2. Experimental

2.1. Chemicals: Potassium iodide, Zinc acetate, ethanol, methanol, THF (tetrahydrofuran), potassium hydroxide and hydrochloric acid HCl 37%, were supplied from BDH Chemicals. Selenium metal powder (Se, 99.5%), sodium hydroxide (NaOH), sodium borohydride (NaBH₄, 98%), cadmium chloride (CdCl₂, 99.99%) and Rhodamine B dye (empirical formula: C₂₈H₃₁ClN₂O₃, dye content 97%, λmax = 553 nm) were obtained from Sigma-Aldrich Corporation. All chemicals were of reagent grade products which were used as received without any additional purification. All solutions were prepared using double distilled water (DDW).

2.2. Photoreactor Setup: Photocatalytic experiments were performed using a 250 mL cylindrical Pyrex batch photoreactor with inner water-cooling apparatus. The photoreactor was equipped with 100 W Xenon lamp. The xenon lamp was installed inside the photoreactor and equipped with a cooling water jacket to maintain the temperature of the reaction mixture. The photoreactor was consecutively washed after every run by DDW within 5 minutes and ethanol for another 5 minutes. The outer wall of the photoreactor is covered with an aluminum foil to minimize light emissions, prevent any outer interactions and to ensure homogeneous irradiation.

2.3. Instruments: The crystal phase of synthesized materials was determined via X-ray diffraction (XRD) analyses using an XRD-6000 instrument (Shimadzu-Japan) with CuKα radiation (1.54056 Å), in the scanning 20 range of 10⁰-80⁰. The surface topography of the nanomaterial was examined by atomic force microscopy (AFM, SPM-AA3000, USA). Powder size and nanoparticle morphology were analyzed by Field Emission Scanning Electron Microscopy (FESEM) on (MIRA3 TESCAN - Czech). The optical properties of as synthesized nanomaterials were tested on an UV-Vis diffuse reflectance spectrum in the range of 200 - 1100 nm (UV-1800 UV-Vis Spectrophotometer, Shimadzu-Japan). The mineralization of Rh.B dye has been confirmed by Chemical Oxygen Demand (COD) measurement using TR 300 COD Thermoreactor with samples that have an expected range
of 0 to 150 ppm. 405 power sonic, Hwashin- Korea ultrasound bath was adopted to break ZnO particles agglomerates and increase dispersion property. The absorbance of Rh.B dye was monitored by UV-vis spectroscopy at its $\lambda_{\text{max}}$ (553 nm) using PC 1650 UV-Visible Spectrophotometer, Shimadzu-Japan.

2.3. Synthesis of nanomaterials: synthesis of the CdSe NPs includes following steps, in the first step, selenium metal (25 mg) was mixed with DDW (30 mL), then sodium borohydride (30 mg) was added to this solution. Then the solution was stirred vigorously via magnetic stirrer for 1 h at 25 °C under N$_2$ atmosphere. After complete dissolving of selenium in solution, the obtained black-gray solution converts to yellow-green color before finally becoming colorless. Furthermore, cadmium chloride aqueous solution (0.016M) was prepared. Then, CdCl$_2$ aqueous solution was transferred to a 50 mL round-bottomed flask with strong agitating continued followed by slow addition of colorless selenide ion solution (3mL). Immediately the solution color changed to reddish brown when adding of selenide ion solution, as a result of formation cadmium selenide nanoparticles. After that, the solution was stirred for a further 4 hour at 70 °C and the solution was aged in a Teflon lined stainless steel autoclave for 24 hours at 70 °C [29]. In contrast, the ZnO nanoparticles were synthesized via sol gel technique via dissolving zinc acetate dehydrate (2.195 g) into 100 mL DDW/ethanol, and stirring in an ambient condition. After that, 1.122 g of NaOH was dissolved into 10 mL DDW and was added to zinc acetate dehydrate solution drop wise with assisting continuous stirring. A few minutes later, the solution turned into jelly of a milky white color. Then, the mixture was heated for an additional 3 h without agitating at 90 °C. After that, ZnO nanoparticles were separated from suspension by centrifugation at 6000 rpm, and then was mixed with DDW and sonicated. Then, the final product after drying overnight at 70 °C, it stayed as a white fine powder [30]. CdSe-ZnO nanocomposites were synthesized by CBD method, whereas Se powder was dispersed into the pre-prepared NaBH$_4$ aqueous solution (Solution A, NaHSe). The synthesized ZnO NPs were added to a beaker containing CdCl$_2$ solution (Solution B). Meanwhile, to approach a homogenous distribution of the composite components, the solution B has been stirred continuously and then gradually added to the solution A. Afterwards, the CdSe-ZnO nanoparticles were centrifuged at 6000 rpm, successively washed several times by DDW and ethanol and then were dried in oven and then calcined at 450 °C for 4 [31]. The CdSe-ZnO powders have been synthesized via varying the CdSe to ZnO molar ratio, hence three molar ratios (1%, 5%, and 10%) of CdSe were synthesized.

