PHOTODEGRADATION OF ERIOCHROME BLACK T USING HIGH SURFACE AREA LaCrO₃ NANOMATERIAL PREPARED BY SONICATED SOL GEL COMBUSTION METHOD

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ABSTRACT: Combustion derived lanthanum chromite (LC) catalyst was prepared by sonicated sol gel combustion method from lanthanum nitrate hexahydrateLa(NO₃)₃.6H2O(LN),chromium nitratenonohydrate Cr(NO₃)₃.9H₂O(CN),glycine and urea as combination fuel.Nanocrystalline LaCrO₃ powder was formed after heating at 165ºC for five minutes. Synthesized powder was characterized by using FT-IR, X-ray diffraction, TG-DTA, EDS, SEM. Average particle sizeof synthesized powder was determined by Debay Scherrer'sequation andwas found 28.86 nm. BET surface area of LaCrO₃ by flow BET nitrogen adsorption method was found 22.7 m²/g.Photoreactivity of LaCrO₃ was studied for degradation of Eriochrome Black T indicator.100% degradation efficiency is achievedat 10 ppm solution,6 volume H₂O₂ and 8.2 pH in 40 minutes. Reusability of catalyst reveals green nature of catalyst.

KEYWORD- LaCrO₃, Sonicated sol gel Combustion method, FT-IR, EDS, X-ray diffraction, SEM TG-DTA, BET, Eriochrome Black T.

INTRODUCTION

Green house effect, pollution, envirnoment are today's important global regards. Various multicomponent compound like oxide,nitrite,carbide,halide affect nature.Sevaral synthetic techniques are available for preparation of multicomponent oxides including co-precipitation [1],Pechini method[2]conventional method[3],oxalate route[4],micro wave heating method[5],hydrothermal method[6], sol gel combustion method[7-10],hydrazine method[11].Synthesis of complex metal oxide by sol gel combustion method has several advantages over other conventional preparation techniques.

By using sol gel combustion method we could achieve product at low temperature within short period .High degree of conversion to reactive powder in relatively simple way using simple equipments.Combustion system involves use of different redox system in which oxidant i.e.nitrate & fuel like glycine, urea,citric acid are mixed in appropriate molar ratio. Fuel also serves as complexing agent limiting precipitation of individual precursor component prior to ignitation[12-17]

Perovskite LaCrO3 has interest in high temperature electrochemical application of solid oxide fuel cell.It was captured as reforming catalyst due to its good stability under strongly reducing conditions, high electrical conductivity, high temperature corrosion resistance [18-25].Dye pollutants are non biodegradable and cause severe problems. To control it heterogeneous photocatalysis is branch of advanced oxidation process (AOPs) which generate active radical oxidants as hydroxyl or superoxide radical in solution and help in waste water treatment without forming hazardous byproducts.[26-29]

Present work is aimed to prepare nanolanthanum chromite powder in more simple way, to report investigation of structural properties and testing catalytic activity of LaCrO₃ nanopowder.Experimental parameter in decolorisation of Eriochrome Black T were studied to achieve better degradation efficiency of dye using LaCrO₃. In this paper we achieve, LaCrO₃ in short time at low temperature using sol gel combustion method in good yield.

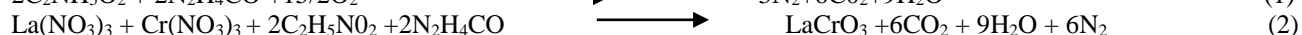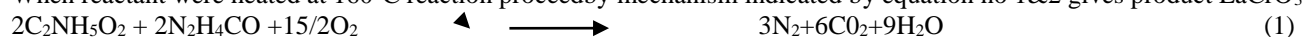## MATERIALS AND METHODS
2.1 Experimental

