Modified $\text{Y}_2\text{O}_3$-coated biosilica with Dysprosium nanomaterials: synthesis, characterization, and optical study with enhanced catalytic activity

Younes Hanifehpour

Department of chemistry, Sayyed Jameoddin Asadabadi University, Asadabad, Iran

ABSTRACT

Dy-doped $\text{Y}_2\text{O}_3$ coated biosilica nanostructures with variable Dy$^{3+}$ contents were synthesized by a facile hydrothermal technique. The products were characterized by means of energy dispersive X-ray photoelectron spectroscopy (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), UV-Vis diffuse reflectance spectroscopy, and photoluminescence spectroscopy techniques. XRD demonstrated that the particles were crystallized excellently and attributed to the cubic phase of $\text{Y}_2\text{O}_3$. The substitution of Dy$^{3+}$ ions into $\text{Y}_2\text{O}_3$ lattice caused a redshift in the absorbance and a decrease in the band gap of as-prepared coated compounds. The pore volume and BET specific surface area of Dy-doped $\text{Y}_2\text{O}_3$-coated diatomite were greater than uncoated biosilica. The sonophotocatalytic activities of as-synthesized specimens were evaluated for the degradation of Reactive Blue 19. The effect of various specifications such as ultrasonic power, various scavenger, and catalyst amount was investigated. The results revealed that diatomite coated with Dy$^{3+}$-incorporated yttrium oxide nanoparticles could be utilized in various experimental cycles with no significant decrease in photocatalytic activity.

INTRODUCTION

The degradation of hazardous organic contaminants in industrial wastewater through AOPs (advanced oxidation processes) has attracted a great deal of research attention. Production of •OH radicals is the primary mechanism of AOPs, which have higher oxidation potential and can help to obtain efficient and faster degradation of the pollutants. The AOP process is particularly suitable for cleaning up non-degradable or toxic materials, such as petroleum constituents, pesticides, volatile organic compounds in wastewater, and aromatics [1–4].

Sonocatalysis is one type of AOPs that has recently been applied for degrading organic dyes [5–7]. The chemical influence of ultrasound (US) is caused by acoustic cavitation, leading to the formation, growth, and collapse of bubbles within a solution. By collapsing the bubbles, localized hot spots are produced with very high pressure and temperature. Due to such severe circumstances, the water molecules and dissolved oxygen undergo direct thermal dissociation to create highly reactive radical species including •OH, oxygen (•O), and hydrogen (•H), which, in turn, play a pivotal role in oxidizing organic pollutants in water [8–11].

The combination of sonocatalysis and photocatalysis appears to improve the degradation share of organic pollutants owing to synergistic effects [12]. In addition to the formation of reactive oxygen species (ROS) through cavitation, the use of US in photocatalytic processes has a number of other benefits; these include incrementing the

This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.
active surface area of the catalyst (by preventing the aggregation of particles, increasing the pollutants' mass transfer between the solution and catalyst surfaces), preventing catalyst deactivation (by means of continuously cleaning absorbed molecules from the catalyst surface by micro streaming and micro bubbling), and incrementing the number of high pressure and temperature regions (through breaking up microbubbles made via the US into smaller ones in the presence of catalyst particles) [12–14].

Diatomite (diatomaceous earth), fossilized diatoms, is already used as adsorbent and carrier material. In addition, the porous structure of diatom makes it a potential heterogeneous catalyst [15-17]. Yttrium oxide (Y$_2$O$_3$) is an essential engineering compound in various fields due to its physical and chemical properties, including relatively large band gap energy, high melting point, and high permittivity [18, 19]. It has been extensively utilized in luminescent devices and transparent ceramics. To obtain better material performance, many investigations have been conducted on controlling the morphology and size of Y$_2$O$_3$. Yttria has found many high-technology applications because of its well-defined crystal structures and outstandingly high affinity for oxygen and sulfur; these properties can be qualified by substituting different kinds of ions into the lattice [20]. Lanthanide-doped nanostructured semiconductors have recently been used as active photocatalysts and sonocatalyst. Rare earth cations with empty 5d orbitals and partly occupied 4f orbitals could also notably enhance the separation rate of photo-induced charge carriers within semiconductor sonocatalysts and improve significantly the sonocatalytic activity [1,21–23]. However, no report exists on the sonocatalytic degradation of Reactive Blue 19 (RB 19) in the presence of coated-diatom with dysprosium-doped Y$_2$O$_3$.