2.4. Photocatalytic activity

In a typical process, the photocatalyst was dispersed 100 mL of aqueous solution of RhB dye by sonication for 15 min. After dispersion of photocatalyst, it was kept in the dark for 80 min under continuous agitation to reach the adsorption–desorption equilibrium of the dye on the photocatalyst surface. Next, the suspension was irradiated with visible light generated by 100 W-Xenon lamp. During the reaction, and to keeping the homogeneously of suspension, it was agitated continuously using magnetic stirrer. Samples were
withdrawn before and at given time intervals during the photocatalytic process, centrifuged at 6000 rpm for 15 min, and then filtered through a 0.45 μm filter paper in order to separate ZnO NPS. Finally, the absorbance of supernatant dye solution was measured using UV-Vis spectrophotometer at maximum wavelength of RhB (\(\lambda_{max} = 553\) nm), then the decolonization efficiency was calculated using following equation [32] :

\[
\text{Efficiency (\%)} = \frac{C_o - C}{C_o} \times 100\%
\]

(1)

Where \(C_o\) and \(C\) are the initial concentration and concentration at a given irradiation time \((t)\) of RhB dye \((\text{mg/L})\) respectively. The experiments were performed by varying initial pH \((4-12)\), catalyst dosage \((0.25-3.0 \text{ g/L})\) and initial dye concentration \((5-50 \text{ mg/L})\). The COD values of irradiated RhB aliquot samples were measured by colorimetric analysis method using COD standard solution range of 0 - 150 mg/L with TR 300 COD Thermoreactor.

3. Results and Discussion

CBD is known to be a simple, low temperature and inexpensive large-area deposition technique, it is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions.

3.1- Materials Characterization

3.1.1- XRD patterns: X-ray powder diffraction (XRD) is good analytical tool to investigate a phase structure of crystalline materials. XRD patterns of as synthesized nanomaterials are displayed in Figure (1). For ZnO nanoparticles, all the reflection peaks of X-ray diffraction corresponding to cubic structure with the results in good agreement with the previous works [15, 32, 33]. The diffraction peaks observed at 20 values of 32.0253, 33.6686, 35.4966, 46.7734, 55.8286 and 63.0893 degrees corresponding to the lattice planes \((100), (002), (101), (102), (110)\) and \((103)\) respectively. The peaks observed in the CdSe XRD patterns at 20 value of 25.461, 29.223, 43.921, 48.195, 62.000 and 75.342 nearly match with the \((111), (220), (311), (400), (331)\) and \((422)\) lattice planes respectively. Peaks breadth in XRD pattern of the CdSe powder, is an indication about smallest of grains and nanocrystalline nature. Also, cubic crystal structure can be observed in CdSe XRD pattern[17, 31]. After deposition of CdSe on ZnO nanostructure, major diffraction peaks of ZnO are still identifiable, suggesting that the deposition of CdSe does not affecting the ZnOcrystalline phase structure. Additionally, The XRD pattern of CdSe-ZnO nanocomposites exhibits an appearance of new diffraction peaks centered at 30.0314 ,42.394 ,50.1366, and 68.2835 degrees [17, 34]. The appearance of such peaks indicates the heterogeneously growth of CdSe NPs onto ZnO nanostructure. This suggests that CdSe NPs were successfully deposited onto ZnO NPs to form CdSe-fZnO in a core-shell growth like structure, whereas the surface is partially coated.
Fig. 1. XRD patterns of ZnO, CdSe and CdSe (10\%) - ZnO nanocomposite

