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Application of CdTe/CdS/ZnS core/multi-shell QDs as a high-performance nanocatalyst for degradation of methylene blue from water

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ABSTRACT

The application of nanocatalysts for the removal of dyes from industries' wastewater and effluents has attracted great attention these days. In this paper, CdTe/CdS/ZnS core/multi-shell quantum dots were used as a nanocatalyst for the degradation and removal of methylene blue, methylene orange, and rhodamine b dyes from water. The obtained results showed that CdTe/CdS/ZnS nanocatalyst had excellent ability for removal of methylene blue dye from water and after 60 min reaction time, methylene blue dye was completely degraded (100%). Also, the degradation percentage of rhodamine b and methylene orange dyes was obtained at about 80.2% and 55.2%, respectively. The radical scavenger experiment was used to study which active radicals play a key role in the photocatalyst process of CdTe/CdS/ZnS nanocatalyst with methylene blue dye and results showed that electrons play a key role in the degradation process. The successful formation of CdTe/CdS/ZnS core/multi-shell QDs was studied by XRD, EDS, PL, absorbance, and TEM analysis.

1. Introduction

Water pollution is one of the most important global concerns. Dye pollution is one type of water pollution. Dye molecules have a wide range of applications in the textile, leader, paper, and pigment industries [1-3]. The presence of dyes in industrial effluents and wastewater causes pollution and irreparable damage to the environment because these dyes are very toxic and also have high stability which can't be removed easily from water [2-6]. Hence, the treatment of industrial effluents is an important issue. There are many methods for the treatment of wastewater and effluents from organic dyes such as absorption, ion exchange, advanced oxidation process (AOPs), reverse osmosis, etc [5-8]. Among these treatment methods, AOPs methods due to their cost efficiency, dye degradation efficiency, and high potential to be used in small industries have attracted great attention among scientists [9,10]. The photocatalyst degradation process is one of the AOP methods in which the degradation process is done in the presence of a semiconductor catalyst [11]. II-VI_B semiconductor QDs especially CdTe QDs due to their unique optoelectric properties and suitable bandgap have a good potential to be used as high-performance nanocatalysts for the treatment of wastewater and effluents from organic dyes [12-16]. Li et al. reported the photocatalyst activity of CdTe/TiO_2 nanoparticles with rhodamine b dye [17]. Molaei et al. reported the application of CdTe/ZnS QDs as a photocatalyst material for the degradation of rhodamine b, methylene blue, and methylene orange dyes from water [18]. Subramanian et al. reported the photocatalyst activity of CdTe/$NiTiO_3$ nanostructure for the treatment of methylene blue dye from industrial effluents [19]. Benavente et al. investigated the

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photocatalyst activity of H2Ti3O7/CdTe nanocomposite for the degradation of methylene orange and 4-chlorophenol dyes from water [20]

In this work, CdTe/CdS/ZnS core/multi-shell QDs were synthesized by a facile and one-pot photochemical method. X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), photoluminescence (PL), and absorbance analysis were done for studied successful formation of CdTe/CdS/ZnS core/multi-shell structure. The photocatalyst ability of CdTe/CdS/ZnS core/multi-shell nanocatalyst was studied by methylene blue, methylene orange, and rhodamine b dyes under different conditions. In addition, the radical scavenger experiment was done to investigate which radical species has a main role in the photodegradation process.

2. Materials and methods

2.1. Materials

Cadmium acetate dihydrate ($C_4H_6CdO_4*2H_2O$), Zinc acetate dihydrate ($C_4H_6O_4Zn*2H_2O$), Tellurium powder (%99), Thioglycolic acid (TGA), and Sodium borohydride ($NaBH_4$) were purchased from Merck company. Sodium selenite (Na_2SeO_3) was obtained from Sigma-Aldrich company. All used materials were of the analytical grade and were utilized without further purification.

2.2. Synthesis of CdTe/CdS/ZnS core/multi-shell QDs

CdTe core QDs were synthesized by a microwave method which was reported previously [21]. CdS and ZnS shells were grown around CdTe QDs with a photochemical method [22]. Briefly, 0.1 g cadmium acetate and 0.08 g zinc acetate were dissolved in 30 ml DI, separately. Then, 100 µL TGA was added to cadmium bakear and after stirring for a few minutes, pH was adjusted to 9 by NaOH. At the end, prepared solutions were mixed and 20 ml of synthesized CdTe QDs (with 1 mg/ml concentration) were added. The final solution was placed under a high-pressure mercury lamp (250 w) as a UV irradiation source for as long as 10 minutes.