This study aimed to describe a simple hydrothermal route for the preparation of coated-diatom with dysprosium-doped Y$_2$O$_3$ (Dy$_x$Y$_2$O$_3$) nanomaterials. We assessed the nanoparticles’ sonocatalytic activity for RB 19 (see Table 1). In addition, we examined and optimized the sonophotocatalytic degradation of organic dye. We also investigated the influence of inorganic ions on the degradation effectiveness of RB19.

**EXPERIMENTAL METHODS**

**Chemicals and materials**

The chemicals used in this study had analytical grades and were utilized with no further purification. Diatomaceous earth (97.5% SiO$_2$), YCl$_3$ (99.99%), ethanol (99%), and Dy(NO$_3$)$_3$.5H$_2$O were purchased from Sigma-Aldrich. RB19 was acquired from the Zhejiang Yide Chemical Company (China).

**Characterization**

The samples’ crystal phase composition was determined using XRD characterization at room temperature through a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with monochromatic high-intensity Cu Ka radiation (λ=1.5406 Å), an emission current of 30 mA, and accelerating voltage of 40 kV. Elemental analyses were obtained using a linked ISIS-300, (Oxford Instruments, Abingdon, UK) (energy dispersion spectroscopy) detector. Using an electron microscope (SEM, S-4200, Hitachi, Tokyo, Japan), the surface state and the

---

**Table 1. The characteristics of C.I. Reactive blue 19**

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Reactive Blue 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color index name</td>
<td>C$<em>{22}$H$</em>{16}$N$_2$Na$<em>2$O$</em>{11}$S$_3$</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>219-949-9</td>
</tr>
<tr>
<td>Color index number</td>
<td>592</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>592</td>
</tr>
<tr>
<td>$M_W$ (g/mol)</td>
<td>626.54</td>
</tr>
</tbody>
</table>
morphology were observed. A diffuse reflectance UV-Vis spectrophotometer was utilized to obtain the samples' optical absorption spectra (Varian Cary 3 Bio, Varian Ltd., Artarmon, Australia). The specific surface areas were measured through a single point BET technique utilizing Micrometrics Gemini V and Gemini 2375. Cell parameters were calculated with the Celref program from powder XRD patterns, and reflections were determined and fitted using a profile fitting procedure with the Winxpow program. The reflections observed in 2θ = 10–70° were used for the lattice parameter determination.

Preparation of Dy-doped Y$_2$O$_3$ nanoparticles

Dy-doped yttrium oxide compounds with different Dy contents (0–8 mol%) were made hydrothermally. In a typical synthesis, first, Dy (NO$_3$)$_3$·5H$_2$O and proper molar ratios of YCl$_3$ were dissolved in 30 ml of deionized water. Next, EDTA (0.3 g) and 1 mmol NaOH were added dropwise to the solution while stirring it at moderate speed. The above solution was transferred into a 100-ml autoclave with Teflon-lined stainless-steel. Then it was settled in an oven at 230°C for 48 h and finally allowed to cool naturally to room temperature. Gathering the as-prepared Dy$_x$Y$_{2-x}$O$_3$ nanoparticles, they were rinsed numerous times with absolute ethanol and distilled water to remove residual impurities, and then dried at vacuum for 2 h at 55°C. The result was a white powder.

Diatomite coated with Dy-doped Y$_2$O$_3$ nanoparticles

The diatom was weighted and added to 25mL deionized water and was continuously stirred to spread evenly. Then, 1 g Dy-doped Y$_2$O$_3$ compounds with various Dy content were added to the above solution to fully disperse. After 1 h ultrasonic irradiation, the solution was transferred into a 100-ml autoclave with Teflon-lined stainless-steel, settled in an oven at 140°C for 10 h and then cooled down naturally to room temperature. The final coated-diatom was obtained after washing and drying the precipitates at 60°C.

Evaluation of catalytic activity

The sonophotocatalytic activity of the diatom biosilica coated with Dy-doped yttria nanomaterial was assessed to decolorize of RB19 as a model organic pollutant. Within a characteristic procedure, suspending the nanocatalyst (0.1 g) was performed in an aqueous solution of the model dye (100 mL) with an identified initial concentration at pH=6.5. Then, the suspension was irradiated by a 40W compact fluorescent visible lamp armed with a cutoff filter to present visible light illumination ($\lambda$ of higher than 420 nm) into the ultrasonic bath. A UV–Vis spectrophotometer was utilized to determine the removal of dye via the absorbance at $\lambda_{max}$ = 592 nm. The decolorization efficiency (DE) was determined as follows:

$$DE(\%) = \left(1 - \frac{C}{C_0}\right) \times 100$$

where C and C$_0$ are the dye's final and initial concentrations within the solution (mg/L), respectively. To test the nanocatalyst’s reusability, the utilized catalyst was separated from the solution, rinsed with distilled water, and utilized in a fresh test after drying at 70°C.

