Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nano-strontium titanate as the nanophotocatalyst

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Abstract Research on photocatalytic degradation rate of azo dyes using nano-strontium titanate in photocatalysis process was the main goal of present study. In this regard, the influence of the main operating parameters such a photocatalyst concentration, dye concentration, temperature, pH and the presence of hydrogen peroxide upon dye removal rate under UV irradiation was studied. The absorbance of samples was measured by a UV–Vis spectrophotometer. The structure and morphology of nano-powder were investigated using scanning electron microscopy and crystalline structure by X-ray diffraction spectroscopy. The results reveal that nano-strontium titanate has high and significant photocatalytic activity and in comparison with nano-titanium dioxide was superior photocatalyst.

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1. Introduction

Environmental problem of toxic wastewater and infected waters is one of the main subjects that researchers work on. Due to this, organic dyes are one of the main industrial wastewater pollutions. More than 50% of textile dyes is azoic dyes which are recognized by nitrogen π-bound (Song et al., 2008; Lee et al., 2006). Textile and industrial dyes contain large groups of organic compounds that produce more than 7,00,000 ton per year. About 1–20% of world dye products enter into textile wastewater during the dyeing process (Madhavan et al., 2010; Isaev et al., 2009; Mahvi et al., 2009).

The common biological processes of degradation and discoloration on modern dyes are ineffective because of high degree of aromatic groups in dye molecules. The traditional physical methods such as using active carbon, filtration, reverse osmosis and coagulation are costly; moreover these methods do not degrade the dye and just change its phase (Janus and Morawski, 2007; Kaur and Singh, 2007). In recent years, advanced oxidation processes (AOPs) have been developed to deal with the problem of destruction of dyes in aqueous systems. The researches show that AOPs based on photocatalysts are effective. The benefits of this method are mineralization of organic compounds, no wastewater problem
and processing in mild pressure and mild temperature (Vinu et al., 2010; Chen, 2009; Foleto et al., 2009; Pouretedal et al., 2009; Wang et al., 2009; Konstantinou and Albanis, 2004). The use of semi-conductors such as TiO$_2$, ZnO, Fe$_2$O$_3$, and CdS as photocatalyst is interesting for the degradation of organic pollution. Due to optical and electrical properties, low cost, high photocatalytic activity, chemical stability and non-toxicity of nano-titanium dioxide, it is used as a common photocatalyst (Xua et al., 2008; Hegde et al., 2005).

Band gap larger than 3.2 eV causes low efficiency of nano-TiO$_2$, and the separation of nano-titania from the wastewater after photocatalytic dye degradation which is very difficult due to the small particle size (Wang et al., 2006; Zyoud et al., 2010; Ueda, 2004). Therefore, there is a need to find novel materials with high performance for the use in heterogeneous photocatalysis. The perovskite oxides recognition as photocatalyst has ABO$_3$ formula; where A is a rare earthmetal with a large ionic radius or alkaline earthmetal, B is a transition metal with a small ionic radius. Alkali metal acts as the ionic balance (place in A) and the titanate framework plays the main role in the structure and properties with Ti in the B sites (Boudali et al., 2009; Subramanian et al., 2006; Wang et al., 2003; Niishiro et al., 2005). The presence of Sr in SrTiO$_3$ gives more ionic properties in comparison to SrO, and Ti is more covalent in SrTiO$_3$ than in TiO$_2$, so this causes the reduction of the acidity of Ti ions and increase of covalent property. Thus, bond formation properties might be different with titania and can lead to different photocatalytical reactions (Chang et al., 2008). In comparison with other oxidants, the multi-cation oxide of SrTiO$_3$ is more capable of tuning the chemical and physical properties by altering the compositions and also has larger number of photocatalytic sites (Wei et al., 2008). The photocatalytic degradation of synthetic dyes using nano-strontium titanate has been reported in less scientific researches (Subramanian et al., 2006; He, 2009; Tsumura et al., 2009; Puangpetch et al., 2008). In the present study degradation of Direct Green 6 and Reactive Orange 72 with nano-strontium titanate under 20 and 400 W UV irradiation is investigated. The effect of various parameters such as dye and photocatalyst concentration, solution pH, temperature and presence of hydrogen peroxide will be investigated in turn and photocatalyst degradation rate of nano-strontium titanate and nano-titania on dyes will be compared next.

