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Photodegradation Study of Evan's blue in Presence of Strontium Chromate

Monika Jangid[1*], Suresh C. Ameta[1] and Ajay Sharma[2]

1. Department of Chemistry, PAHER University, Udaipur-313003 (Raj.), **INDIA**
2. P.G. Department of Chemistry, Govt. P. G. College, Sirohi-307001 (Raj.), **INDIA**

Email: monikajangid24@gmail.com

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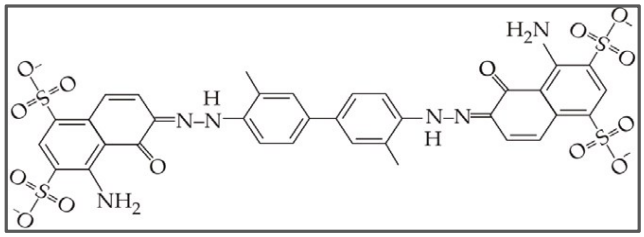
ABSTRACT

The photocatalytic degradation of Evans blue has been studied under visible light in the presence of $SrCrO_4$ as a photocatalyst. Strontium chromate was synthesized by precipitation method in a wet chemical process. The photocatalytic activity of strontium chromate was compared by investigating the photodegradation of Evans blue dye under visible light. The effect of various parameters such as pH, the concentration of dye, amount of semiconductor and light intensity on the rate of degradation was also studied. It was observed that strontium chromate has the highest catalytic activity in basic medium. A tentative mechanism for the reaction has been proposed.

Graphical Abstract



Structure of Evan's blue.

Keywords: Evans Blue dye, Photocatalytic degradation, Strontium Chromate.

INTRODUCTION

Water is one of the most important natural resource for human kind. On the Earth, water is the most precious and biggest gift of God to mankind. All life and peripheral activities are ceased without water. In present, water pollution is a major problem for all of us. Dye wastes are major pollutants because they can be easily identified by the human eye and are not easily biodegradable. Textile and dyeing industries produces large volume of wastewater containing synthetic organic dyes. Synthetic organic dyes contain toxic materials such as organic compounds, color pigments and metals. These organic compounds are responsible for high chemical oxygen demand (COD) level in wastewater; thus, cause serious problems in the environment. Therefore, decontamination and decolourization of dye wastewater is an urgent requirement for protecting environment.

Azo dyes are the largest and most important class of synthetic organic dyes. It has been observed that azo dyes are used more than 50% of all the dyes used, because of their chemical stability and versatility [**1**]. Azo dyes are not biodegradable by aerobic treatment processes [**2**] and under anaerobic condition, they give potentially carcinogenic aromatic amines, which because long-term health concerns [**3**]. Evans blue or T-1824 is an azo dye, which has a very high affinity for serum albumin. Devi *et al*., studied photodegradation of methyl orange, an azo dye by advanced Fenton process using zero valent metallic iron, influence of various reaction parameters and its degradation mechanism [**4**]. Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes was reported by Neamtu *et al* [**5**].

Antonin *et al*., studied degradation of Evans blue diazo dye by electrochemical processes based on Fenton's reaction chemistry [**6**]. A solution with 0.245 mM of the diazo dye Evans blue and 0.50 mM Fe^{2+} catalyst of pH 3.0 was comparatively degraded by electrochemical Fenton processes like electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF). Evans blue degradation obeyed pseudo-first order kinetics. The mineralization rate was found to increase in the following order:
EF < PEF < SPEF

Tambe and Kothari studied oxidative photodegradation of Evans blue using N-doped ZnO. N-doped ZnO was prepared by the solvent free method [**7**]. The effect of different parameters like pH, concentration of the dye, amount of N-doped ZnO and light intensity on the rate of degradation was also studied. It was revealed that the N-doped zinc oxide photocatalyst shows higher photocatalytic activity compared to pure zinc oxide.

Pillai *et al*., prepared C-TiO_2 nanophotocatalyst and used it for degradation of Evans blue [**8**]. The reaction followed pseudo-first order kinetics. Participation of $^{\bullet}OH$ free radical was confirmed by scavenger studies. Optimum conditions were determined by variation of operational parameters.

