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Environmental remediation of Cr(VI) solutions by photocatalytic reduction using Ag–Er(OH)₃ nanocomposite



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ABSTRACT

A hydrothermal method was use to prepare $Er(OH)_3$ nanoparticles, and a photoassisted deposition method was used to deposit silver onto the surface of those nanoparticles. $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites were characterized by BET, XRD, XPS, PL, UV–Vis and TEM measurements. The photocatalytic performance of the nanoparticles with respect to the photocatalytic reduction of chromium(VI) under UV light irradiation was determined. The results reveal that the silver particles were well dispersed onto the surface of the $Er(OH)_3$ nanoparticles. Additionally, the surface area of the $Ag/Er(OH)_3$ nanocomposites was observed to be smaller than that of the $Er(OH)_3$ nanoparticles due to the blocking of some pores of the $Er(OH)_3$ nanoparticles by the deposition of silver particles. The $Ag/Er(OH)_3$ nanocomposites (0.15 wt%) exhibit the lowest band gap and highest photocatalytic activity for the reduction of Cr(VI). The photocatalytic performance of the 0.15 wt% $Ag/Er(OH)_3$ nanocomposites was stable after the reuse of the nanoparticles for the reduction of Cr(VI) after five uses.

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1. Introduction

Photocatalysis describes the change in the rate of a photoreaction in the presence of a catalyst. In a photocatalytic reaction, light is absorbed by a semiconductor. Any photoreaction that occurs in the presence of a catalyst depends on the ability of the semiconductor to create electron-hole pairs to proceed, which consequently generates free radicals, such as hydroxyl radicals, that in turn are able to undergo further reactions. Since the discovery of TiO₂ for use in the electrolysis of water [1], the commercially used process has been referred to as the advanced oxidation process (AOP). There are various methods for developing an advanced oxidation process via the synthesis of new photocatalysts that can function more efficiently than TiO₂. The synthesis of new semiconductors that function as photocatalysts, e.g., for the degradation of organic contaminants and water splitting using solar energy, is inevitable. TiO₂, the most widely used photocatalyst, is photoactive for UV photons and inactive under visible light because of its large band gap (3.20 eV) [2-6]. The UV region covers only approximately 4% of the entire solar spectrum, whereas visible light covers 45% of the spectrum. Therefore, research efforts focus on visiblelight-sensitive photocatalysts as the most inexpensive source of photocatalysts for environmental cleanup. As previously mentioned, the energy gap of TiO_2 is 3.2 eV, which is equivalent to a photon in the UV region with a wavelength of 380 nm. Therefore, TiO₂ requires near-UV light to act as a photocatalyst. The holes that are formed in TiO₂ are highly oxidizing, which leads to the formation of OH radicals. Therefore, inorganic species that possess more positive reduction potentials relative to the conduction band of a semiconductor provide more electrons for reaction. In recent years, increasing attention has been focused on the photocatalytic reduction of inorganic contaminants. TiO₂ photocatalytic reduction is well reported to be effective in removing various toxic metal ions, such as mercury [9,10], arsenic [11,12] and chromium [13–17]. The physical and chemical properties of chromium depend on the molecular structure of the chromium compounds considered. These compounds primarily exist in two oxidation states: Cr(III) and Cr(VI). Cr(VI) compounds are more toxic, more soluble and more mobile (because of being weakly adsorbed on the inorganic surfaces) than Cr(III) compounds. According to the United States EPA, Cr(VI) is considered a high priority hazard due to the dangers of the presence of chromium in drinking water. Chromium electroplating, leather tanning and paint industries are the main sources of Cr(VI). Efforts have been undertaken to remove Cr(VI) by reducing it to Cr(III), which is 100 times less toxic and less mobile. The reduction process involves the neutralization or alkalization of the containing solution by precipitating Cr(OH)₃. Further reduction