RESULTS AND DISCUSSION

Characterizing the synthesized samples

Fig. 1 presents the XRD pattern of uncoated diatomite, Y$_2$O$_3$, and diatom-coated with Dy-doped Y$_2$O$_3$. The diatomite XRD pattern was indexed readily to SiO$_2$ (JCPDS card no. 00-001-0647), while the four broad and strong peaks with attributed reflections of (222), (400), (440), (622) and 2θ = 29.1, 33.7, 48.6 and 58.2° were related to cubic structure of yttria, respectively (JCPDS card no. 41-1105) [24]. The indistinguishable forms of the XRD patterns of Y$_2$O$_3$ and the compounds coated with Dy$_x$Y$_{2-x}$O$_3$ suggest that the surface of diatom was equally covered. As illustrated in Fig. 1, in substitution of yttria by Dy$^{3+}$, only the peaks related to Y$_2$O$_3$ were still noticed and no other peaks corresponding to Y(OH)$_3$, Dy$_2$O$_3$, or other impurities were detected, which demonstrates that the dy$^{3+}$ ions substitute Y$^{3+}$ ions in the yttoria structure. A slight shift was found to lower diffraction for diatomite-coated with Dy-dopedY$_2$O$_3$ samples.

The cell parameters of the synthesized materials were calculated from the XRD patterns. By increasing dopant content ($x$), a, b and c parameters for Dy$^{3+}$ increased (Fig. 2). The trend for lattice constants could be correlated to the effective ionic radii of the Ln$^{3+}$ ions, which resulted in greater amount of lattice parameters for Dy$^{3+}$-doped materials.

Fig. 3 displays SEM images of the diatom-
coated with 6% Dy-doped Y$_2$O$_3$ and uncoated sample produced by the hydrothermal route. The skeletal-remain biosilica with high porosity structure is shown in Fig. 3a. High porosity and the surface morphology of diatom can be employed as a template to enhance the potential of functional materials. Fig. 3b represents the image of 6% Dy-doped Y$_2$O$_3$ nanoparticles, the diameter of which was around 25–70nm. Following the immobilization of 6% Dy-doped yttrium oxide, the SEM image of diatomite is seen in Fig 3c, d. Changing the mass ratio of the substrate–diatomite and the coating material–doped-Y$_2$O$_3$ controlled the thickness of the coating layers. To achieve smooth, stable and uniform coating, the optimum ratio was 1.5.

The elemental mapping of O, Y, Dy and Si in the diatom-coated with Dy-doped Y$_2$O$_3$ sample is shown in Table 2 confirming the XRD outcome. Fig. 4a shows the absorbance spectra of Dy-doped Y$_2$O$_3$ coated diatomite compounds. A redshift in absorbance spectra is seen by increasing dopant content.

The as-prepared compound's band gap energy can be determined from the interception of the resultant linear area with the energy axis according to (hνα)$^2$ versus (hν) (Tauc plot)(Fig.4b). The doped Y$_2$O$_3$ had lower Eg values compared to the pure sample, which were reduced by increasing the dopant. Table 3 lists the band gap energy for Dy-doped Y$_2$O$_3$ coated diatomite nanoparticles.

Adsorption/desorption isotherm of nitrogen for uncoated and coated diatomite with 6% dy$^{3+}$-substituted Y$_2$O$_3$ are shown in Fig. 5. In the case of both specimens, two isotherms with obvious hysteresis loop were noticed in the pressure range of 0.3–1.0 p/p$_0$. The BET specific surface area of biosilica is 1.65 m$^2$/g. Additionally, the BET specific
Figure 3. SEM images of natural diatomite (a), 6% Dy-doped Y$_2$O$_3$ (b) and 6% Dy-doped Y$_2$O$_3$-coated diatomite at different magnification (c,d)

Table 2. The atomic percent of 6% Dy-doped Y$_2$O$_3$-coated diatomite.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line Type</th>
<th>Wt%</th>
<th>Atomic %</th>
<th>Factory Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>K series</td>
<td>56.50</td>
<td>67.38</td>
<td>Yes</td>
</tr>
<tr>
<td>Si</td>
<td>K series</td>
<td>37.50</td>
<td>29.37</td>
<td>Yes</td>
</tr>
<tr>
<td>Y</td>
<td>L series</td>
<td>4.86</td>
<td>2.31</td>
<td>Yes</td>
</tr>
<tr>
<td>Dy</td>
<td>M series</td>
<td>1.14</td>
<td>0.94</td>
<td>Yes</td>
</tr>
<tr>
<td>Total:</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Absorbance spectra of diatom coated with Y$_2$O$_3$ (a), diatom coated with 4% Dy-doped Y$_2$O$_3$ (b), diatom coated with 6% Dy-doped Y$_2$O$_3$ (c) and diatom coated with 8% Dy-doped Y$_2$O$_3$ (d) at room temperature
The surface area of diatomite coated with 6% Dy-substituted $\text{Y}_2\text{O}_3$ (8.85 m$^2$/g) considerably exceeds that of uncoated diatom. A superior adsorption performance is expected for coated-diatom with dysprosium-doped $\text{Y}_2\text{O}_3$ nanoparticles.