Paliwal *et al*., reported enhanced photocatalytic activity of bismuth ferrite for degradation of Evans blue by doping it with cobalt [**9**]. The progress of the reaction was monitored spectrophotometrically by measuring the absorbance of the reaction mixture at definite time intervals. Doping of bismuth ferrite by cobalt was found to increase the rate of photocatalytic degradation due to narrowing of the band gap. Undoped bismuth ferrite has the highest catalytic activity in basic, while the Co-doped catalyst in acidic medium.

Dangi *et al.*, studied photocatalytic activity of CdS-ZnS composite and their components. A composite of CdS and ZnS was prepared by simple solid state mechanochemical method and it was used for photocatalytic degradation of Evan's blue [**10**]. The photocatalytic efficiency of CdS-ZnS composite was compared with pure CdS and ZnS. It was found that coupled chalcogenides (CdS-ZnS) showed better photocatalytic activity as compared with pure CdS and ZnS for the degradation of Evan's blue in the presence of visible light.

Rao *et al*., investigated ionic liquid assisted synthesis and characterization of ZnO nanoparticles. A green approach has been developed for the synthesis of nanocrystalline zinc oxide with the aid of room-temperature synthesized ionic liquids (RTILs) as crystal growth modifiers by low-temperature precipitation technique. The role of RTILs (propylammonium acetate (PAA), propylammonium formate (PAF), 3-hydroxy propylammonium acetate (3-HPAA), 3-hydroxy propylammonium formate (3HPAF) and the effect of their concentration on the particle size has been studied in this protocol. XRD spectra of nanoparticles exhibited typical diffraction peaks of hexagonal phase with wurtzite ZnO structure [**11**]. TEM results revealed that spherical nanoparticles were obtained with an average particle size in the range of 5-20 nm. UV-Vis-DRS spectra of the ZnO nanoparticles showed blue shift as compared to the bulk ZnO which is attributed to quantum confinement effect.

Kalantri *et al*., synthesized $PbTa_2O_6$ by solid state method and used it for photocatalytic degradation of Evans blue. $PbTa_2O_6$ photocatalyst was prepared by a green chemical approach. Band gap of synthesized $PbTa_2O_6$ was found to be 4.38 eV. XRD pattern confirmed hexagonal crystal phase while SEM showed agglomerated crystalline particles [**12**]. The photocatalytic property of synthesized catalyst was examined by photodegradation of Evans blue as a model dye systematically. The degradation follows first order kinetics with rate constant 4.0×10^{-3} min^{-1}.

Paliwal *et al.*, has studied photodegradation of malachite green using CuO/Al_2O_3 as a photocatalyst [**13**]. Sanasi *et al.*, prepared Thiourea modified nanotitania (NT) particles and used it for degradation study of Congo red dye from the waste water [**14**]. Narkhede *et al*., approach towards a green synthesis of iron oxide (Fe2O3) nanoparticles, which is used for degradation of methyl orange exists in waste water of various industries for environmental remediation [**15**].

Chen *et al*., reported that $SrTiO_3$is an effective photocatalyst for NO degradation under UV light irradiation [**16**]. Bhati *et al*., studied the photocatalytic degradation of fast green using $CeCrO_3$ as photocatalyst [**17**]. Asai *et al*., suggested visible light responsive rhodium and antimony-codoped $SrTiO_3$ photocatalyst loaded with an IrO_2 cocatalyst for solar water splitting [**18**]. Chen *et al*., reported the theoretical investigation of the metal doped $SrTiO_3$ photocatalysts for water splitting [**19**]. Synthesis of highly active rhodium doped $SrTiO_3$ powders in Z-scheme systems for visible light driven photocatalytic overall water splitting was carried out by Kato *et al* [**20**]. Composite $Sr_2TiO_4/SrTiO_3$ (La,Cr) hetero junction based photocatalyst for hydrogen production under visible light irradiation was reported by Jia *et al* [**21**]. Very little work has been carried out on $SrCrO_4$ as photocatalyst and therefore, in the present work, $SrCrO_4$ has been used as a photocatalyst for the degradation of Evan's blue.