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is performed to obtain Cr(0) [7,8]. The following semiconductors (photocatalysts) have been used for the photoreduction of Cr(IV) to the less toxic Cr(III):ZnO, Hombikat UV 100, Degussa P25 and WO₃ [18]. These semiconductors have been studied as a function of the pH of the slurry, the initial Cr(VI) concentration and the amount of the semiconductor used in the slurry. All of these quantities produce increasing amounts of the Cr(VI) reduced photoproduct with a decrease in pH. It has been suggested that the reaction mechanism is acid-catalyzed. The reaction mechanism varies to first order with the initial concentration of Cr(VI). Note that other non-photocatalytic methods (mainly analytic techniques) are used to remove Cr(VI) ions from industrial wastewater via different techniques, such as reduction [19,20], reduction followed by chemical precipitation [21], adsorption on activated charcoal [22], solvent extraction [23], freeze separation and reverse osmosis [24], ion exchange [25] and electrolytic methods [26]. The removal of chromium [27] from inorganic waste can be accomplished by conventional techniques, such as chemical precipitation, ion exchange, electrochemical and adsorption. Each of these techniques has its own disadvantages, for example, an inability to meet health and hazards regulations, high energy consumption and highly toxic hazardous waste. The best of these techniques should meet the maximum pollutant level (Cr = 0.05 mg/L) at a low cost. To the best of our knowledge, there are no reports on the reduction of chromium(VI) in aqueous solution by Er(OH)₃. The present study presents the synthesis and characterization of Ag/Er(OH)₃ and the evaluation of its photocatalytic activity for the reduction of chromium(VI) in the aqueous phase.

2. Experimental

2.1. Preparation of photocatalyst

A hydrothermal method was used to prepare $Er(OH)_3$ nanoparticles. All of the chemicals used as starting materials were provided by Sigma–Aldrich. In a typical synthesis, 2 mmol of erbium(III) nitrate pentahydrate, 15 mmol of urea and 1 g of cetyltrimethylammonium were dissolved at room temperature in 70 ml of water and then stirred for 30 min. The resulting mixture was kept in a Teflon-lined stainless steel autoclave at 100 °C for 24 h. The obtained mixture was washed with distilled water and ethanol absolute several times and finally dried for 24 h at 60 °C. PAD-Ag/Er(OH)₃ (containing 0.05, 0.10, 0.15 or 0.20 wt% of Ag metal) was synthesized using the following photo-assisted deposition (PAD) route: Ag metal was deposited onto $Er(OH)_3$ with an aqueous solution of silver nitrate under UV-light irradiation. The samples were dried at 60 °C and treated via H₂ reduction (20 ml min⁻¹) at 80 °C for 2 h.

2.2. Characterization techniques

X-ray diffraction (XRD) analysis was performed at room temperature with a Bruker axis D8 using Cu K α radiation ($\lambda = 1.540$ Å). The specific surface area was calculated from N₂-adsorption measurements, which were obtained using a Nova 2000 series Chromatech apparatus at 77 K. Prior to the measurements, the samples were treated under vacuum at 100 °C for 2 h. The band gap of the samples was identified by UV-visible diffuse reflectance spectroscopy (UV-Vis-DRS), which was performed in air at room temperature over the wavelength range of 200–800 nm using a UV/Vis/NIR spectrophotometer (V-570, JASCO, Japan). Transmission electron microscope (TEM) analysis was conducted with a JEOL-JEM-1230 microscope, and samples were prepared by suspension in ethanol, followed by ultrasonication for 30 min. Subsequently, a small amount of this solution was placed onto a carbon-coated copper grid and dried before loading the sample into the TEM. X-ray photoelectron spectroscopy (XPS) studies were performed using a Thermo Scientific K-ALPHA, XPS, England. Photoluminescence (PL) emission spectra were recorded using a Shimadzu RF-5301 fluorescence spectrophotometer.

2.3. Photocatalysis experiment

The application of the synthesized nanoparticles for the photoreduction of chromium(VI) was studied under UV irradiation. The experiments were performed using a horizontal cylinder annular batch reactor. The photocatalyst was irradiated using a xenon lamp (300 W). In a typical experiment, the desired weight of the catalyst was suspended in 500 ml of a 150 mg/l K₂Cr₂O₇ solution. The reaction was performed isothermally at 25 °C, and the samples in the reaction mixture were analyzed at different time intervals for a total reaction time of 1 h. The concentration of chromium(VI) in the samples was estimated with a UV–Vis spectrophotometer (V-570, JASCO, Japan) at 540 nm using the standard diphenylcarbazide method [28].