2.3. Photocatalyst activity section

For investigating the photocatalyst ability of CdTe/CdS/ZnS core/multi-shell QDs, absorbance spectrum was used. Methylene blue (MB), methylene orange (MO), and rhodamine b (RB) dyes have characteristic peaks at about 664 nm, 465 nm, and 554 nm, respectively. The photodegradation of dyes could be measured by the characteristic peak reduction. For preparation of the photocatalyst process solution, different amount of CdTe/CdS/ZnS nanocatalyst was added to 25 ml of 10 ppm dye solution. After that, the prepared solution was dispersed in darkness for as long as 20 minutes for absorption-desorption equilibrium. In the end, the final solution was placed under a UV lamp (250 w) and irradiated at different times.

2.4. Characterization section

Field Emission Scanning Electron Microscopy (EDX-FESEM) was carried out on a ZEISS (SIGMA VP). X-ray diffraction (XRD) data was recorded by D8-Advance Bruker X-ray diffractometer using Cu-Kα radiation at the wavelength of 1.54 Å. The optical absorption spectrum was recorded using an Avantes spectrometer (AvaSpec-2048 TEC). Transmission electron microscope (TEM) images were obtained using a LEO912 AB electron microscope operating at the bias voltage of 200 kV.

3. Results and discussion

3.1. Structural and morphology study of CdTe/CdS/ZnS QDs

Fig. 1 illustrates XRD patterns of synthesized CdTe and CdTe/CdS/ZnS core/multi-shell QDs. CdTe QDs have three main peaks at about 23.7°, 40.1°, and 47.1° which are related to (111), (220), and (311) planes of CdTe cubic structure, respectively [21]. In the XRD pattern of synthesized CdTe/CdS/ZnS core/multi-shell QDs, these three peaks are observable yet with a slight shift. This shift of diffraction peaks to the higher angles is a reason for the successful formation of CdS and ZnS shells around CdTe core QDs and the successful formation of CdTe/CdS/ZnS core/multi-shell QDs. Due to the Bragg equation, after the synthesis of CdS and ZnS shells around CdTe core QDs, the lattice constant of CdTe QDs decreases and it results in an increase of diffraction peaks to the higher angles. The Bragg equation is:

$$2d\sin\theta = n\lambda \quad (1)$$

In this equation, λ is the X-ray wavelength, n is a positive integer, θ is the diffraction angle, and d is the spacing of diffracting planes.

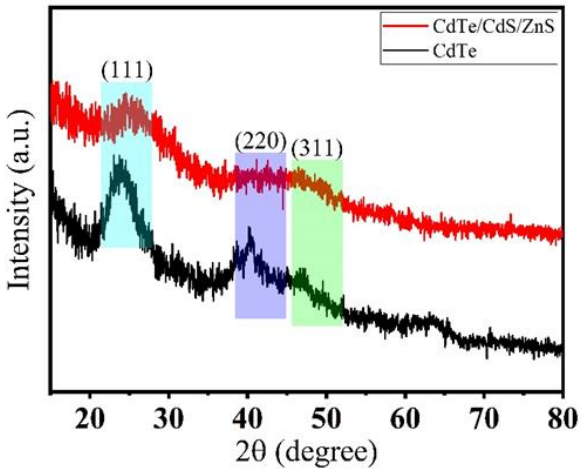

Fig. 1. XRD pattern of CdTe and CdTe/CdS/ZnS core/multi-shell QDs

Fig. 2A depicts the PL spectrums of CdTe and CdTe/CdS/ZnS core/multi-shell QDs. CdTe QDs have green photoemission with a PL peak at about 535 nm. After the formation of CdS and ZnS shells around CdTe core QDs, the PL intensity of CdTe QDs increased significantly which is another reason for the successful formation of CdTe/CdS/ZnS core/multi-shell structure [22]. Figure 2B shows the absorbance spectrums of CdTe and CdTe/CdS/ZnS core/multi-shell QDs. As is shown in this picture, the absorbance band edge of CdTe QDs after the

formation of CdS and ZnS shells increased which is a reason for the synthesis of CdS and ZnS shells around CdTe QDs and increasing of nanoparticle size [22].