3.1.2- FE-SEM analysis: SEM technique can detect and analyze surface topographical, morphological and compositional properties for micro and nanostructures. The morphology of as synthesized materials was studied by FE-SEM technique. As Figure (2) shows, the FE-SEM images display that the ZnO nanoparticles were produced with a monomodal particle size distribution and high formed in a uniform cubic shape and few particles appeared in a spherical manner, whereas the CdSe nanoparticles seem to be more uniformly in a cubic morphology. FE-SEM image of CdSe-ZnO shows the presence of good amount of CdSe-ZnO present in the core-shell structure, that growth of CdSe particles onto ZnO surface present in the core-shell like structure. Also, some aggregations can be seen in CdSe-ZnO nanoparticles, the reason behind aggregation is the reaction conditions, especially the annealing process at high temperature, whereas there is a great chance of interaction between CdSe and ZnO nanoparticles. Also, aggregation process could directly influence the homogeneity of the nanoparticle’s distribution.
Fig. 2. FE-SEM images of ZnO NPs, CdSe NPs and CdSe(10%) –ZnO nanocomposite.

3.1.3 - Atomic Force Microscopy: One of the most important tools for imaging of nanomaterials is AFM technique. Generally, AFM is used to investigate the dispersion and aggregation of nanomaterials, in addition to their size, shape, surface topography. Figure (3) shows 2D and 3D AFM images of the CdSe-ZnO nanocomposite scanned over a surface area of 1 μm × 1 μm using tapping mode. AFM micrograph confirms that the CdSe NPs are uniformly distributed on ZnO NPs. The Surface topographic parameters of synthesized photocatalysts are calculated and presented in Table (1).

Table 1. Surface topographic parameters of synthesized photocatalysts.

|          | \( R_{\text{a(nM)}} \) | \( R_{\text{s(k)}} \) | \( R_{\text{q}} \) | \( R_{\text{ku}} \) |
|----------|-----------------|-----------------|----------------|-----------------|
| CdSe     | 5.53 nm         | -0.234          | 6.23nm         | 1.91            |
| ZnO      | 1.5 nm          | 0.0111          | 17.3nm         | 1.79            |
| CdSe-ZnO | 1.42 nm         | 0.121           | 1.77 nm        | 2.86            |

\( R_{\text{a}} \): roughness average, \( R_{\text{s(k)}} \): surface skewness, \( R_{\text{q}} \): Root mean square Roughness, \( R_{\text{ku}} \): surface kurtosis.

The results indicate the bumpiness of CdSe-ZnO surface where peaks are more than the surface valleys. Also, because aggregation in the CdSe-ZnO nanoparticles, the roughness average of ZnO/CdSe NPs seem to be lesser than ZnO NPs and CdSe NPs.
Fig. 3. 2D and 3D AFM topographic micrograph of CdSe (10%)-ZnO

3.1.4- Diffuse reflectance UV–vis Spectra (DRS): The band gap and optical properties of semiconductors provide an important information about electronic structure and conductivity which is directly related to their energy band structure and hence the strength of optical transitions in such semiconductors. The optical properties of semiconductors depend to their electronic structure and particles size. Nanoscale materials exhibit significantly enhanced or altered characteristics, for instance, an increasing of the semiconductor band gap due to electron confinement [35]. The DRS (Tauc’s plot) of CdSe(10%)-ZnO nanocomposite is displayed in Figure (4) A. The energy band gap (Eg) values of as synthesized photocatalysts are estimated from the plots and are listed in Table (2). The band gap of CdSe (10 %)/ZnO is red shifted to 2.90 eV as listed in Table 2. The band gap energy values obtained from absorption spectra using Tauc’s plot method [36].

| Photocatalyst | Eg, eV |
|---------------|--------|
| ZnO           | 3.26   |
| CdSe-ZnO (1%) | 3.09   |
| CdSe-ZnO (5%) | 3.00   |
| CdSe-ZnO (10%)| 2.90   |

3.2-Degradation of Rh.B dye: The photocatalytic performance of ZnO and CdSe-ZnO (1%, 5% and 10% of CdSe loading) photocatalysts were investigated by degradation of Rh.B aqueous solution under visible light irradiation. Blank experiments have been first performed under influence of visible light to explore the photolysis effect of the reaction (in the absence of the photocatalyst) and almost insignificant degradation of the dye was achieved. Then, photocatalytic degradation experiments were performed using above nano-photocatalysts, and the decolorization efficiency was calculated using equation (1). From the results Figure (4B), CdSe-ZnO (10%) nanocomposite shows enhanced photocatalytic efficiency in comparison to ZnO, CdS and other binary composites, which may be related with its reduced band gap energy (2.9 eV). The photocatalytic decolonization
efficiency of Rh.B steadily increased from 45% to 99% when ZnO was doped with increasing ratio of CdSe up to 10 wt%.