The photoreduction efficiency of chromium(VI) (%), was measured by applying the following equation:

% photoreduction efficiency = $(C_o - C_t)/C_o \times 100$

where C_0 is the initial concentration of chromium(VI) in the solution at zero time and C_t is the concentration of chromium(VI) in the solution at time *t*.

3. Results and discussion

3.1. Structural, morphological and compositional characterizations

Fig. 1 shows the XRD patterns of the $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites. The results reveal that the nanocomposites are mainly composed of $Er(OH)_3$, which indicates that the lack of diffraction peaks due to Ag in the patterns of the $Ag/Er(OH)_3$ samples is because the wt% of Ag is below the XRD detection limit or perhaps because Ag is well dispersed on surface of the $Er(OH)_3$ nanoparticles.

Fig. 2 shows the XPS spectra of Ag 3d for a sample of Ag/ Er(OH)₃. The results reveal the presence of Ag metal in the sample via the two peaks for Ag $3d_{5/2}$ and $Ag3d_{3/2}$ at 284.7 eV and 287.7 eV, respectively.

Fig. 3 shows TEM images of $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites. The results show that an increase in the wt% of Ag increases the dispersion of Ag on the surface of the $Er(OH)_3$ nanoparticles. Additionally, an increase in the wt% of Ag to 0.15% increases the homogeneity of the Ag particle size on the surface of the $Er(OH)_3$ nanoparticles. This homogeneity decreases at higher concentrations of silver, i.e., 0.20 wt%, which suggests that there is an optimum content for the deposition of Ag ions that controls the size and homogeneity of the doped silver.

3.2. Surface area analysis

The texture parameters of the $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites are presented in Table 1. The S_{BET} values for $Er(OH)_3$ and 0.05 wt% $Ag/Er(OH)_3$, 0.10 wt% $Ag/Er(OH)_3$, 0.15 wt% Ag/ $Er(OH)_3$ and 0.20 wt% $Ag/Er(OH)_3$ were determined to be 53, 47, 45, 43 and 38 m²/g, respectively. The total pore volume of Ag/ $Er(OH)_3$ is smaller than that of the $Er(OH)_3$ sample due to the blocking of some pores by the deposition of Ag metal. The presence



Fig. 1. XRD patterns of Er(OH)₃ and Ag/Er(OH)₃ nanocomposites.



Fig. 2. XPS spectra of Ag 3d for the 0.15 wt% Ag/Er(OH)₃ sample.

of mesopores in all samples was confirmed by the similar values of S_{BET} and S_t in most samples, as presented in Table 1.

3.3. Optical characterization

Fig. 4 shows the UV–Vis diffuse reflectance spectra of the $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites. The results demonstrate that the deposition of silver metal onto the surface of $Er(OH)_3$ leads to a shift in the absorption edge of $Er(OH)_3$ from 325 nm to 394 nm. The UV–Vis spectra were used to calculate the direct band gap of the $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites based on a method used by Mohamed [29]. The band gap energies were calculated using the following equation:

 $E_{\rm g}=1239.8/\lambda$

where E_g is the band gap (eV) and λ is the wavelength (nm) of the absorption edges in the spectrum; the results are tabulated in Table 2.

The results reveal that an increase in the wt% of silver from 0.05 wt% to 0.15 wt% decreases the band gap from 3.81 eV to



Table 1

Texture parameters of Er(OH)₃ and Ag/Er(OH)₃ nanocomposites.

Sample	$S_{\text{BET}} (m^2/g)$	$S_t (m^2/g)$	$S_{\rm micro}~({\rm cm}^2/{\rm g})$	$S_{\rm ext} ({\rm cm}^2/{\rm g})$	$V_p (\text{cm}^3/\text{g})$	$V_{\rm micro}~({\rm cm}^3/{\rm g})$	$V_{\rm meso}~({\rm cm}^3/{\rm g})$	r (Å)
Er(OH) ₃	53.00	56.00	32.00	21.00	0.200	0.164	0.050	30.00
0.05 wt% Ag/Er(OH)3	47.00	50.00	30.00	17.00	0.145	0.120	0.025	40.00
0.10 wt% Ag/Er(OH)3	45.00	48.00	29.00	16.00	0.122	0.100	0.022	50.00
0.15 wt% Ag/Er(OH)3	43.00	44.00	28.00	16.00	0.115	0.095	0.020	55.00
0.20 wt% Ag/Er(OH) ₃	38.00	39.00	21.00	14.00	0.098	0.055	0.018	50.00

Note:

 (S_{BET}) \blacktriangleright BET-surface area (S_t) \blacktriangleright surface area derived from V_{1-t} plots.

