1. Introduction

Dyestuffs produced by Textile industries always constitute a largest number of organic compounds which increases environmental hazards. Due to the presence of a large degree of aromatic groups in dye molecules and the stability of modern dyes, traditional and conventional techniques have been unsuccessful for the discoloration and degradation of dyes. Therefore, investigation of new methods are required which could conduct complete decomposition of dyes [1].

Purification of contaminated water through complete mineralization of pollutants has been used extensively. Titania is a very versatile material with attractive applications as cosmetics, in the production of electrochemistry electrodes, capacitors, solar cells, catalysis and photocatalysis [2-7]. However, TiO$_2$ presents a relatively high electron-hole recombination rate due to its wide band gap energy (ca. 3.0 eV for rutile and 3.2 eV for anatase), and as a result retards its photoactivity. In this sense, doping with metals could make a double effect: firstly, it could reduce the band gap energy, thus shifting the absorption band to the visible region. Secondly, metals could provoke a decrease in electron-hole recombination rate, acting as electron traps. Therefore, few examples were found in literature about titanates doping.
with transition metals such as Ni (II) [8], Cu (II) [9,10], Nb (V) [11], Cr (III) [12,13], Fe (III) [14–17], Sn [18], Ag [19], Au [20] and Pd [21]. Recently Wang and Virkutyte et al. found that nitrogen and metal doped TiO$_2$ nanoparticles showed visible light photoactivity [22,23]. In addition, titania doped with metal molybdates [24] were reported to have improved photocatalytic properties with enhanced absorption of visible/ultraviolet light.

The photocatalytic activity of a multicomponent system also depends on the synthetic procedure and their compositions. In recent years, binary metal oxides such as TiO$_2$/Fe$_2$O$_3$, TiO$_2$/WO$_3$, TiO$_2$/MoO$_3$, TiO$_2$/SiO$_2$ and TiO$_2$/ZrO$_2$ have been widely studied for their unique chemical, physical and photocatalytic properties [25–29]. Jiang Yin et al. reported that MCrO$_4$ (Ba, Sr) has photocatalytic properties [30] but interestingly no one have studied on the photocatalytic properties of SrCrO$_4$/TiO$_2$ mixed oxides.

Furthermore, photoactivity is highly dependent on surface area, crystallinity or crystal sizes which, in turn, are influenced by the titania synthetic method. As far as such methods are concerned, the catalytic properties are closely related to their structure and depend on the method of preparation and on the thermal treatment. Both single phase and multiphase SrCrO$_4$/TiO$_2$ mixed oxides in different mole ratio [strontium chromate in TiO$_2$ is 1 mol% (SCT1), 3 mol% (SCT2) and 5 mol% (SCT3)] were prepared by co-precipitation technique and their photocatalytic activities were evaluated by the photo-oxidations of different dyes like Rhodamine 6G (Rh6G), Methyl orange (MO), Thymol blue (TB) and Bromocresol green (BG) under UV light (400-W Hg lamp; $\lambda = 364$ nm) irradiation. The advantages of this approach are that the use of voluminous solutions and complicated operations as well as the high sintering temperature of the final product can be avoided.

2. Experimental

2.1. Synthesis of SrCrO$_4$/TiO$_2$ photocatalysts

Nano-sized mixed oxide photocatalysts (strontium chromate in TiO$_2$ is 1 mol%, 3 mol% and 5 mol%) were prepared by co-precipitation method. The total synthesis was carried out in two steps. In the first step, the stock solutions of ammonium dichromate, strontium nitrate and titanium tartrate solutions were prepared. The titanium tartrate synthesis was reported in elsewhere [31,32]. In the second step the stoichiometric amount of titanium tartrate, strontium nitrate and ammonium dichromate solutions were taken in a beaker. In this case in any condition no precipitation should appear in the mixture. Then the aqueous ammonia was added drop wise via vigorous stirring to the above solution to adjust pH to about 9 and a light orange amorphous precipitate was formed. The precipitation was filtered and washed with distilled water until alkali phases were removed from precipitation. The prepared samples were dried at 100°C for 15 h in an oven and photocatalytic activity was studied. The same method was followed for the synthesis of TiO$_2$ and SrCrO$_4$ systems. The heat treatment of the sample at a temperature higher than 200°C had poor photocatalytic activity.

2.2. Chemicals

Titanium dioxide (analytical reagent), Sr(NO$_3$)$_2$ (analytical reagent), (NH$_4$)$_2$Cr$_2$O$_7$ (analytical reagent), HNO$_3$ (65%), NH$_4$OH (25%), HF (40%), Rhodamine 6G (Rh6G), Methyl orange (MO), Thymol blue (TB), Bromocresol green (BG) and 4-nitrophenol (4-NP) were A.R. reagents procured from MERCK India.