Fig. 3A depicts the EDS analysis of CdTe/CdS/ZnS core/multi-shell QDs. The presence of the constituent elements of the CdTe/CdS/ZnS structure means Cadmium (Cd), Zinc (Zn), Sulfur (S), and Tellurium (Te) elements are observable in this picture, which confirms the successful formation of CdTe/CdS/ZnS structure. Figure 3B shows a TEM image of synthesized CdTe/CdS/ZnS QDs. This picture shows that the synthesized CdTe/CdS/ZnS nanocatalysts were spherical.

3.2. Study of photocatalyst ability of CdTe/CdS/ZnS nanocatalyst

For investigating the photocatalyst activity of CdTe/CdS/ZnS core/multi-shell QDs, 30 mg of nanocatalyst was added to 25 ml 10 ppm MB dye solution. Figure 4A shows the absorbance spectrum of MB dye during the photocatalyst process. As is shown in this picture, with increasing UV irradiation time absorbance characteristic peak of MB dye decreased which is related to MB photodegradation of MB dye during the photocatalyst process. The obtained results showed that MB dye after 60 min photocatalyst process completely degraded. Figure 4B shows the logarithmic during MB concentration with irradiation time. The photocatalyst rate of CdTe/CdS/ZnS nanocatalyst was obtained by the following equation:

$$-ln\ C/C_0 = kt \qquad (2)$$

In this equation, t is the irradiation time (min), C_0 is the initial concentration of MB, C is the MB concentration at a particular time, and k is the pseudo-linear first-order kinetic constant. The pseudo-linear photodegradation rate of MB was obtained at about 3×10^9.

For investigating the effect of catalyst mass on the photocatalyst process, different amounts of CdTe/CdS/ZnS nanocatalyst (20 mg, 25 mg, 30 mg, and 35 mg) were tested. As is shown in Figure 5A, with increasing of nanocatalyst mass from 20 mg to 30 mg, the photocatalyst process was increased but with increasing of nanocatalyst mass from 30 mg to 35 mg the photocatalyst process didn't have any change. So, the 30 mg of CdTe/CdS/ZnS nanocatalyst mass was chosen as the optimum mass.

For studying of photocatalyst activity of CdTe/CdS/ZnS nanocatalyst, two different dyes were examined. Figures 5 C & D show the absorbance spectrums of MO and RB dyes in the photocatalyst process, respectively. The obtained results showed that after 60 min from the photocatalyst process, 55.2% of MO dye and 80.2% of RB dye were degraded. The obtained results confirmed that the CdTe/CdS/ZnS nanocatalyst had the best degradation with MB after RB and MO dye.

In the photocatalyst process, different active species such as e^-, h^+, and OH^- are present. In this section, silver nitrate ($AgNO_3$), ethylenediaminetetraacetic acid (EDTA), and sodium iodide (NaI) were used as e^-, h^+, and OH scavengers, respectively [23-25]. The radical scavenger results are plotted in Figure 6. As is shown in this picture, without any scavenger, the photocatalyst process was done in 60 min. With the addition of EDTA and NaI, the photocatalyst process didn't stop and confirmed that h^+ and OH radicals didn't have any effective role in the photocatalyst process. Still, with the addition of $AgNO_3$ the photocatalyst process decreased dramatically. This result showed that electrons had a main role in the photodegradation of MB dye with CdTe/CdS/ZnS nanocatalyst

