

Hydrothermal synthesis of $\text{Pr}_x\text{Cd}_{1-x}\text{Se}$ nanoparticles: Investigating the enhanced photocatalytic activity under visible light

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ABSTRACT

In the present study, undoped and praseodymium doped CdSe ($\text{Pr}_x\text{Cd}_{1-x}\text{Se}$) nanoparticles were prepared via a facile hydrothermal method at 150 °C for 24 h. The products were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). These analyses confirmed the nonometric diameter of as-synthesized samples. The photocatalytic activity of Pr-doped CdSe nanoparticles was investigated by the decolorization of malachite green (MG) solution under visible light irradiation. The color removal efficiency of pure CdSe and $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ was 35.65 % and 94.96 % after 180 min of treatment, respectively. The significantly enhanced photocatalytic activity of the Pr-doped CdSe photocatalyst was mainly attributed to the suppression of electron/hole recombination on the surface of the catalyst due to the Pr loading. In this study, 6 mol % was the most suitable content of Pr^{3+} in CdSe, at which the recombination of photoinduced electrons and holes could be effectively inhibited and thereby the highest photocatalytic activity was formed. The reusability tests were done to test the stability of the used photocatalysts. There was almost no loss of photocatalytic activity after ten cycles of repeated experiments.

1. INTRODUCTION

The release of the colorful wastewaters in the environmental water resources is a dramatic source of aesthetic pollution, eutrophication and perturbations in the aquatic life. As international environmental standards are becoming more severe, technological systems for the removal of organic pollutants, such as dyes are becoming more advanced. Conventional methods of physical, chemical and biological techniques are frequently used technologies for removal of refractory organic pollutants from industrial wastewater effluents. But among the used methods for water treatment, heterogeneous

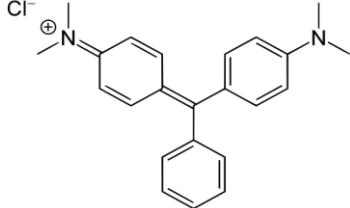
photocatalysis by the use of the semiconductor photocatalysts has been considered as an efficient alternative method for polluted water treatment (Fathinia 2010). Different semiconductors have been used to exhibit photocatalytic behavior. TiO₂ and ZnO are the most commonly utilized semiconductors for organic pollutant degradation (KimLim 2008, Khataee 2011). But, TiO₂ and ZnO are wide band gap semiconductors (band gap around 3.2 eV and 3.37 eV for TiO₂ and ZnO, respectively) which adsorb light only in the UV region (Xiao 2008, Saif 2013). One of the disadvantages of these wide band gap semiconductors is that they can only be activated under UV irradiation (HoYu 2006). To overcome this problem, various composite and hybrid materials were produced to be used under visible light range (HoYu 2006, Wu 2013, Robel 2006). Among these materials, CdSe, an n-type semiconductor, has been extensively investigated owing to its small band gap energy which was reported to be from 1.65 to 1.8 eV (BiswalParida 2013, Chen 2012). CdSe could be excited and produce electron/hole pairs when the light wavelength of irradiation source is less than or equal to 730 nm (Robel 2006, Chen 2012).

Up to now, modified CdSe nanomaterials have been used for decolorization of organic pollutant. However, some issues are reported regarding the low efficiency CdSe under visible light irradiation which prevent its practical application including low adsorption capacity and separation efficiency of electron/hole pairs (Xiao 2008, Saif 2013, Ma 2010).

Generally, the adsorption capacity of CdSe particles could be improved by producing CdSe nanomaterials containing enhanced specific surface area. The recombination of electron/hole pairs could be efficiently inhibited by preparing hybrid or composite semiconductor materials containing CdSe. Regarding this context, CdSe-Pt nanorods (Elmalem 2008), hybrid CdSe-Au nanostructures (Costi 2008), carbon nanomaterials-CdSe composites including graphene (Oh 2011, Ghosh 2013) and graphene oxide (Ghosh 2013) and fullerene-CdSe composites (Meng 2012) have been successfully prepared and reported for degradation of various organic compounds. Nevertheless, there have been no reports regarding the improvement of CdSe photocatalytic properties under visible light irradiation via doping of transition rare earth metals such as Pr, a lanthanide metal.