2. Experimental

2.1. Materials and equipments

Nano-strontium titanate powder (P.N.517011) and nano-titania (p25) were provided by Sigma Aldrich and Degussa Company, respectively. The specification of nano-materials was presented in Table 1. Commercially available Direct Green 6 and Reactive Orange 72 were obtained from Alvan Sabet Company, Iran, and their structures are shown in Figs. 1 and 2, respectively. Hydrogen peroxide, sodium hydroxide and nitric acid were prepared from Merck Company.

The dye’s solution was mixed with a magnetic stirrer during reaction (MR Hei, Heidolf, Germany). Samples after photocatalytic treatment were filtered through Millipore filter (0.45 µm) membrane. The pH of the solution was measured using ELICO, India, Li 120 pH meter and concentrations of dyes were determined by Varian Carry 100 UV–Vis spectrophotometer.

UV-A 20 W lamp (Sylvania, Belgium), with 365 nm wavelength radiation and light intensity of 0.2–0.4 µW cm$^{-2}$, and UV 400 W (Philips, HPA 400 s, Belgium), with higher radiation of wavelength between 300 and 400 nm along with light spectrum having intensity of 800 µW cm$^{-2}$ for UV-A, 115 µW cm$^{-2}$ for UV-B and 25 µW cm$^{-2}$ for UV-C were used as light source.

Scanning electron microscopy (Philips, SEM, XL30, The Netherlands) was used to determine the structure and the morphology of nano-materials. The crystalline structure of the photocatalysts was characterized by X-ray powder diffraction (XRD; Bruker D8 Discover X-ray diffractometer, Germany).

2.2. Procedure

The concentration of dye in the solution was calculated by a computer program using calibration curve. The program determines absorbance of dye solution at maximum wavelength of dyes: Direct Green 6 – 623 nm, Reactive Orange 72 – 433 nm. The first step was the preparation of dye solution by distilled water. Then, nano-materials with different percent were added. Firstly, the solution mixture was stirred for 15 min without irradiation in order to get equilibrium of dye adsorption. Then the solution was irradiated with two lamps (20 and 400 W) for 3 h and during irradiation it was continuously stirred with a rate of 200 rpm and temperature of 25 °C and the real dye solution pH for direct and reactive dye was 6.6 and 6.4, respectively. After irradiation, the samples were purified with Millipore filter. The decolorization and photocatalytic degradation efficiency have been calculated as

\[
\text{Efficiency(%) = } \frac{C_0 - C_f}{C_0} \times 100
\]

where $C_0$ and $C_f$ correspond to the initial and final concentration of dye before and after photo-irradiation. In this equation E% shows the dye photocatalyst degradation percent (Chen, 2009). The variable parameters of research were photocatalyst concentration (in range of 0.01–0.3%, on weight of bath (O.W.B.)), dye concentration (in range of 20–60 g/L), temperature (between 30 and 50 °C), pH (3–11) and presence of hydrogen peroxide (0.1–0.4 mL). Basic parameters were photocatalyst concentration of 0.1%, 20 mg/L dye, 25 °C temperature, 3 h irradiation and real pH. Finally for investigation of nano-strontium titanate photocatalytic efficiency, its degrada-

<table>
<thead>
<tr>
<th>Kind of nano-powder</th>
<th>Ave. particle size (nm)</th>
<th>Appearance</th>
<th>Solubility in water</th>
<th>Density (g/cm$^3$)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>&lt; 100</td>
<td>White and without odor</td>
<td>Insoluble</td>
<td>4.81</td>
<td>2060</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>21</td>
<td>White and without odor</td>
<td>Insoluble</td>
<td>3.8</td>
<td>1850</td>
</tr>
</tbody>
</table>
tion percent in various concentrations were compared with nano-TiO$_2$.