Fig. 4. A- Optical band gap energy (Tauc's plot) of CdSe(10%)-ZnO, B- Decolonization

Efficiencies ratios of RhB under visible light irradiation using various photocatalysts. pH = 6.3, Rh.B conc. (10 mg/L), and photocatalyst dosage 1.5 g/L, reaction duration 240 min and 298 K

3.3- Decolonization of Rh.B by CdSe (10%)-ZnO nanocomposite

3.3.1- Adsorption of Rh.B: To describe the effect of agitating time on the adsorption behavior of RhB from aqueous solution, sorption experiments were carried out via adding 0.1 g. of CdSe(10%)-ZnO to 100 mL of Rh.B solutions (10 mg/L, initial pH 6.3). The suspension was kept in a chamber under dark conditions and continuous magnetic stirring for at 298 K up to beyond the equilibrium time. The suspensions of 5 mL were withdrawn during stirring at preset time intervals and the adsorbent was separated from the solutions by centrifugation at 6000 rpm for 10 minutes. Then the absorbance of supernatant dye solution was analyzed using UV-Vis spectrophotometer at the wavelength of maximum absorbance for Rh.B (λmax=553 nm). The result in Figure (5 A) showed that the adsorption equilibrium was attained within 80 min using 10 mg/L as an initial dye concentration.

3.3.2-Effect of CdSe(10%)-ZnO dosage: The reaction performance of the heterogeneous photocatalyst CdSe(10%)-ZnO included a study of catalyst loading on photocatalytic efficiency. The effects of various amounts of catalyst dosage have also been investigated, whereas, the experiments were conducted under direct visible light by adding various amounts of CdSe(10%)-ZnO within 0.25 to 3.0 g/L to Rh.B dye solutions (10 mg/L, initial pH 10 ) with continuous magnetic stirring for 240 min at 298 K. The decolorization efficiency for different CdSe(10%)-ZnO loadings has been displayed in Figure (5B). It has been is observed that the decolorization efficiency increases with increase in CdSe(10%)-ZnO dosage exhibiting maximum rate of degradation at photocatalyst dosage 1.5 g/L loading and behind this amount the efficiency steadily descend. The results proved that the optimal catalysis dosage was found to be 1.5 g/L. Hence, this suggest that an increase in photocatalyst dosage lowered the catalytic activity due to the sintering and aggregation
of ZnO NPs, thus causing poor dispersion and leading to the reduction of the active surface area. Additionally reduce irradiation field due to light scattering by the photocatalyst NPs causing a decrease in the passage of irradiation leading to a lower quantity of exposed surface [37, 38].

![Figure 5](image)

**Fig. 5.** A- Time of adsorption equilibrium B- influence of CdSe(10%)-ZnO (10%) dosage (Rh.B conc. 10 mg/L, pH 10, 298 K and reaction duration 240 min)

### 3.3.3 Effect of pH:

As wastewater contains dyes mixed with various contaminants at a variety of pHs values, therefore the pH of the medium plays an important role in decolorization of wastewater contaminations, and it is necessary to investigate the impact of pH on removal efficiency of such water pollutants [37]. Because of the amphoteric nature and amphoteric surface functionality of most metal oxide semiconductors, the pH would affect the surface charge properties of the respective photocatalysts used in photocatalytic degradation reactions [8,39]. The surface charge properties of ZnO were also found to change with a change of pH value due to the amphoteric behavior of semi conducting ZnO. In current study, to investigate the impacts of pH on decolorization efficiency, a range of pH values (4-12) were studied at the dye concentration 10 mg/L and catalyst dosage 1.5 g/L at 25 °C. Figure (8) illustrates the removal of RhB at different pH initial values after 180 min irradiation. The results showed that the decolorization efficiencies of RhB all increase with increase solution pH up to 10. The maximum removal value was achieved at pH 10. No significant impact for removal efficiency at pH values of 11 and 12 regarding Rh.B removal. This behavior could be explained by point of zero charge (pzc) of ZnO surface, as well as the molecular nature of RhB dye (nature of charges). The point zero charge of ZnO exists around a pH value of 9.0 [40]. In reported literatures, the surface charge properties of ZnO were also found to change with a change of pH value due to the amphoteric behavior of semi conducting ZnO[41]. Therefore, at pH values less than pH$_{pzc}$, the ZnO NPs carried with a positive charge, while at pH above pH$_{pzc}$ the surface of ZnO NPs is negatively charged. Thus, as Rh.B is a cationic dye, it's adsorption on ZnO surface is favored in the alkaline media. Also, in the alkaline media, the presence of a large amount of hydroxyl ions on the
ZnO NPs surface favors the formation of hydroxyl radicals which enhances the removal of dye.

