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ORIGINAL ARTICLE

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.

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

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and processing in mild pressure and temperature (Vinu et al., 2010; Chen, 2009; Foletto 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_2O_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

$$\text{Efficiency}(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 and C_e 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 1 Specification of nano-materials.

Kind of nano-powder	Ave. particle size (nm)	Appearance	Solubility in water	Density (g/cm^3)	Melting point (°C)
$SrTiO_3$	< 100	White and without odor	Insoluble	4.81	2060
TiO_2	21	White and without odor	Insoluble	3.8	1850