So, in the present work we present a new method to prepare cubic CdSe nanoparticles using cadmium acetate as a cationic source and sodium selenite as an anionic source in the presence of ethylenediaminetetraacetic acid (EDTA), as template agent to avoid further aggregation of synthesized nanoparticles, using a hydrothermal method. The hydrothermal technique is a “one-pot chemical process”, which facilitates the control of particle size, particle morphology, phase composition, and surface chemical properties by adjusting experimental parameters such as temperature, pressure, process duration and the pH value of the solution (Oh 2011). The physical properties of the synthesized samples were characterized by XRD and SEM. Also, the prepared CdSe and Pr_xCd_{1-x}Se nanoparticles were used as a photocatalyst for decolorization of MG as an anionic dye (See Table 1). Moreover, the performance of synthesized samples in terms of decolorization efficiency and kinetic rate constant was studied and compared. To the best of our knowledge, there is no previous literature report concerning the use of CdSe and Pr_xCd_{1-x}Se nanoparticles for the removal of MG.

Table 1. Characteristics of Malachite Green.

Color index name	Chemical structure	Molecular formula	λ_{\max} (nm)	Color index number	Mw (g/mol)
C.I. Basic Green 4		C ₂₃ H ₂₅ CIN ₂	619	42000	364.91 1

2. EXPERIMENTAL DETAILS

2.1 Materials

All chemicals used in this study were of analytical grade and were used without further purification. Cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 98%), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ 80%), sodium selenite (Na_2SeO_3 99%) were purchased from Loba Chemie Co. (India), and NaOH was obtained from Merck. praseodymium (III) nitrate hexahydrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.99%), was purchased from Aldrich. EDTA ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$) was purchased from Rankem Co. (India), MG and ethanol (90%). $\cdot 4\text{H}_2\text{O}$ was purchased from Shimi Boyakhsaz Co. (Iran) and Iran Daru Co. (Iran), respectively.

2.2 Synthesis of CdSe and Pr-doped CdSe samples

CdSe and Pr-doped CdSe nanoparticles with variable Pr mole fractions (0-10 % mol) have been prepared by hydrothermal method using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as the reducing agent. In a typical synthesis, 1 mmol Na_2SeO_3 powder and 1 mmol NaOH and appropriate molar ratios of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were first dissolved in 70 mL distilled water. Under middle speed stirring, 1 mmol EDTA was dissolved in 20 mL distilled water and added to the above solution. After being stirred uniformly, hydrazine was added drop wise to the above solution. The resulting solution was moved into a 110 mL Teflon-lined stainless-steel autoclave, placed in an oven at 180 °C for 24 h, and then the autoclave was allowed to cool to room temperature naturally. As-synthesized CdSe and $\text{Pr}_x\text{Cd}_{1-x}\text{Se}$ nanoparticles were collected and washed with distilled water and ethanol several times in order to remove residual impurities, and then dried at 60 °C for 5 h. The final black powders were obtained as a result.

2.3 Characterization instruments

XRD (D8 Advance, Bruker, Germany) was used to identify the crystal structure, mean crystal size and phase purity of the CdSe and Pr-doped CdSe nanoparticles with monochromatic high-intensity CuKa radiation ($\lambda=1.5406 \text{ \AA}$). The accelerating voltage of 40 kV and emission current of 30 mA were used. The Debye–Scherrer formula was employed to calculate the average crystalline size of the catalysts (Patterson 1939). SEM (S-4200, Hitachi, Japan) was used to observe the surface state and structure of the prepared nanoparticles using an electron microscope.