3. Result and discussion

3.1. Effect of photocatalyst concentration

In photocatalyst process, one of the main parameter of discoloration of dye solution is photocatalyst concentration. Fig. 3 showed that by increasing nano-strontium titanate concentration, degradation of dye was increased but practically there was no degradation more than 0.15% nano-strontium titanate, even in some samples it decreased and caused the aggregation of nano-strontium titanate in dye solution that due to the decrease of nano-material photocatalytic activity. So, given no difference between photocatalyst degradation of 0.1 and 0.15, besides being more cost effective compared with 0.15% SrTiO$_3$, 0.1% SrTiO$_3$ was chosen as the base parameter of bath weight.

For both direct and reactive dye, the percentage of photocatalyst degradation with 400 W UV lamp was higher than 20 W. This occurs for two reasons, first of all there is more radiation intensity and the second one is lower wavelength that resulted in electron exiting of nano-materials.

The higher degree of discoloration of the reactive dye compared with the direct dye is due to the chromophore structure of the dyes, which is monoazo and trisazo, respectively (Karimi et al., 2010).

3.2. Effect of dye concentration

The dyes’ concentrations in the experiment ranged from 20 to 60 mg/L. The results illustrated in Fig. 4 reveal that by increasing dye concentration, photocatalyst degradation is reduced. The results are similar to that of previous studies (Habibi and Talebian, 2007). When the dye concentration increased, the quantity of intermediates increased as well, competing through side reactions with the parent dye decomposition.

![Figure 1](image1.png)  
**Figure 1** Structure of Direct Green 6 (CI 30295).

![Figure 2](image2.png)  
**Figure 2** Structure of Reactive Orange 72 (CI 17754).

![Figure 3](image3.png)  
**Figure 3** Comparison diagram of photocatalytic reactive and direct dye degradation with different percent of nano-strontium titanate based on weight of bath.
At higher dye concentration, the UV light might be absorbed by dye rather than the SrTiO3 particles and reduces the photocatalytic degradation efficiency.

3.3. Effect of temperature

To evaluate the effect of temperature on photocatalytic degradation, the temperature of solution was changed in the range of 30–50 °C by the use of electromagnetic heater while the other parameters were kept constant. The results were shown in Fig. 5. The degradation efficiency of dyes gradually increased as the temperature increased. With the increase of temperature, the bubble of solution rose causing the production of free radicals. Furthermore, the increase in temperature helped the reaction to compete more efficiently with electron–hole recombination. Furthermore, the increasing temperature may increase the oxidation rate of dye at the interface.

3.4. Effect of pH

The effect of pH on photocatalyst degradation of dye solution in the range of 3–11 was investigated while other parameters were constant. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of nitric acid or sodium hydroxide. Fig. 6 compares the results of photocatalyst degradation of dyes as a function of reaction pH.

It is clear from Fig. 6 that lower pH causes the increase of dye degradation. Less pH cause to produce hydroxide radicals in photocatalytic processes and also cause to enhance active area of strontium titanate and contact area, thus photocatalyst degradation is more.

3.5. Effect of hydrogen peroxide

The effect of hydrogen peroxide from 0.1 to 0.4 mL on the photocatalyst degradation at real pH, a temperature of 25 °C with 0.1% of perovskite under 20 and 400 W UV irradiation for 3 h is illustrated in Fig. 7. Due to producing hydroxide radicals and the prevention of recombination of electrons and holes (e−/h+) (according to Eqs.(1)–(3)) dyes degradation improved by adding H2O2 (Saquib et al., 2008):

\[ \text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2, \]  
\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot\text{OH}, \]  

Figure 4  Comparison diagram of photocatalytic dye degradation with different dye concentrations.

Figure 5  Comparison diagram of photocatalytic dye degradation in temperature range of 30–50 °C.
H$_2$O$_2$ + e$^{-}_{CB}$ → ‘OH + ‘OH’. \( (3) \)

3.6. Nano-material phases and morphology

Nano-material morphology was investigated by scanning electron microscopy and as it is clear in Fig. 8, the particle size was 29 and 66 nm for titania and strontium titanate, respectively.