 $(S_{\text{mic}}) \triangleright$ surface area of micropores $(S_{\text{ext}}) \triangleright$ external surface area.

 $(V_p) \triangleright$ total pore volume $(V_{mic}) \triangleright$ volume of micropores.

 (V_{mes}) > volume of mesopores (r^{-}) > mean pore radius.



Fig. 4. UV–Vis absorption spectra of Er(OH)₃ and Ag/Er(OH)₃ nanocomposites.

Table 2Band gap energy of $Er(OH)_3$ and $Ag/Er(OH)_3$ nanocomposites.

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Sample	Band gap energy, eV
Er(OH) ₃	3.81
$0.05 \text{ wt\% Ag/Er(OH)}_3$	3.52
0.10 wt% Ag/Er(OH) ₃	3.37
0.15 wt% Ag/Er(OH) ₃	3.11
0.20 wt% Ag/Er(OH) ₃	3.14

3.11 eV. However, there is no significant effect on the band gap at a high wt% of silver greater than 0.15. Therefore, there is an optimum content of deposited silver that controls the band gap.

We investigate the separation and recombination of photogenerated charge carriers and the transfer of the photogenerated electrons and holes by gathering photoluminescence (Pl) emission spectra. The results indicate that an increase in the wt% of silver deposited on the $Er(OH)_3$ nanoparticles from 0.05 wt% to 0.15 wt% leads to a decrease in the Pl intensity. However, there is no significant effect on the Pl intensity at a high wt% of silver above 0.15. Therefore, there is an optimum content of deposited silver that yields the carrier lifetime required for e–h recombination, in agreement with the UV–Vis results (see Fig. 5).

3.4. Photocatalytic activities

Fig. 6 shows the effect of the wt% of Ag on the photocatalytic activity of $Er(OH)_3$ nanoparticles for the reduction of Cr(VI) under UV irradiation; the experiment was performed under the following



Fig. 5. PL spectra of Er(OH)₃ and Ag/Er(OH)₃ nanocomposites.



Fig. 6. Effect of the wt% of Ag on the photocatalytic activity of $Er(OH)_3$ nanocomposites for the reduction of Cr(VI).

conditions: $K_2Cr_2O_7$ concentration of 125 ppm, $K_2Cr_2O_7$ volume of 500 ml and photocatalyst weight of 0.30 g. The results reveal that the photocatalytic activity increased from 48.5% to 100% with an increase in the wt% of silver from 0 wt% to 0.15 wt%. However, further increasing the wt% of silver above 0.15 wt% led to a decrease in the photocatalytic activity from 100% to 97%. This decrease was observed because a high wt% of silver hinders the penetration of light to the surface of Er(OH)₃, thereby decreasing



Fig. 7. XPS spectra of Cr 2p for the 0.15 wt% $Ag/Er(OH)_3$ sample after being used for the reduction of Cr(VI) solution.



Fig. 8. Effect of loading of the $0.15 \text{ wt\% Ag/Er(OH)}_3$ sample on the photocatalytic reduction of the Cr(VI) solution.

the photocatalytic performance of $Er(OH)_3$ with respect to the reduction of Cr(VI). Fig. 7 shows the XPS spectra of Cr 2p for the 0.15 wt% Ag/Er(OH)_3 sample after it was used to reduce a Cr(VI) solution. The results reveal the presence of Cr(III) in the sample by the two peaks for Cr $2p_{3/2}$ and Cr $2p_{1/2}$ (Fig. 7), which confirm that Cr(VI) was reduced to Cr(II).