MATERIALS AND METHODS

Synthesis of strontium chromate: Strontium chromate was synthesized by precipitation in a wet chemical process with water-soluble strontium chloride and sodium chromate, It was characterized by SEM-EDS techniques. 66.66 g of strontium chloride and 58.52 g of sodium chromate was taken in separate beakers and distilled water was added. Strontium chloride and sodium chromate solutions are mixed, giving precipitates of deep lemon yellow colored strontium chromate. Then, it was filtered, washed with water many times and dried at 80°C.

Photocatalytic process: The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of Evan's blue dye. A stock solution of dye (1.0×10^{-3} M) was prepared by dissolving (0.096 g) of dye in 100 mL doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics model 335), and the desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The reaction mixture containing 0.10 g photocatalyst was exposed to a 200 W tungsten lamp, and about 3 mL aliquot was

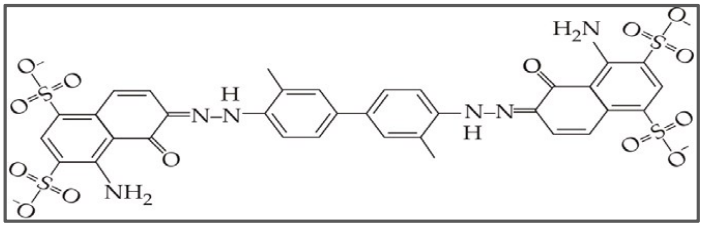


Figure 1. Structure of Evan's blue.

taken out every 10 min. Absorbance (A) was measured at λ_{max}=620 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM 201). The

absorbance of the solution at various time intervals was measured with the help of spectrophotometer (Systronics Model 106). It was observed that the absorbance of the solution decreases with increasing the time of exposure, which indicates that the concentration of Evan's blue dye decreases with increasing time (Figure 1).

Characterization of composite

EDS Analysis: Energy-dispersive X-ray spectroscopy (EDS) detects X-rays emitted from the sample during bombardment by electron beam to characterise the elemental composition. It is based on an interaction of source of X-ray excitation and sample. The results are reported in table 1 and presented in figure 2.

Table 1. EDS data of strontium chromate

Element	Series	Norm. C [wt.%]	Atom. C [at.%]
Strontium	L Series	38.17	18.91
Chromium	K Series	46.13	38.51
Oxygen	K Series	15.70	42.59
Total		100.00	100.00

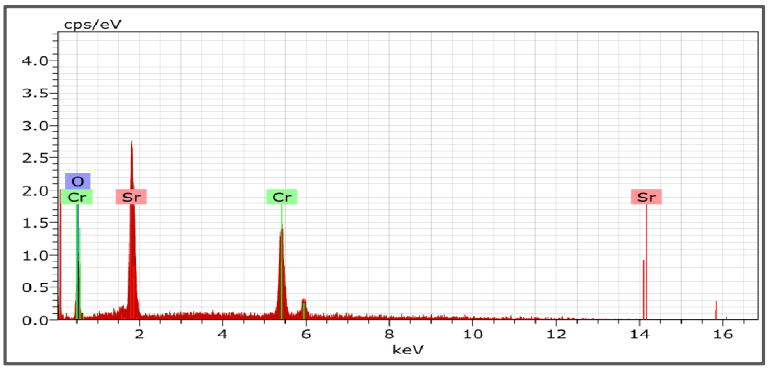


Figure 2. EDS of strontium chromate

XRD-Analysis: X-ray diffraction is a method to determine crystallinity of a compound. The crystal size of the composite was determined by the X-ray diffractometer (XRD) (XPERT-PRO model) using CuKα radiation (λ = 0.154060 nm) in the 2θ scanning ranges from 20^0 to 80^0 with a scan rate at 10^0 min^{-1}. The applied voltage and current were 45 kV and 40 mA, respectively. The powder XRD pattern of as-prepared $SrCrO_4$ nanomaterials is given in figure 3.