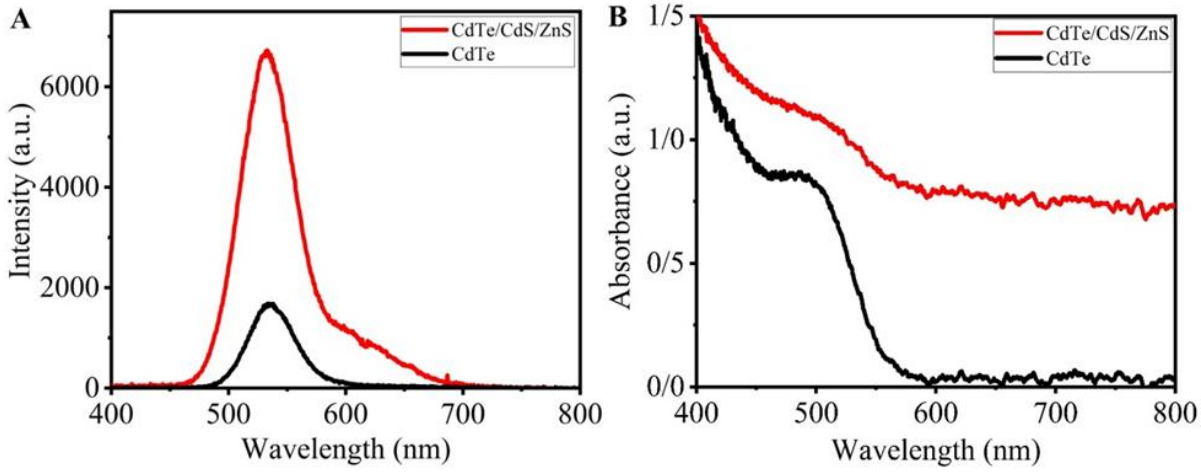

Fig. 2. PL (A) and absorbance (B) spectrums of CdTe and CdTe/CdS/ZnS core/multi-shell QDs