Fig. 8 shows the effect of loading the 0.15 wt% Ag/Er(OH)₃ sample on the photocatalytic reduction of the Cr(VI) solution under UV irradiation; the experiment was performed under the following conditions: $K_2Cr_2O_7$ concentration of 125 ppm, $K_2Cr_2O_7$ volume of 500 ml and a 0.15 wt% Ag/Er(OH)₃ nanocomposites photocatalyst. The results reveal that photocatalytic performance, in terms of *a*%, after 60 min was increased from 84% to 100% with an increase in the weight of the photocatalyst from 0.3 g/l to 0.6 g/l. The reaction time required to complete the reduction of Cr(VI) was decreased to 60 min, 50 min and 30 min as the weight of the photocatalyst was increased to 0.6 g/l, 0.9 g/l and 1.2 g/l, respectively. However, the reaction time required to complete the reduction of Cr(VI) was increased again to 40 min with an increase in the weight of the photocatalyst above 1.2 g/l; that is, the optimum weight of the photocatalyst is 1.2 g/l.



Fig. 9. Effect of the initial Cr(VI) solution concentration on the photocatalytic reduction of the Cr(VI) solution.



Fig. 10. Recycling and reuse of photocatalysts for the photocatalytic reduction of the Cr(VI) solution.

Fig. 9 shows the effect of the initial Cr(VI) solution concentration on the photocatalytic reduction of the Cr(VI) solution under UV irradiation, which was studied by varying the initial Cr(VI) solution concentration from 25 ppm to 150 ppm in the presence of 0.15 wt% Ag/Er(OH)₃ photocatalyst. The results demonstrate that the photocatalytic activity remained nearly unchanged with an increase in the initial Cr(VI) solution concentration from 50 ppm to 125 ppm after the 30 min of reaction time required to complete the reduction of Cr(VI). However, for initial Cr(VI) solution concentrations above 125 ppm, the reaction time required to complete the reduction of Cr(VI) was increased to 40 min and 55 min by increasing the initial Cr(VI) solution concentration to 150 ppm and 200 ppm, respectively. The photocatalytic activity depends on the hydroxyl free radicals reaching the surface of the catalyst and then reacting with the Cr(VI) solution; therefore, increasing the initial Cr(VI) solution concentration increases the probability of a reaction between the free radicals and the Cr(VI) solution, thereby increasing the photocatalytic activity. A further increase in the initial Cr(VI) solution concentration decreases the

photocatalytic activity because the active sites of the photocatalyst are blocked by the Cr(VI) solution, which prevents UV light from penetrating the surface of active sites.

Fig. 10 shows the results obtained regarding the recycling and reuse of photocatalysts for the photocatalytic reduction of the Cr(VI) solution. The experiment was carried out under the following conditions: a reaction time of 30 min, a Cr(VI) solution concentration of 125 ppm and 1.2 g/l of 0.15 wt% Ag/Er(OH)₃ nanocomposite. The results show that the photocatalytic activity remains nearly unchanged after five uses, which means that the photocatalyst is stable in the photocatalytic reduction of the Cr(VI) solution. The XRD patterns of the 0.15 wt% Ag/Er(OH)₃ sample obtained before and after being reused five times are shown in Fig. 1. It was also observed that the shape of the composite XRD patterns after the first five cycles was similar to the shape observed before the reaction. This finding indicates that the structure of the 0.15 wt% Ag/Er(OH)₃ does not change during the photocatalytic process. In addition, the UV–Vis spectra of the 0.15 wt% Ag/Er(OH)₃ sample before and after being reused five times are shown in Fig. 4. It was also observed that the absorption spectrum of the 0.15 wt% Ag/Er(OH)₃ sample after the first five cycles was similar to that observed before the reaction. This result indicates that the structure of 0.15 wt% Ag/Er(OH)₃ does not change during the photocatalytic process. Therefore, this photocatalyst can be separated and recycled while maintaining its stability, making it a promising material for environmental remediation.

4. Conclusions

In summary, a Ag/Er(OH)₃ nanocomposite photocatalyst was successfully synthesized and proven to be a promising catalyst due to its high efficiency in reducing the pollutant Cr(VI) under UV light. The band gap of the Er(OH)₃ photocatalyst can be controlled by controlling the weight percent of silver that is deposited onto the surface of the photocatalyst. The results of photocatalytic studies reveal that the highest photocatalytic activity and stability were obtained for the 0.15 wt% Ag/Er(OH)₃ nanocomposite photocatalyst, which can be used to reduce 100% of Cr(VI) to Cr(III) after 30 min.

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