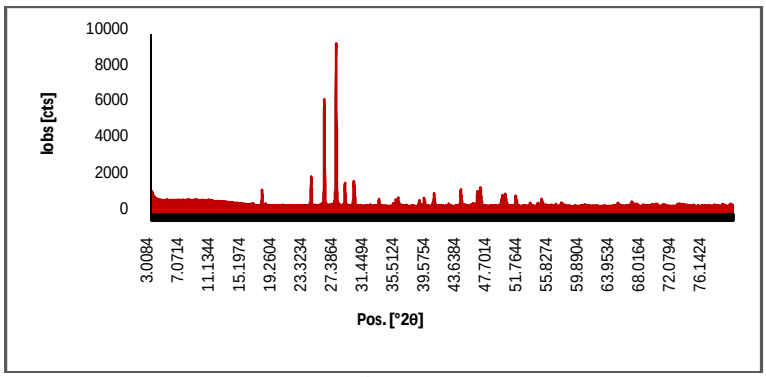


Figure 3. XRD of strontium chromate.

The crystal size (D) was calculated using the Debye-Scherrer's formula:

$$D = 0.9\lambda/\beta \cos\theta \qquad (1)$$

Where, λ = The wavelength of x-ray source (λ = 0.1540 nm for CuKα), $\beta_{(\text{in radians})}$= The full width at half maximum (FWHM) and θ = The Bragg's angle.

The average crystalline size of prepared composite was found to be 48.97 nm for $SrCrO_4$, which is in the order of nanoscale.

RESULTS AND DISCUSSION

The rate constant was calculated by using the expression:

$$K = 2.303 \times \text{slope} \qquad (2)$$

Typical Run: Typical run is graphically represented in Figure 4 and rate constant is 1.49 x 10^{-4} s^{-1}. pH = 9.5, [Evan's blue] = 1.4×10^{-4} M, Semiconductor = 0.16 g, Light intensity = 40.0 $mWcm^{-2}$.

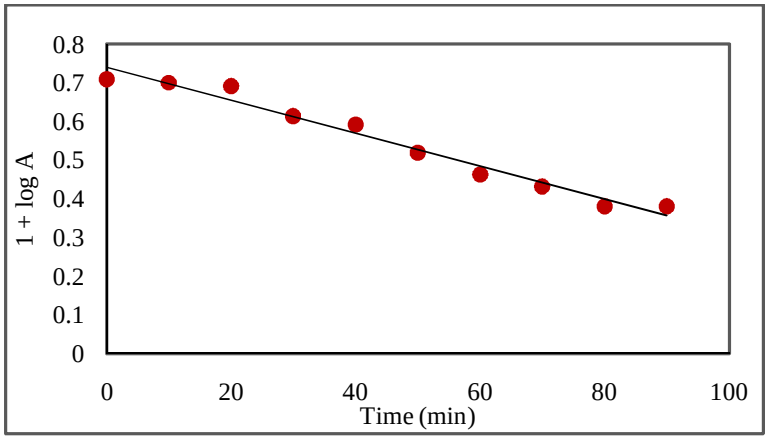


Figure 4. Typical run.

Effect of parameters

pH variation: The effect of variation of pH was studied in the range 7.0-10.5. It was observed that the rate increases with an increase in pH up to 10.5,but the rate of degradation decreases with a further increase in pH.An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\bullet-}$. An increase in the rate of photocatalytic degradation of dye with the increase in pH may be due to the availability of more $O_2^{\bullet-}$ radicals. A decrease in the rate of photocatalytic degradation of the dye may be due to the fact that Evan's blue is present in its anionic form, which will experience a force of repulsion with the negatively charged surface of the semiconductor due to absorption of more OH^- ions on the surface of the photocatalyst. [Evan's blue] = 1.4×10^{-4} M, Semiconductor = 0.16 g, Light intensity = 40.0 $mWcm^{-2}$.

Dye concentration variation: The effect of dye concentration on the photocatalytic degradation of Evan's blue was observed in the range of 0.2×10^{-4} to 2.0×10^{-4} M and results are reported in figure. 6. As the concentration of the dye was increased, it was observed that the dye degradation increases but after 1.4×10^{-4}M (optimum condition), the efficiency of the photocatalytic degradation showed a declining behaviour. Here, the dye will start acting as an internal filter and it will not allow the desired

light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel. pH = 9.5, Semiconductor = 0.16 g, Light intensity = 40 $mWcm^{-2}$.