2.3. Photocatalytic experiment

Photocatalytic experiments were conducted using nanophotocatalysts in the presence of different photo catalytically degradable dyes in water solution. The photocatalytic reaction was carried out under UV light irradiation with slow stirring (using magnetic stirrer) of the solution mixture and SrCrO$_4$/TiO$_2$ photocatalysts. The light source was a 400-W Hg lamp (PHILIPS-HPL-N, G/74/2, MFB-400) and its wave length ($\lambda$) is 364 nm. The container was made of Petridis of volume 200 mL. The reactions were performed by adding nano powder of each photocatalyst (0.1 g) into each set of a 100 mL of different solution of dyes.

2.4. Analytical methods

A small volume (1 mL) of reactant liquid was siphoned out at regular intervals of time for analysis. It was then centrifuged at 1100 rpm for 15 min, filtered through a 0.2 μm-millipore filter to remove the suspended catalyst particles and concentration of dye was measured by absorption spectrometry using UV-VIS spectrometer (PerkinElmer Lambda 35) at absorption maxima.

2.5. Characterization

The crystal structure of the prepared samples was determined by the X-ray diffractometer (XRD) (Model: Philips PW 1710) equipped with a Cu Kα radiation. The accelerating voltage and current used were 40 kV and 20 mA, respectively. The 2θ ranged from 10°-70°.

Crystallite sizes ($D$) of the obtained powders were calculated by the X-ray line broadening technique performed on the direction of lattice using computer software (APD 1800, Philips Research Laboratories) based on Scherer’s formula [33]

$$D = \frac{0.99 \lambda}{\beta \cos \theta}$$

where $D$ is the Crystallite size, $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg’s angle and $\beta$ is half width. The stoichiometry of SrCrO$_4$/TiO$_2$ mixed oxides were examined by energy dispersive X-ray spectroscopy (EDX) (JEOL JMS-5800) which was consistent with the amount taken of SrCrO$_4$ and TiO$_2$ taken during synthesis.

BET surface area measurements were carried out using a BECKMAN COULTER SA3100 through nitrogen adsorption-desorption isotherm at 77 K. The average sizes of nanoparticles were measured in the SEM (JEOL JMS-5800). The electron paramagnetic resonance (EPR) spectrum was obtained by
BRUCKER ER083CS model at room temperature (ca. 298 K). The UV-VIS diffuse reflectance spectra of the prepared powders were obtained by a UV-VIS spectrophotometer (PerkinElmer Lambda 35) at room temperature.

After leaching the SrCrO$_4$/TiO$_2$ solid solution through filtration with whatman-42, the reaction solution (after reaction) was subjected to inductively coupled plasma (ICP) analysis in order to measure the amount of leached SrCrO$_4$/TiO$_2$ solid solution.

3. Results and discussion

3.1. X-ray diffractometer analysis

The XRD pattern of the different mixed oxides (single and multiphase) of SrCrO$_4$/TiO$_2$, heated at 100 °C for 15 h in air atmosphere, was shown in Fig. 1. It was evident from the XRD pattern that the mixed oxide SCT1 (TiO$_2$ doped with 1 mol% of SrCrO$_4$) should almost anatase phase (as per JCPDS No. 72-0746). Following an increase of the SrCrO$_4$ concentrations in TiO$_2$ lattice, the SrCrO$_4$ peaks appeared, as shown in the XRD pattern of SCT3, because SrCrO$_4$ was not resolved in TiO$_2$ lattice and its photocatalytic activity was decreased. The XRD pattern of TiO$_2$ sample showed distinct peaks of the anatase phases, without any indication of rutile phases. Average crystallite sizes of the prepared photocatalysts were calculated using Scherer’s formula and were found to be ~15 nm. The atomic level dispersion of SrCrO$_4$ in TiO$_2$ has been presented in Fig. 2 through an energy dispersive X-ray spectroscopy.

3.2. Specific surface area (BET) analysis

The BET surface area of SCT1 mixed oxides, calcined at 100 °C, was 52.4 m$^2$/g, while the surface area of P25 was 49.1 m$^2$/g. The surface areas of other prepared photocatalysts are presented in Table 1. Among all the prepared photocatalysts the SCT1 was more photoactive for faster degradation of different dyes like Rh6G, MO, TB and BG under UV light irradiation. The photocatalytic activity of SCT1 was 3 times greater than that of P25 TiO$_2$ for degradation of Rh6G.

3.3. Transmission electron microscopy and SEM analysis

The finer detail of the particles and their morphologies was investigated by transmission electron microscopy (TEM) (Model Philips TM-30, Philips Research Laboratories). The bright-field (BF) electron micrograph of the SCT1 powder produced at 100 °C reflected a spherical particle, with an average particle diameter of 90 nm (Fig. 3a). Fig. 3b represents the particle size distribution histogram. In Figs. 3c and 3d represents the SEM images of SCT1 at different resolution. The grains separated by well-defined grain boundaries were visible and uniformly distributed. The average grain size of SCT1 sample was about 100 ± 5 nm. The grain sizes were calculated from the micrographs using UTI image tool software (version 2.0).