**Synergistic effect of photocatalysis and sonocatalysis on the degradation of RB19 using diatomite coated with Dy-doped $\text{Y}_2\text{O}_3$ nanoparticles**

Through some comparative tests, the sonocatalytic, photocatalytic, and sonophotocatalytic behaviors of the synthesized diatomite coated with Dy-doped $\text{Y}_2\text{O}_3$ were determined, for which the findings are presented in Fig. 6. The decolorization efficiency was negligible in the absence of the catalyst particles under light irradiation, which shows that photolysis does not contribute to the RB19 removal from the aqueous solution.

The results of the test conducted in dark conditions revealed that surface adsorption have no significant effect on decolorizing the dye solution. The removal percentage by the photocatalytic procedure was less than 66%. The decolorization efficiency by sonocatalytic degradation (50%) was greater than that of the sonolysis process (7%). The decolorization efficiency was significantly improved in the sono-photocatalytic process (94.15%) as a result of synergistic impacts between sonocatalysis and photocatalysis. This can be summarized as: first, the generation of several ROSs through the integrated photocatalytic procedure and cavitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatom coated with $\text{Y}_2\text{O}_3$</td>
<td>4.93</td>
</tr>
<tr>
<td>Diatom coated with 4%Dy-doped $\text{Y}_2\text{O}_3$</td>
<td>4.74</td>
</tr>
<tr>
<td>Diatom coated with 6%Dy-doped $\text{Y}_2\text{O}_3$</td>
<td>4.66</td>
</tr>
<tr>
<td>Diatom coated with 8%Dy-doped $\text{Y}_2\text{O}_3$</td>
<td>4.55</td>
</tr>
</tbody>
</table>
effects; second, the improved mass transfer rates; third, the catalyst particles disaggregation through US and the larger active surface areas; and fourth, the creation of more hot spots by existing catalyst particles [12–14]. Fig. 7 indicates the spectra of the lamp used for catalytic process.

As demonstrated in Fig. 8, the graph of (−ln (C/C₀) vs. time indicates linear dependence for all three sono-photocatalytic, photocatalytic and sonocatalytic processes, displaying pseudo-
first-order kinetics [1, 25]. It is obvious that the
decolorization efficiency and pseudo-first-order
kinetic constant in sono-photocatalysis (k_{obs, sono-
photo}) are greater than those for photocatalysis (k_{obs-
photo}) and sonocatalysis (k_{obs,sono}). These results
implicitly include the concept of a synergistic effect.

To assess the degradation process’s mechanism
and to discover the main oxidative species,
experiments were conducted in the presence
of appropriate scavengers of active species.
According to Fig. 9, adding t-BuOH (a scavenger
of hydroxyl radicals) led to a reduction of 14% in
the decolorization percentage. By adding oxalate (a
scavenger of h^+_vlp), the decolorization percentage
would be reduced by 14%.
decreased to 54%. In the case of I (scavenger of hole), it reached 30%. When benzoquinone (BQ) was added (a scavenger of superoxide radicals), the dye degradation was inhibited remarkably. Such findings indicate that the $h^+$ and superoxide radicals are the main oxidative species in degrading dye molecules although the hydroxyl radicals also affect the decolorization. Regarding the synergistic impacts of sonocatalysis and photocatalysis, a possible mechanism for the degradation procedure can be suggested \[12,14\]:

1) Both US and light irradiation can excite the catalyst nanoparticles to form electron-hole pairs:

$$\text{Dy-doped Y}_2\text{O}_3 \text{ coated diatom} + (h\nu \text{ and US}) \rightarrow h^+ + e^- \quad (2)$$