3.3.4- Effect of Initial Dye Concentration: Large quantities of organic dyes are lost during dying processes and hence wastewater effluents have different dye contamination depending on their degree of fixation on the fibers and fabrics. Previous researches have reported that the photodegradation efficiency of dye is linearly decreased with increasing the initial dye concentration. This could be due to a decline in the number of surface-active sites available for the photocatalytic reaction which relate with increasing of adsorbed dye molecules and significant amount of visible light is absorbed by the dye molecules rather than catalyst surface. In the present study, as the initial concentrations of RhB dye increase more and more dye molecules are adsorbed on the ZnO surface of the catalyst which lead to formation of several layers of adsorbed dye on the ZnO surface. Hence, the penetration of light to the ZnO surface is decreases [references], therefore, the total number of photons approaching the photocatalyst surface is decreased as a result of visible light absorption by adsorbed dye molecules [42]. The adsorbed Rh.B dyes on the ZnO also impedes reaction of adsorbed molecules with the photo induced positive holes or hydroxyl radicals, since there is no direct contact of the semiconductor with them .In current study and as Figure (6B) illustrates, the kinetics of photocatalytic degradation of Rh.B dye follow the Langmuir-Hinshelwood (L-H) kinetic model:

\[ R = - \frac{d[Rh-B]}{dt} = \frac{kK_{Rh-B}[Rh-B]}{1+K_{Rh-B}+[Rh-B]^n} = k_{app}[Rh - B] \ldots \ldots \ldots (2) \]

\[ \frac{1}{k_{app}} = \frac{1}{kK_{Rh-B}} + \frac{[Rh - B]^o}{k} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3) \]

Were \([Rh.B]^o\) represents the initial Rh.B concentration (mg/L), \(k_{Rh-B}\) is the L-H adsorption equilibrium constant (L/mg), \(k\) represents the kinetic rate constant of the surface reaction (mg/L.min), and \(k_{app}\) represents the apparent first-order degradation rate constants. According to Eq. 3, the plot of \(1/k_{app}\) versus \([Rh-B]^o\) is a straight line with rate constant for the surface reaction is equal of 0.7194 mg/L.min and the adsorption equilibrium constant, \(K_{Rh-B} = 0.04436\) L/mg. This results suggest that the heterogeneous photocatalytic degradation of the Rh.B catalyzed by CdSe(10%)-ZnO nanocomposite fits with the L-H kinetics model.
Fig 6. A- Effect of initial pH on RhB decolorization efficiency (RhB conc. 10 g/L, CdSe(10%)-ZnO dosage 1.5g/L, duration reaction 180 min and T= 298 K), B- Linear transformation of the L-H type expression (RhB conc. range 5–50 mg/L, t=298 k, CdSe%-ZnO dosage 1.5 g/L,pH 10)

3.3.5- Photodegradation Kinetics: Figure (7A) show the time dependent visible spectra of Rh.B dye under visible irradiation using CdSe(10%)-ZnO nanocomposite (RhB conc.10 mg/L, pH 6.3, CdSe%-ZnO dosage 1.5 g/L,T= 298K). The photocatalytic decolorization was evaluated from the UV spectra of RhB dye in aqueous solution under influencing of reaction time. Visible absorption spectra revealed that decolorization of Rh.B dye based photocatalytic system was approached to 99% in 240 min under visible light irradiation. The absorption spectra of Rh.B dye, decreased and finally disappeared under visible light irradiation which confirmed that the dye has been removed and no significant absorption bands were recorded after irradiation for 240 nm. Figure (7B) illustrates the pseudo first order kinetics of Rh.B dye decolorizatin and the results confirm that the appropriate model to describe the photodegradation reaction of RhB dye using CdSe(10%)-ZnO nanocomposite is first order kinetic model:

\[ \ln(C_0/C_t) = kt \] …………. (4)