3.4. Electron paramagnetic resonance spectrum study

The characteristic feature of the EPR spectrum of the SrCrO$_4$/TiO$_2$ recorded at 298 K was a signal at a g-tensor value of 2.001, indicating the presence of Sr$^{2+}$/Cr$^{3+}$ on irradiated TiO$_2$ (Fig. 4). Due to absence of any hyperfine line in ESR spectra, it was suggested that Sr$^{2+}$/Cr$^{3+}$ cations were well separated. No EPR signal was detected on pure TiO$_2$ or SrCrO$_4$ species. The EPR signal of SrCrO$_4$/TiO$_2$ indicated that the ejection of an electron was the crucial role for photooxidation of Rh6G under UV light.

3.5. Photocatalytic activity of the prepared samples

The photo oxidation of Rh6G in the presence of different catalysts SrCrO$_4$/TiO$_2$ (SCT1, SCT2, and SCT3), TiO$_2$, SrCrO$_4$ (SC) under UV light irradiation (Fig. 5a) and represented the concentration changes of Rh6G at 528nm in presence
of SCT1 at different irradiation times (Fig. 5b). Figure 5b represents the Rh6G degradation at different irradiation time in presence of SCT1. Figure 5a indicates that under UV light irradiation, SCT1 mixed oxides exhibited highest photocatalytic activity compared to the other compositions of SrCrO$_4$/TiO$_2$ mixed oxides, P25 TiO$_2$, and strontium chromate. Under the UV lamp, nano TiO$_2$ was excited leading to the accelerated generation of photo-induced hole-electron pairs, which reacted with dissolved oxygen and Rh6G to produce CO$_2$ and water and as a result, concentration of Rh6G was decreased. It was also observed that in absence of a catalyst, the degradation of dyes was not possible under UV light (Fig. 5a). Because its oxidizing ability was not sufficient, UV light can promote the generation of •OH from oxidation of Rh6G but the result was still not satisfactory. The slight changes in concentrations of Rh6G due to the compounds were itself absorbing the dyes. The SCT1 mixed oxide showed a three times higher photocatalytic activity than P25 TiO$_2$ in Rh6G medium. The increment of SrCrO$_4$ concentration beyond 1 mole % led to a lower photocatalytic activity due to formation of multi-phase on mixed oxides of SCT2, SCT3 systems. The photo-oxidation of different colored dyes Rh6G, MO, TB, BG and 4-nitrophenol to colorless solution using the prepared photocatalysts under an UV light irradiation was shown in Fig. 6. UV-VIS spectra of Rh6G, MO, TB, BG and 4-NP were recorded after irradiation of UV in presence of SCT1, SCT2, SCT3, P25 TiO$_2$ and SC mixed oxides and corresponding absorbance maxima of dyes were found.

### Table 1 – Resultant properties of SCT1, SCT2, SCT3, P25 TiO$_2$, and SrCrO$_4$ mixed oxides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction rate constant $k$ (h$^{-1}$)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Crystallite size (nm)</th>
<th>Photo degradation efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rh6G</td>
</tr>
<tr>
<td>SSCT1</td>
<td>7.54</td>
<td>52.4</td>
<td>14.98</td>
<td>97.5</td>
</tr>
<tr>
<td>SCT2</td>
<td>4.56</td>
<td>49.5</td>
<td>15.13</td>
<td>89.1</td>
</tr>
<tr>
<td>SCT3</td>
<td>1.96</td>
<td>37.1</td>
<td>15.48</td>
<td>61.5</td>
</tr>
<tr>
<td>P25 TiO$_2$</td>
<td>2.42</td>
<td>49.1</td>
<td>12.42</td>
<td>84.4</td>
</tr>
<tr>
<td>SrCrO$_4$</td>
<td>0.37</td>
<td>1.1</td>
<td>18.21</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Calculated reaction rate constant after 3 h degradation of Rhodamine 6G under UV light and catalyst. BET surface area measured by dinitrogen adsorption desorption isotherm at 100 °C. Crystallite size in nm calculated from Scherer equation.