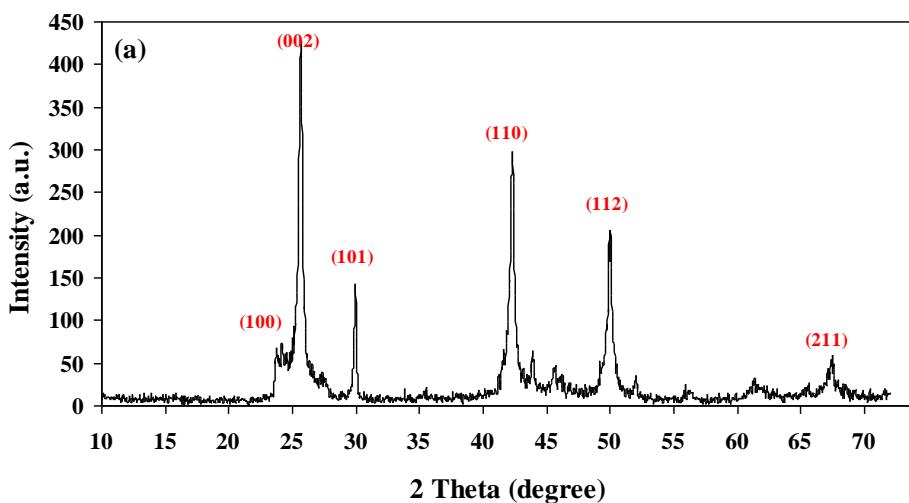
2.4 Measurement of photocatalytic activity

The photocatalytic activity of undoped and Pr-doped CdSe nanoparticles was evaluated by the decolorization of MG in an aqueous solution under visible light. In a typical process, 0.1 g of the photocatalyst powder was added into 100 mL MG solution with an initial concentration of 5 mg/L. The suspension of photocatalyst and MG was magnetically stirred in a quartz photoreactor in the dark for 15 min to establish an adsorption/desorption equilibrium of the dye. Then, the solution was irradiated by a 6W fluorescent visible lamp (GK-140, China) as the light source for a set irradiation time. Visible light irradiation of the reactor was performed for 15, 30, 45, 60, 90 and 120 min. Samples were withdrawn regularly from the reactor, and dispersed powders were removed in a centrifuge. The color removal was evaluated by determining its absorbance at $\lambda_{\max}= 619 \text{ nm}$ by using UV–Vis spectrophotometer, Lightwave S2000 (England). The decolorization efficiency (DE (%)) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one.

3. RESULTS AND DISCUSSION

3.1 Characterization of the synthesized products

The XRD patterns of the CdSe and $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ nanoparticles were depicted in Fig. 1.



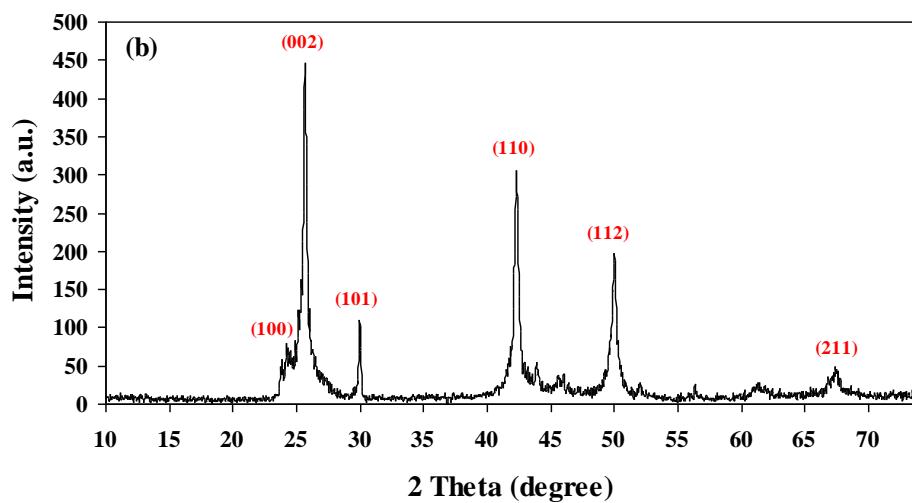
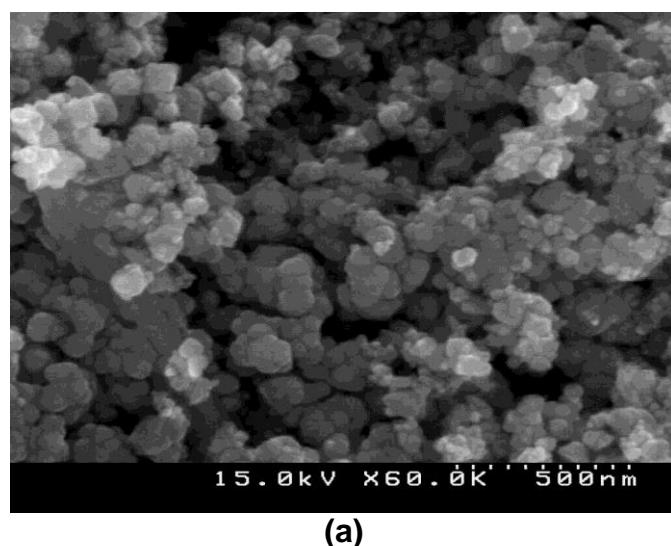