Where \( C_0 \) and \( C_t \) (mg/L) were the Rh.B concentrations at the initial and any time in the solution, respectively. Plotting the left-hand side of equation (4) versus t gave a straight line of slope k indicating that the reaction is first order in Rh.B dye.
3.3.6 Measuring chemical oxygen demand (COD) during dye removal: COD is an indicative method to measure the oxygen amount that required for oxidizing of organic matter in waters. As the change in COD value relates to how efficiency of organic species are degraded, the percentage COD removal for Rh.B dye was studied as a function of visible light illumination under conditions of (initial Rh.B conc. 10 mg/L, catalyst dosage 1.5 g/L, T= 298 K, pH 6.3, and duration reaction 240 nm). Results from this study indicated the percentage of COD removal reached 89 % after illumination for 240 min. Generally, the decline in COD value is less than the decolorization efficiency which attribute to the formation of new smaller colorless organic species through fragmentation of larger dye molecules [37]. Therefore, it seems that to approach almost complete dye mineralization, more irradiation time is required. Hence, after illumination for 360 min, the COD removal was reached ~98%.

3.3.7 Reusability study: The annual costs of the catalyst’s replacements used in industrial processes amounts to very large sums. The durability of catalyst is measured by the total number of catalytic cycles while maintaining its catalytic activity. Therefore, the most sustainable catalyst can enables reactions to produce a variety of required materials, before the process of its replacement [43]. In the present research, a CdSe(10%)-ZnO photocatalyst was used for fifteen times several times and has exhibited high efficiency in the removal of Rh.B dye. Figure (8B) displays the percentages of decolorization and COD removal efficiencies with reuse of CdSe(10%)-ZnO photocatalyst for 15 cycles.
3.3.7- Role of reactive oxygen species (ROS): ROS such as OH•, O$_2$•⁻, and valance band holes (h+) play an important role in photocatalytic degradation of organic pollutants. It is well known that OH• and O$_2$•⁻ species are the most effective species which have the most participation of reactions on the catalyst surface. The hydroxyl radicals are the ultimately strong oxidation and non-selective agents which lead to complete degradation and mineralization of different organic constituents of polluted waters [38]. These OH• radical is the most important species in the degradation process and the rate of degradation increases with an increase in such species [44]. The role of ROS can be estimated and their comparative effect is explored via different scavengers. To investigate the effect of main ROS in photodegradation reaction of Rh.B dye, some inhibitors (scavengers) such as tetrahydrofuran (THF, O$_2$•⁻ scavenger), potassium iodide (KI, h$^+$ and OH• scavenger), ethanol (OH• scavenger) were added [45]. Figure (14) illustrates the influence of ROS on the efficiency of Rh.B removal. The decolorization efficiency could be remarkably decreased by the addition of KI and ethyl alcohol. The decolorization efficiency of dye was 99% after irradiation for 240 min without adding any scavenger on addition of ethanol. When ethanol was introduced, the decolorization efficiency diminished to 34%, and with introduction of THF, the decolorization efficiency is significance reduced to 59%, under the same condition. Meanwhile, the addition of KI causes the decolorization efficiency remarkably reached a smaller value (19%) compared to other scavengers which indicate that iodide ions scavenge adsorbed hydroxyl radicals beside valence band holes [46]. These results show that the hydroxyl radical and superoxide anion are the most powerful intermediates.

Fig. 8. A- Decolorization and COD removal efficiencies, B- Decolorization and COD removal efficiencies with reuse after 15 catalytic cycles using CdSe(10%)-ZnO nanocomposite. CdSe(10%)-ZnO dosage 1.5 g/L, dye conc. 10 mg/L, pH 6.3, 2989 K and illumination time 360 min)
4. Conclusions

In the present study, CdSe-ZnO nanocomposites were successfully synthesized and characterized by XRD, UV-DRS, FE-SEM and AFM techniques. The heterogeneous growth of CdSe nanoparticles on ZnO nanoparticles to form core–shell like morphology. Therefore, the results reveal that as CdSe ratio increases, the band gap energy of ZnO decreases. The as synthesized CdSe-ZnO nanocomposites have been proven to be a promise photocatalysts in the degradation of rhodamine B dye. The results clearly show that CdSe(10%)-ZnO nanocomposite exhibits a higher efficiency performance than other photocatalysts in the photocatalytic degradation of Rh.B dye in aqueous solution. The decolorization efficiency has been studied at different catalyst dosage, dye concentrating and pH. The maximum decolonization efficiency of 99% was achieved within 180 min by use 1.5 g/L of CdSe(10%)-ZnO at pH of 10, while COD analysis showed 98% reduction in COD after 360 min of illumination with visible light.

5. References

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