Fig. 3 – (a) Transmission electron microscopy of SCT1, (b) particle size distribution of SCT1, (c) scanning electron microscopy of SCT1 calcined at 100 °C for 2 h at resolution 5000, and (d) at resolution 7500.
Among all the four dyes including 4-NP, the rate of degradation of Rh6G was faster in the presence of SCT1 and UV light. The time required for degradation of Rh6G was 5.2 hours. For all the cases, the catalysts were taken at 1 g/L and different dye concentration was about 10 mM. The degradation rate constant (k) of Rh6G, MO, TB and BG using SCT1, SCT2, SCT3, P25 TiO₂, SC photocatalysts have been presented after 3 h for degradation of dye solutions in Table 1. The catalytic efficiency of SCT1 on different dyes under UV light irradiation is shown in Fig. 7. The photo-oxidation efficiency among all of the dyes of Rh6G, MO, TB, BG and 4-nitrophenol, Rh6G was fastest.

3.6. Stability of the catalyst

To examine the stability of the SCT1 photocatalyst, the photocatalytic degradation properties of the photocatalyst was investigated by repeating Rh6G photocatalytic degradation experiments five times. After each cycle, the SCT1 photocatalysts were washed thoroughly with water, and a fresh solution of Rh6G was added before each photocatalytic run in the reactor. Fig. 8 indicates that the photocatalytic efficiency of SCT1 decreased slowly with increase the repetition of the cycles. After the fifth cycle the efficiency of SCT1 catalysts decreased about 2% compared to the total degradation of Rh6G. This is due to the loss of catalysts during the water washing of catalysts, which was not observed in the naked eye. Thus suggests that SCT photocatalysts have excellent stability and reliability for photodegradation of pollutants.

3.7. Effect of heat-treatment temperatures

The effect of calcinations on the photocatalytic activity of mixed oxides was also investigated. Fig. 9 shows the profiles of the photo-oxidations of Rh6G under UV light irradiation using SCT1 mixed oxide calcined at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C. The samples calcined at 100 °C showed the highest photocatalytic activity than that calcined at other temperatures. It seems that the increase of the calcination temperature decreased the number of defect-states on the surface. Above 100 °C temperature, the activity of catalyst decreased with an increase of crystallite sizes of mixed oxides. It was also observed that adsorption of the dyes (Rh6G, TB, MO, and BG) decreased with an increase of the calcination temperature of the catalyst. This may probably due to a decrease in the number of defect-structure on the surface of solid catalyst. However, the
Fig. 6 – Effect of SCT1 on different dyes under UV light.

Fig. 7 – Catalytic efficiency of SCT1 on different dyes under UV light. 4-NP: 4-nitrophenol; BG: bromocresol green; MO: methyl orange; Rh6G: rhodamine 6G; TB: thymol blue.

Fig. 8 – Stability of SCT1 catalysts after 5 recycle processes on rhodamine 6G.

Fig. 9 – The effect of calcinations temperature of SCT1 on rhodamine 6G and study of their photocatalytic activity. The catalyst concentration is \( C_{\text{catalysts}} = 1 \text{ g/L} \). Rhodamine 6G concentration is \( C_{\text{Rh6G}} = 10 \text{ mM} \), 400-W Hg lamp (\( \lambda > 280 \text{ nm} \)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination Temperature (°C)</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCT1</td>
<td>100</td>
<td>52.4</td>
<td>14.98</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>49.5</td>
<td>15.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>33.1</td>
<td>15.49</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>21.1</td>
<td>16.42</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>12.5</td>
<td>18.21</td>
</tr>
</tbody>
</table>

Table 2 - BET Surface Area of SCT1 at different calcination temperature.
decrease in the activity may also be attributed to a decrease in the surface area of the photocatalysts. This was also evident from the change in surface area of the samples calcined at different temperature (Table 2).

4. Conclusions

In summary, we report the novel synthesis of nano spherical SrCrO$_4$ and TiO$_2$ mixed oxides by co-precipitation technique in comparison to traditional solid-state process, allowing the oxidation of the Rh6G synthesis temperature up to 100°C. The incorporation of SrCrO$_4$ in the TiO$_2$ lattice was confirmed by XRD. The XRD data showed the formation of mixed oxides having anatase structure with no free SrCrO$_4$ up to 1 mole % of SrCrO$_4$/TiO$_2$. SCT1 have average crystallite sizes, particle sizes and grain sizes about 15 nm, 90 nm and 100 ± 5 nm, respectively. The SCT1 has highest photocatalytic activity which is 3 times higher than P25 TiO$_2$ for the oxidation of Rh6G. Photocatalytic degradation of Rh6G in presence of UV light was rationalized by production of photo-induced hole-electron pairs in the presence of TiO$_2$ nanoparticles, which would react with dissolved oxygen and Rh6G to produced CO$_2$ and water and as a result concentration of Rh6G decreased. The EPR spectrum of SCT1 was evidence for the formation of electron/hole pair in the reaction time.

Acknowledgements

Author is grateful to the Department of Science and Technology (DST) as “Fast Track Scheme for Young Scientists” (SR/FT/CS-021/2010), New Delhi, India for the financial support of this work.

References