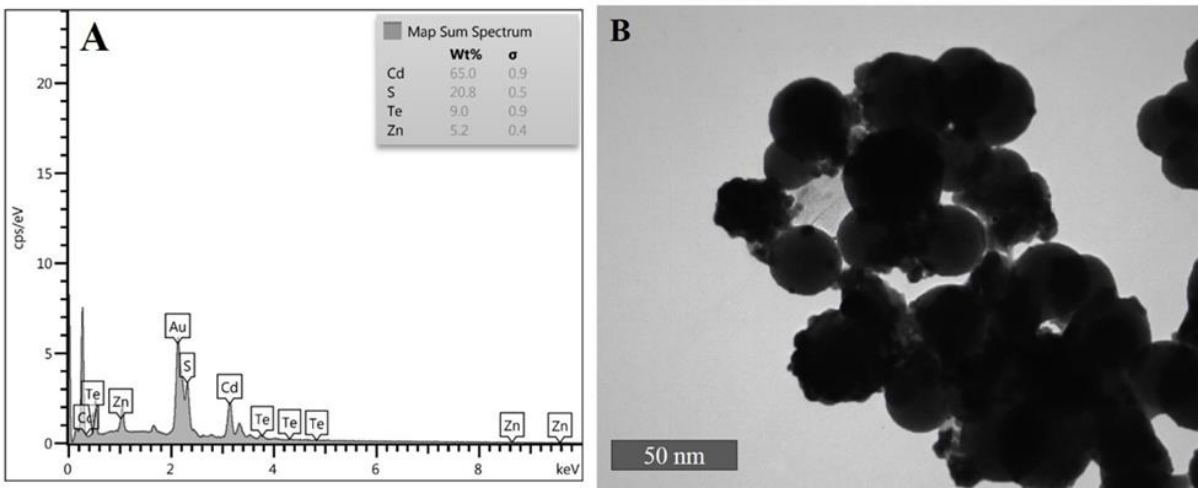

Fig. 3. EDS analysis (A) and TEM image (B) of CdTe/CdS/ZnS core/multi-shell QDs

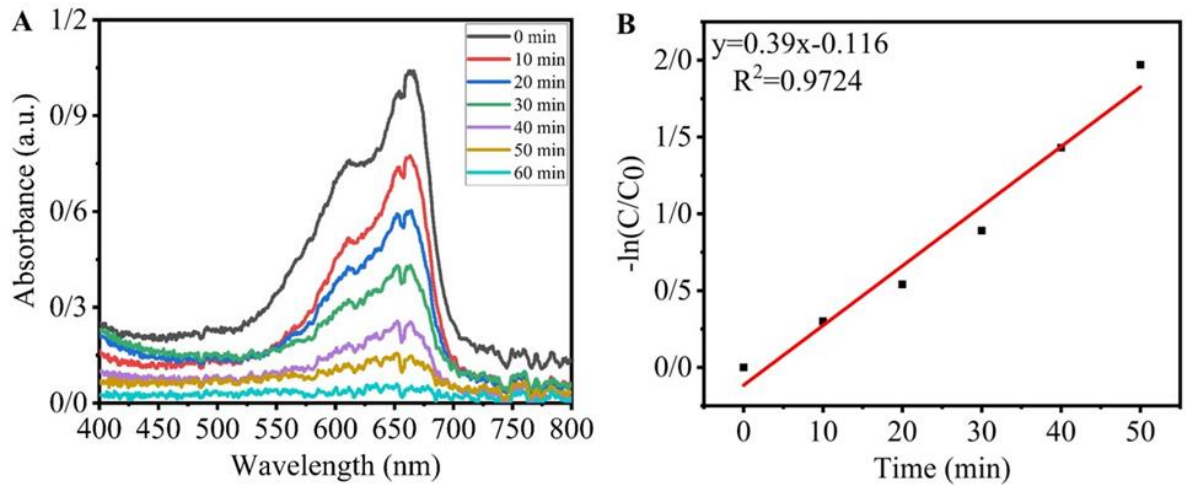

Fig. 4. Absorbance spectrum of MB dye during photocatalyst process (A) and its corresponding logarithm of the relative concentration of samples vs. irradiation time (B)

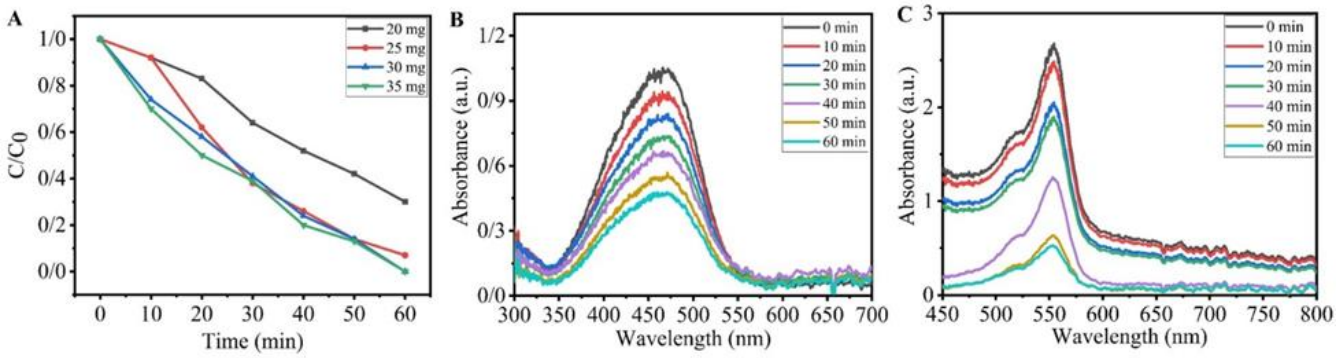

Fig. 5. Degradation of MB dye by different catalyst mass (A), the absorbance spectrum of MO (B), and RB (C) dyes during the photocatalyst process

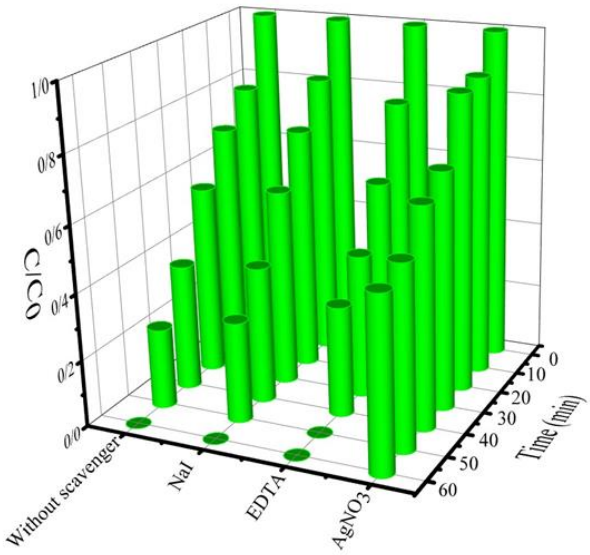

Fig. 6. Effect of different radical scavengers on the photodegradation of MB dye by CdTe/CdS/ZnS nanocatalyst.