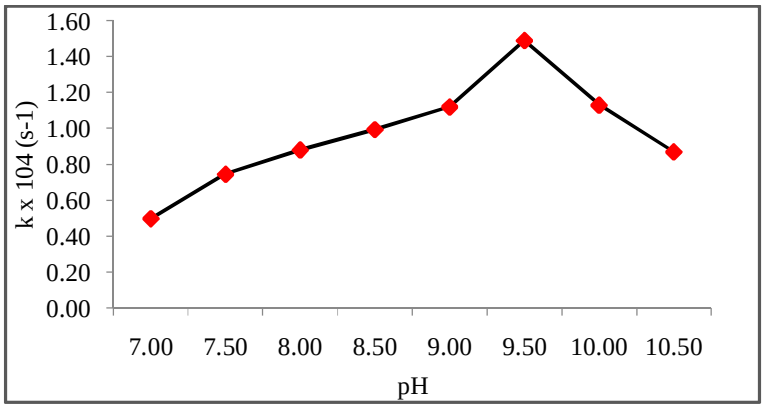


Figure 5. Variation of pH.

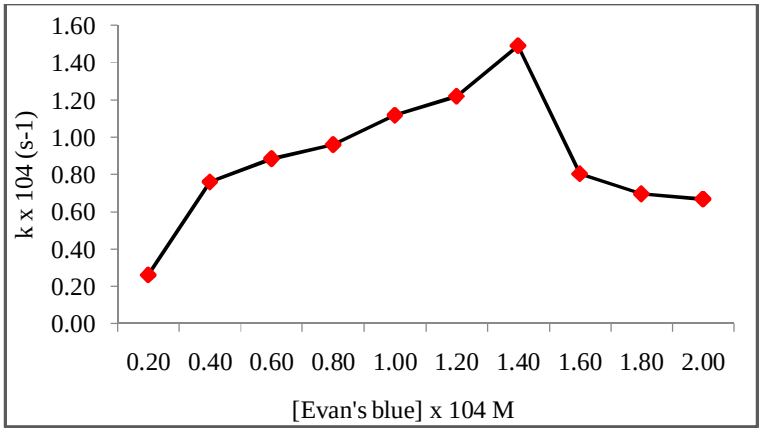


Figure 6. Variation of dye concentration.

Amount of photocatalyst variation: The effect of variation of the amount of catalyst on the rate of dye degradation has been studied in the range from 0.02 to 0.20 g. The results of variation of rate constant with semiconductor are represented in figure 7. It was observed that as the amount of photocatalyst was increased, the rate of photocatalytic activity increases. The rate of degradation was optimum at 0.16 g of the semiconductor. Beyond 0.16 g, the rate constant decreases slightly. Because after this value, an increase in the amount of photocatalyst will only increase the thickness of the photocatalyst layer and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. This slight decline may be due to the fact that excessive amount of photocatalyst may create hindrance and blocks light penetration. pH = 9.5, [Evan's blue] = 1.4×10^{-4} M , Light intensity = 40.0 $mWcm^{-2}$.

Light intensity variation: The distance between the light source and exposed surface area of photocatalyst was varied from 20.0 to 70.0 mW cm^{-2} to determine the effect of light intensity on the photocatalytic degradation. Rate constants with different light intensity are represented in figure 8. It was observed that photocatalytic degradation of Evan's blue was more on increasing the intensity of light as the number of photons striking per unit area of photocatalyst surface per unit time will also increase. The maximum rate was observed at 40.0 mW cm^{-2} for degradation of Evan's blue. On further increasing the intensity above 40.0 $mWcm^{-2}$, there was a slight decrease in the rate of

photodegradation. This may be due to some thermal effects or side reactions. pH = 9.5, [Evan's blue] = 1.4×10^{-5} M, Semiconductor = 0.16 g.