Fig. 1 Powder X-ray diffraction pattern of (a) CdSe and (b) $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ samples. The XRD diffraction peaks at 2θ of 25.4° , 42° , and 49.6° can be classified to the (100), (002), (101), (112) and (211) plane reflections and is associated with cubic crystal structure CdSe according to the standard powder diffraction data (JCPDS 65-2891 for CdSe, cubic) (Raevskaya 2006, Ghosh 2013). Also, the same typical peaks for CdSe were detected for $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ sample indicating that there is no change in the crystal structure upon Pr doping. No peak for impurities was detected, confirming that the applied hydrothermal method in this study was successful in synthesizing the mentioned samples. Calculating from the Debye–Scherrer formula (Patterson 1939), the average size of the nanoparticles was about 15 nm. In order to further clarify the size and the crystal structure of the nanoparticles, SEM image was taken at different magnifications. Fig. 2 shows the SEM microphotographs of the CdSe and Pr doped CdSe particles, respectively. According to Figs. 2a and 2b, the diameter of these particles is around 50-100 nm. Also, these figures confirm that doping of Pr^{3+} into the structure of CdSe does not change the morphology of CdSe nanoparticles.



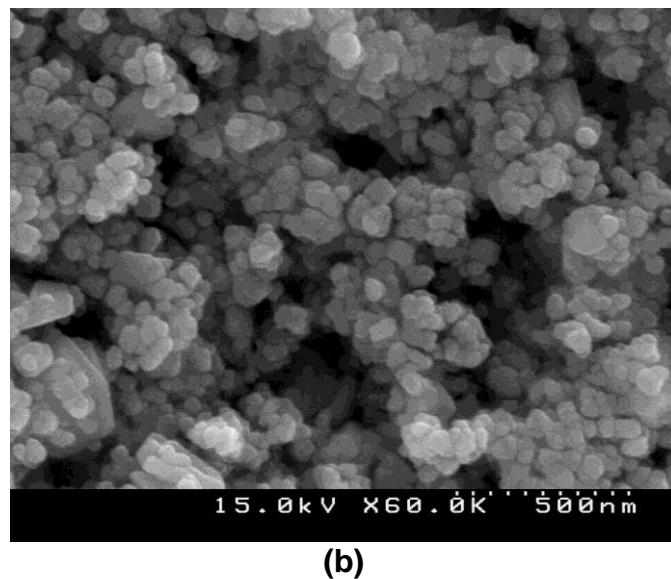
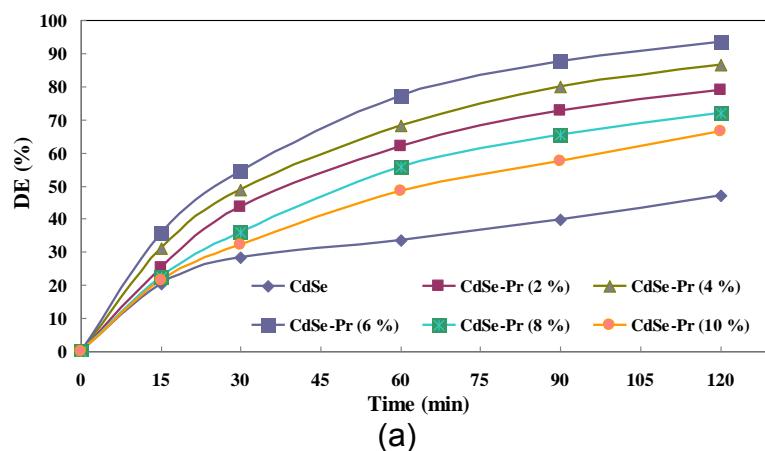


Fig. 2 SEM images of (a) CdSe and (b) $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ nanoparticles synthesized at 150 °C and 24 h.