3.3. Mechanism of photocatalyst process

The possible mechanism of photodegradation of dyes with CdTe/CdS/ZnS core/multi-shell QDs could be explained as follows. CdTe QDs are a semiconductor nanomaterial, under UV irradiation, CdTe valence band (VB) electrons transfer to the conduction band (CB) and create excitons. These electrons and holes react with water molecules and dissolved oxygens and create hydroxyl (OH^-) and superoxide radicals (O_2^-). These active radicals react with dye molecules and cause dye degradation. Figure 7 illustrates the schematic of the photocatalyst process of CdTe/CdS/ZnS nanocatalyst.

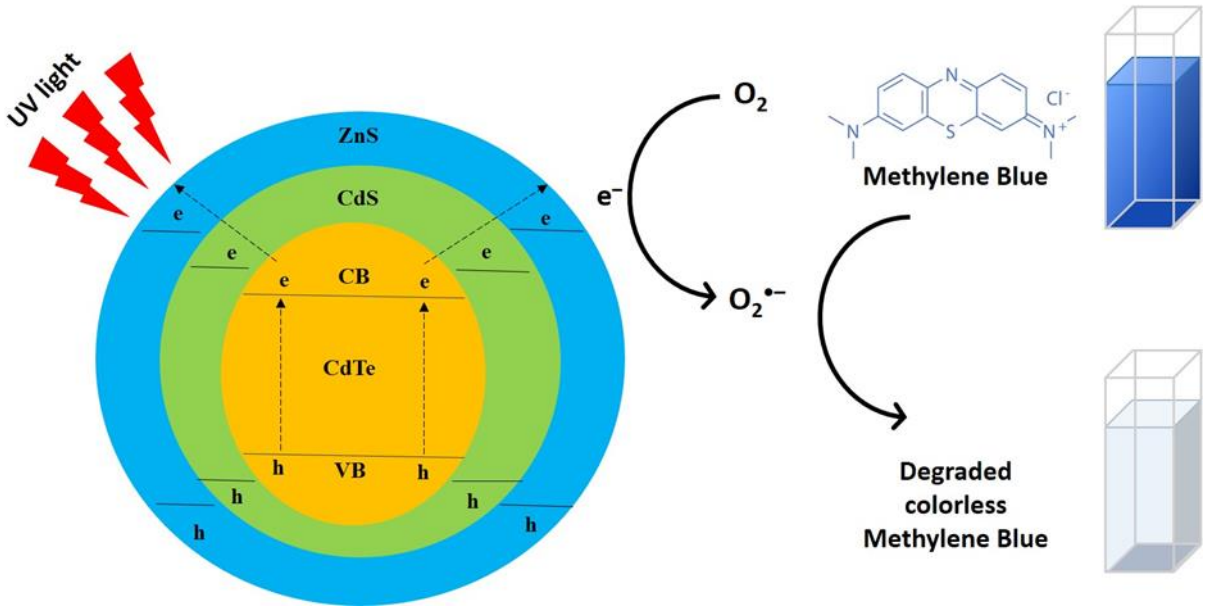

Fig. 7. Schematic illustration of the photocatalyst process of CdTe/CdS/ZnS nanocatalyst

4. Conclusion

In this research, the photocatalyst performance of the CdTe/CdS/ZnS nanocatalyst was studied. At first, CdTe/CdS/ZnS core/multi-shell QDs were synthesized by a simple and fast photochemical method. XRD, EDS, PL, absorbance, and TEM analysis confirmed the successful formation of CdTe/CdS/ZnS core/multi-shell structure. The photocatalyst activity of CdTe/CdS/ZnS nanocatalyst was investigated by MB, MO, and RB dyes, separately. The obtained results showed that MB dye after 60 min of photocatalyst process was completely (100%) degraded but RB and MO dye degradation percentages were 80.2% and 55.2%, respectively. The radical scavenger experiment results showed that electrons play a key role in the photocatalyst process of CdTe/CdS/ZnS nanocatalyst with MB dye. Based on the experimental results of this paper, CdTe/CdS/ZnS QDs have excellent potential to be used as a

nanocatalyst for the removal of MB dye from industries' wastewaters and effluents.

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Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

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