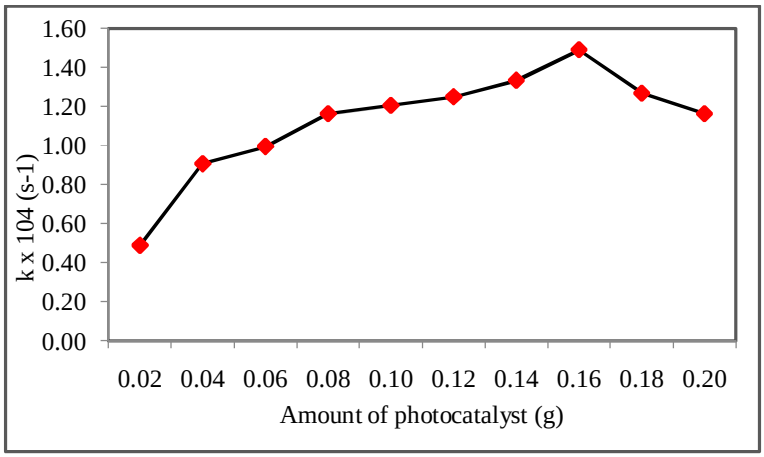


Figure 7. Variation of photocatalyst amount.

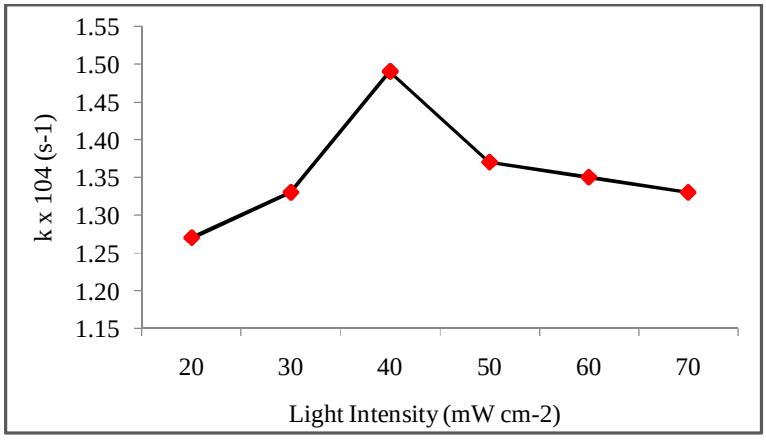


Figure 8. Variation of light intensity.

Mechanism: On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of Evan's blue in the presence of strontium chromate. Evan's blue absorbs radiations of suitable wavelength and transforms to singlet excited state and then to its triplet excited state through intersystem crossing (ISC). The semiconductor also absorbs light to excite an electron from its valence band (VB) to its conduction band (CB), which will be abstracted by dissolved oxygen to generate $O_2^{\bullet-}$ (in basic media). These radicals can degrade dye to its leuco form and ultimately to products.

$$^1EB_0 \xrightarrow{h\upsilon} {}^1EB_1$$

$$^1EB_1 \xrightarrow{ISC} {}^3EB_1$$

$$SC \xrightarrow{h\upsilon} SC\ h^+ (VB) + e^- (CB)$$

$$O_2 \text{ (Dissolved Oxygen)} + e^- (CB) \longrightarrow O_2^{\bullet-}$$

In basic medium

$$^3EB_1 + O_2^{\bullet -} \longrightarrow \text{Leuco EB}$$

$$\text{Leuco EB} \longrightarrow \text{Products}$$

It was found that the reaction rates were unaffected in the presence of $^{\bullet}OH$ radical scavenger, 2-propanol. This shows that there was no involvement of $^{\bullet}OH$ radicals in this reactions as an active oxidizing species.

APPLICATION

Recent developments in technology allow us to fabricate different semiconductors with large surface area and different surface functionalities for successful removal of toxic organic substances. Higher photocatalytic activity is useful in such materials for treatment of industrial effluents because of their advantages, such as low cost, reusability, stability and better performance. These are also used for converting solar energy into storable chemical energy. Applications of photocatalysis are not limited to dyes and are extended to organic molecules, inorganic compounds, industrial pollutants, pesticides, insecticides, phenol, and substituted organic compounds, etc.

CONCLUSION

Strontium chromate was synthesized by precipitation in a wet chemical process and used for the photocatalytic degradation of Evans blue dye. The particle size of synthesized as catalyst is 48.97 nm. Different rate affecting parameters like pH, dye concentration, catalyst amount and light intensity were studied. Photocatalytic treatment is likely increase the quality of polluted water. The observation of present work will provide new awareness for possible use of other photocatalysts for better photocatalytic performance.

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