3.2 Effect of operating conditions on the photocatalysis of MG

3.2.1 Effect of Pr^{3+} content of $\text{Pr}_x\text{Cd}_{1-x}\text{Se}$ nanoparticles

Fig. 3 represents the photodegradation of MG in the presence of $\text{Pr}_x\text{Cd}_{1-x}\text{Se}$ with different mole fraction ($x = 0.00, 0.02, 0.06, 0.08$ and 0.10) under visible light irradiation. Fig. 3a and 3b show the linear relationship of MG decolorization and the related kinetic constant during the photocatalytic reaction at different Pr^{3+} mole fractions by the pseudo first-order model. Fig. 3c shows that the kinetic constant of photocatalytic reaction increases with increasing the Pr^{3+} content up to 6 % and then decreases.



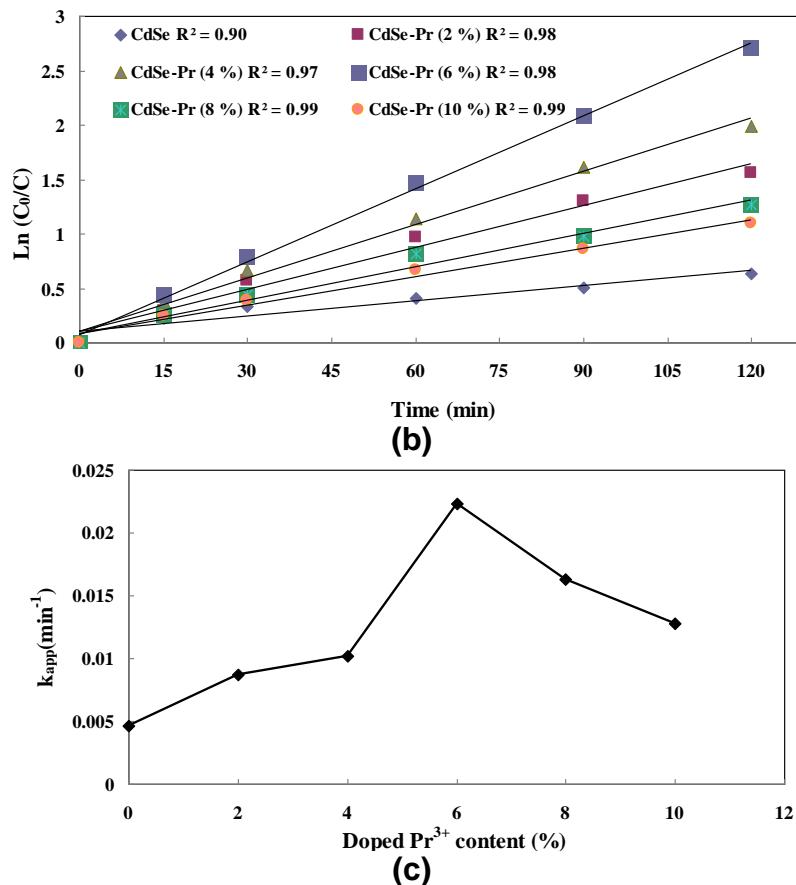


Fig. 3 (a) The effect of Pr³⁺ dopant content on the decolorization of 5 mg/L MG (catalyst loading 1.0 g/L); (b) Apparent pseudo first-order reaction kinetic and (c) Variation of apparent kinetic constant for MG decolorization during the photocatalytic reaction at different Pr³⁺ contents