2) The conduction-band electrons can react with adsorbed oxygen molecules to create $\cdot\text{O}_2^-$, $\cdot\text{HO}_2^-$, and $\text{H}_2\text{O}_2^-$:

$$e^- + O_2 \rightarrow \cdot\text{O}_2^- \quad (3)$$

$$\cdot\text{O}_2^- + H^+ \rightarrow \cdot\text{HO}_2^- \quad (4)$$

$$e^- + H^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 \quad (5)$$

3) Hydroxyl anions or water molecules can be oxidized by the photogenerated holes to form hydroxyl radicals:

$$\text{OH} + h^+ \rightarrow \cdot\text{OH} \quad (6)$$

$$h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \quad (7)$$

4) The water molecule pyrolysis can be promoted by the existence of ultrasonic irradiation to produce hydrogen and hydroxyl radicals:

$$\text{H}_2\text{O} + \text{US} \rightarrow \text{H}^+ + \cdot\text{OH} \quad (8)$$

$$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (9)$$

5) Ultimately, the dye molecules can be degraded by the created active spices:

Reactive blue 19 + reactive oxygen species (ROSs) \rightarrow degrading dye molecules

**Effect of Dy$^{3+}$ Content of diatom coated Dy-doped Y$_2$O$_3$ Nanoparticles**

The removal effectiveness of RB 19 over diatomite coated Dy-doped Y$_2$O$_3$ sonocatalysts during 70 min of sonophotolysis is shown in Fig. 10. The doped samples with proper content of...
Dy$^{3+}$ ion had much better catalytic performance compared with uncoated biosilica. For diatom coated 6 % Dy doped Y$_2$O$_3$ nanoparticles, the highest decolorization efficiency was achieved. Two mechanisms can explain these findings. First, rare-earth cations like Dy$^{3+}$ restrain the electron–hole recombination and act as an electron scavenger. Second, the new energy level under the conduction band edge of Y$_2$O$_3$ is created by the substitution of Dy$^{3+}$ into yttria lattice [26].

\begin{align*}
\text{Dy}^{3+} + e^- & \rightarrow \text{Dy}^{2+} \quad (10) \\
\text{Dy}^{2+} + \text{O}_2 & \rightarrow \text{Dy}^{3+} + \text{O}_2^- \quad (11) \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- \quad (12) \\
2\text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2^- \quad (13)
\end{align*}

•OH, H$_2$O$_2$ and O$_2^*$ radicals are well-known powerful oxidants for the degradation of organic dye [27].

The UV–Vis absorption spectra of RB 19 at various irradiation periods for the sonophotocatalytic process are shown in Fig. 11. Reducing the concentration of RB 19 during the catalytic process is used to examine the performance of the catalyst.

**Effect of sonication energy**

The decolorization percentage of RB19 under different ultrasonic power in the range of 60 to 150 W was also investigated. Employing the sonication power of 50 to 150 W/L, the degradation percentage increased from 81.32 % to 94 % (Fig.12). Enhanced degradation ratio was achieved through increasing the ultrasonic power, which increased the production of •OH radicals. Moreover, the disturbance of the solution was elevated with significant power, which accordingly promoted the mass transfer rate of dye, reactive species and intermediates between catalyst's surface and the bulk solution [28]. In order to save energy, the experiments were set on 120 W due to slight contrast of degradation percentage between 120 and 150 W.

**Photocatalyst recycling and photostability**

Fig. 13 displays the reusability of diatomite coated 6% Dy-doped yttrium oxide, which
was tested at a reaction period of 70 min, a dye concentration of 20 mg/L, and 1.25 g/L of catalyst powder. These conditions were the optimum operational parameters confirmed by the experiments. After five repeated runs, the decrease in the sono-photocatalytic process was negligible, which confirms the synthesized nanoparticles' reusability and high potential stability.

**CONCLUSION**

Dysprosium-doped Y$_2$O$_3$-coated diatomite nanomaterials were prepared using a facile
hydrothermal route and employed for the degradation of reactive blue 19 in an aqueous solution. The substitution of Dy³⁺ into yttrium oxide lattice led to a redshift in absorption spectra and reduction of band gap, respectively. The decolorization effectiveness of the synthesized compounds was much higher in sono-photocatalytic process than that of other methods. 6% Dy³⁺-incorporated Y₂O₃ coated diatom exhibited the best degradation ratio. Radical scavengers reduced the sonophotocatalytic degradation percentage of RB 19 particularly subject to 1,4 benzozquinone. The results revealed that diatomite coated with Dy³⁺-incorporated yttrium oxide nanoparticles can be utilized in various experimental cycles with no significant drop in photocatalytic activity.

ACKNOWLEDGMENTS
This work was funded by the Sayyed Jamaleddin Asadabadi University.

CONFLICTS OF INTEREST
The authors declare no conflict of interest.

REFERENCES
8. Saharan P, Chaudhary GR, Sata S, Mehta SK, Mor S. Ultra fast and effective treatment of dyes from water with the syner-