X-ray diffraction was used to determine the crystalline phase of nano-materials. The results show that 24.2% of strontium titanate structure is the same as anatase structure of titania (Wei et al., 2008). Crystalline phase of nano-strontium titanate is cubic and crystalline phase of titania is anatase and rutile with 84.4% and 15.6%, respectively. XRD spectrum of titania and nano-strontium titanate is shown in Fig. 9.

![Figure 6](image1.png) Comparison diagram of photocatalytic dye degradation with pH range of 3–11.

![Figure 7](image2.png) Comparison diagram of photocatalytic dye degradation in presence of different hydrogen peroxide concentrations and 0.1% nano-strontium titanate.

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![Figure 8](image3.png) SEM image of (A) nano-strontium titanate powder and (B) nano-titania powder.
The average crystal size of nano-strontium titanate and nano-titania are 43.13 and 20.02 nm calculated by XRD. One of the effective parameters in photocatalytic process is specific surface area which is calculated according to:

$$S_{BET} = \frac{6}{s \times d}$$

In this equation “$S$” is surface area, “$s$” is crystal size (nm) and “$d$” is bulk density which is 5.13 and 4.1 g/cm³ for nano-strontium titanate and titania, respectively (He, 2009). Calculated surface area is 27 and 73 m²/g for strontium titanate and titania that shows both photocatalysts having high surface area.

3.7. Nano-SrTiO₃ and nano-TiO₂ photocatalyst comparison

To investigate the amount of photocatalytic degradation of Direct Green 6 and Reactive Orange 72 by titania, the same concentration of nano-strontium titanate was added to dye solution in same conditions (20 mg/L dye concentration, temperature of 25 °C, real pH and 3 h irradiation). The compared...
diagram of photocatalyst degradation of nano-strontium titanate and nano-titania is shown in Figs. 10 and 11. The results show photocatalyst degradation percent of nano-strontium titanate between 0.01% and 0.1% which is the same as titania but greater than 0.1% photocatalyst degradation for TiO₂ which is greater than SrTiO₃.

The results of this study showed larger nano-particle size and lower surface area of nano-strontium titanate in comparison with titania. Particle size and surface area are the effective parameters of photocatalytic activity of nano-materials, but despite these, photocatalytic degradation of nano-SrTiO₃ is the same as nano-TiO₂ that demonstrates the higher photocatalytic activity of nano-strontium titanate than titania. So in the same particle size, photocatalytic degradation of nano-SrTiO₃ is higher than nano-TiO₂ (Wei et al., 2008; He, 2009).

The main advantage of nano-strontium titanate in comparison with titania is higher oxidation activity and smaller band gap energy (Miyauchi et al., 2002). Considering the changes of nano-strontium titanate structure, its multi-cationic oxidant activity is higher than the other photocatalysts and has more photocatalysis capacity (Chang et al., 2008; Wei et al., 2008; He, 2009; Tsumura et al., 2009). The reason of reducing dye degradation in high concentration of nano-materials is due to the aggregation of nano-particles in solution. Because of the bigger size of nano-SrTiO₃ than nano-TiO₂, this aggregation for strontium titanate happens in 0.1% and more percent of nano-materials. However this aggregation happens in 0.2% or higher percentages for titania because of its smaller particle size.

4. Conclusion

In this study azoic dye degradation with photocatalyst process using nano-strontium titanate was investigated. The results show that by increasing nano-strontium titanate concentration in solution, dye degradation will be increased but due to aggregation of nano-strontium titanate in 1 g/L concentration and higher, it suddenly drops down. Also, the results demonstrated that increasing dye concentration reduced the photocatalyst degradation. On the other hand in acidic pH, nano-SrTiO₃ surface area was higher and so photocatalyst degradation
was increasing temperature of process and adding H2O2 caused the increase of dye degradation. The obtained results of XRD and SEM showed the bigger particle size and smaller surface area of nano-SrTiO3 than nano-TiO2, but it proved that photocatalyst dye degradation of nano-strontium titanate was the same as titania. So, it was concluded that the use of nano-strontium titanate photocatalyst in purification based on advanced photocatalyst oxidation process is more efficient.

References