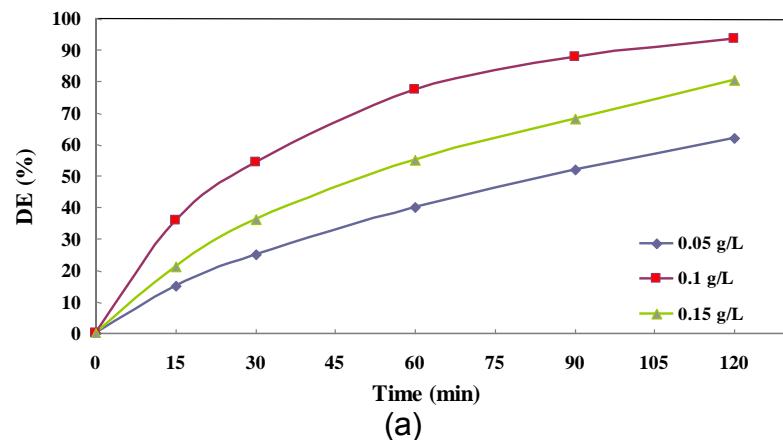
So, it is clear that, the optimum content of Pr is 6 %, which has the best photocatalytic activity. The variation of decolorization efficiency with Pr concentration could be understood by the following mechanism. Under the irradiation of Pr_{0.06}Cd_{0.94}Se, Pr³⁺ works as electron scavenger, which may react with the superoxide species and prevents the electron/hole pairs recombination, and thus increases photo-oxidation efficiency (ChiouJuang 2007). The possible reaction is represented in Eq. (1):



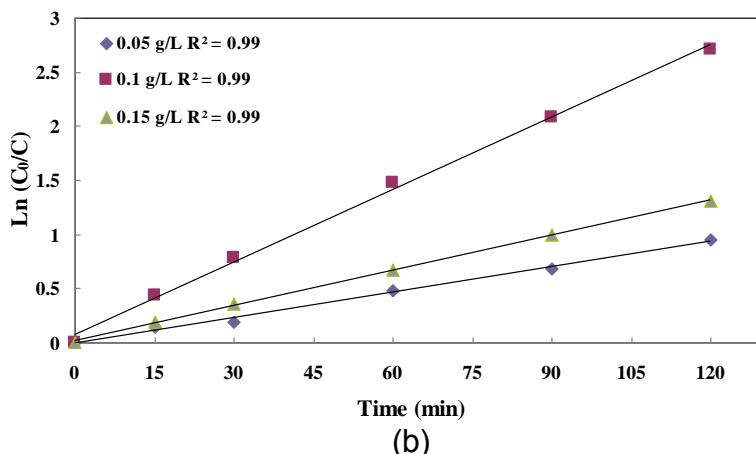
On the other hand, too many Pr³⁺ ions and related vacancies and defects may capture both electron/hole pairs which increase the recombination of electron/hole pairs and decrease their life time (Cong 2007, Asiltürk 2009). This might lead to a further decrease in degradation efficiency. So, an optimum content of Pr³⁺ is essential to separate photoinduced electron/hole pairs and increase the life time of charge carries.

3.2.2 Effect of photocatalyst dosage and reusability

The initial rate of photocatalytic decolorization process is dependent on the photocatalyst concentration (Ghosh 2013, Ghosh 2013, Asiltürk 2009). In order to compare the effect of different dosages of $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ (0.05–1.5 g/L), on the removal efficiency of MG, a series of experiments were done in the 5 mg/L initial concentration of MG. The results were presented in Fig. 4. As can be seen, the color removal efficiency significantly increased with an increase in the amount of photocatalyst from 0.05 to 1.0 g/L, however, a further increase in catalyst dosage (1.5 g/L) slightly reduces the photodegradation efficiency. These results indicated that the photocatalyst dosage of 1.0 g/L would be the optimum amount. In principle, the photodegradation rate of pollutants is affected by not only the active sites but also the photo-absorption of the catalyst used. Adequate dosage of the photocatalyst increases the generation rate of electron/hole pairs for enhancing photodegradation, but a high dosage of the photocatalysts will decrease the light penetration by the suspension and reduce the degradation rate (Xiao 2008, Asiltürk 2009).



(a)



(b)

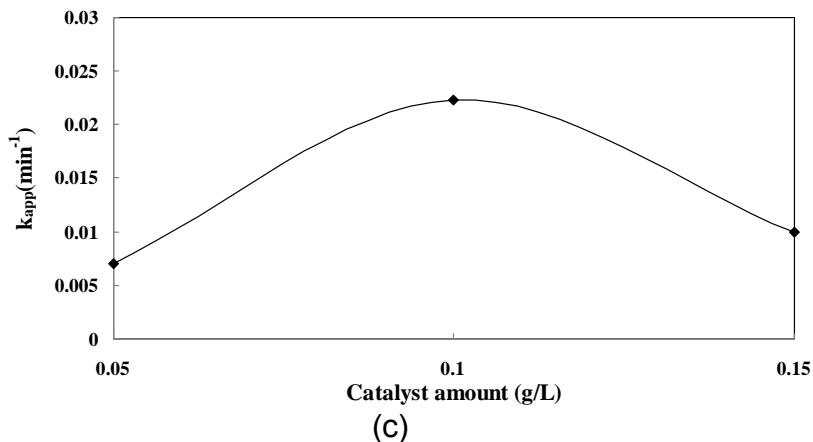


Fig. 4 (a): The effect of photocatalyst loading on the decolorization of 5 mg/L MG by the $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$; (b): Apparent pseudo first-order reaction kinetics and (c): Variation of apparent kinetic constant for MG decolorization during the photocatalytic reaction at different photocatalyst concentration.

Fig. 5 shows the reusability tests of $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ photocatalyst in the decolorization of MG, during 10 cycle experiments under optimum conditions as: 5 mg/L of MG, 1.0 g/L of $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ photocatalyst and irradiation time of 120 min. After each decolorization experiment, the photocatalyst was washed with distilled water and then dried at 60 °C for 5 h and then used for new experiment.

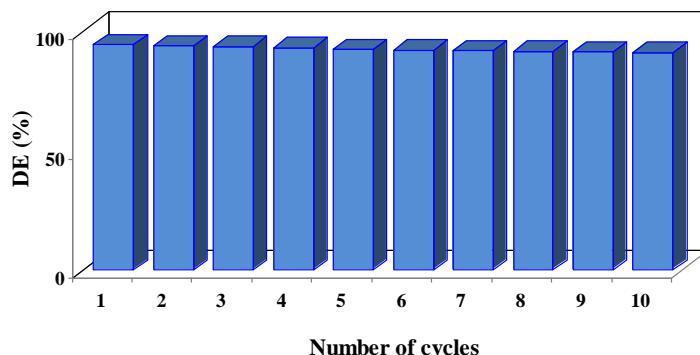


Fig. 5 Reusability behavior of $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ as photocatalyst in photodecolorization of 5 mg/L of MG in the presence of 1.0 g/L of $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ photocatalyst and irradiation time of 120 min.

Fig. 5 exhibited that the reused photocatalyst does not show any considerable change in the color removal of MG during 4 cycles of photocatalytic process. The obtained results emphasize the excellent chemical stability of the catalysts that is advantageous for practical applications.

4. CONCLUSIONS

In this research, a simple and efficient hydrothermal method was applied for the synthesis of CdSe and Pr doped CdSe nanoparticles as a new visible light activated semiconductors.

The results from XRD and SEM analysis confirmed that the doping of Pr^{3+} ions into CdSe structure neither change the crystal structure nor the morphology of CdSe nanoparticles. In photodecolorization studies, the CdSe and Pr doped CdSe nanoparticles were used as a photocatalyst for efficient removal of MG under visible light irradiation. The decolorization efficiency was 35.65 % for CdSe and 94.96 % for $\text{Pr}_{0.06}\text{Cd}_{0.94}\text{Se}$ at 120 min of photocatalytic process. The mole fraction of 0.06 of Pr in nanoparticles showed the highest photocatalytic activity for dechlorination of 5 mg/L MG in the presence of 1.0 g/L of catalyst within 120 min. The reusability tests confirmed that there was almost no loss of photocatalytic activity after 10 cycles of repeated experiments.

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