Nanolanthanum chromite powder was synthesized by sol gel combustion method using glycine & urea as combination fuel. All chemical reagents were analytical grade & used without further purification.One mole reagent of lanthanum nitrate hexahydrate La(NO₃)₃.6H₂O(LN),chromium nitrate nonohydrate Cr(NO₃)₃.9H₂O(CN), 1.5 mole of glycine , 1.5 mole of urea were mixed well by stirring for five minutes. Dark green solid free clear solution was obtained, was treated by ultrasonication for 10 minutes at 60ºC at 5Hz frequency using D-compact 1317 instrument of sonicator.Solution subjected to autocombution on hot plate.Nanocrystalline LaCrO₃ powder was formed at 160ºCin five minutes. .BET surface area of LaCrO₃ was measured by flow bed nitrogen adsorption method was found to be 22.7 m²/gm.

2.2 Degradation Procedure of Eriochrome Black T Dye

To study photodegradation of Eriochrome Black T 5ppm, 10ppm,15ppm,20ppm solution of dye was prepared. Solution of 6%H₂O₂, 0.025 mg catalyst, 250ml prepared dye solution was stirred in dark for 30 minutes.pH is adjusted using NaOH and H₂SO₄.Solution photoexposed for photodegradation in May 2018 at 12-2pm with continuous stirring. Time for degradation was noted.After certain time 2-3 ml solution centrifuged to separate catalyst. Absorbance of solution measured at 200-300 nm.separated catalyst reused for photodegradation up to five run with 100 % efficiency.

RESULT AND DISCUSSION

When reactant were heated at 160ºC reaction proceedby mechanism indicated by equation no 1&2 gives product LaCrO₃

$$2C_2NH_5O_2 + 2N_2H_4CO + 15/2O_2 \longrightarrow 3N_2 + 6CO_2 + 9H_2O \tag{1}$$

$$La(NO_3)_3 + Cr(NO_3)_3 + 2C_2H_5NO_2 + 2N_2H_4CO \longrightarrow LaCrO_3 + 6CO_2 + 9H_2O + 6N_2 \tag{2}$$

3.1 XRD Of $LaCrO_3$

X-ray diffraction measurement were performed on Bruker D2 phasermodel using Cu Kα 1.54056 radiation.XRD pattern shown in fig no (1) shows formed $LaCrO_3$ is orthorhombic perovskite oxide.XRD data show good matching with JCPDS Card No 01-075-0441.Average crystalline size of $LaCrO_3$ by using Scheer's formula $t = 0.9\lambda/\beta\cos\theta\beta$[28,29]is 28.86 nm.
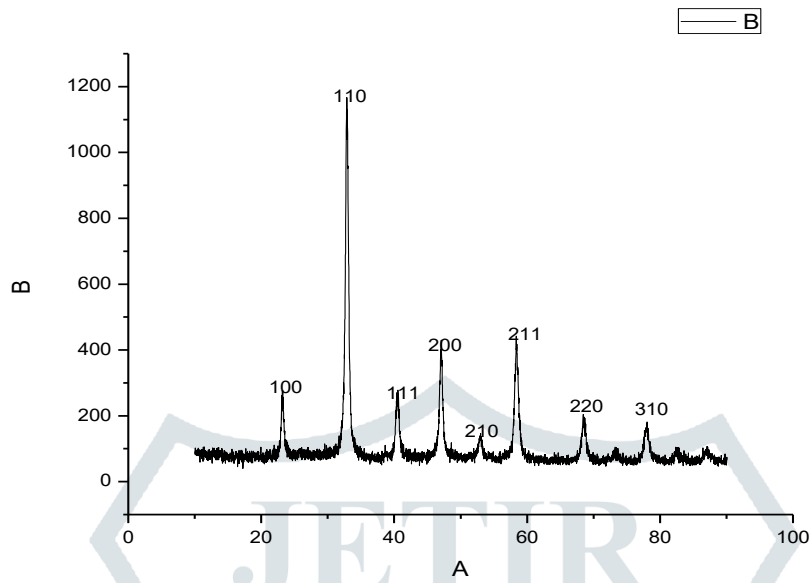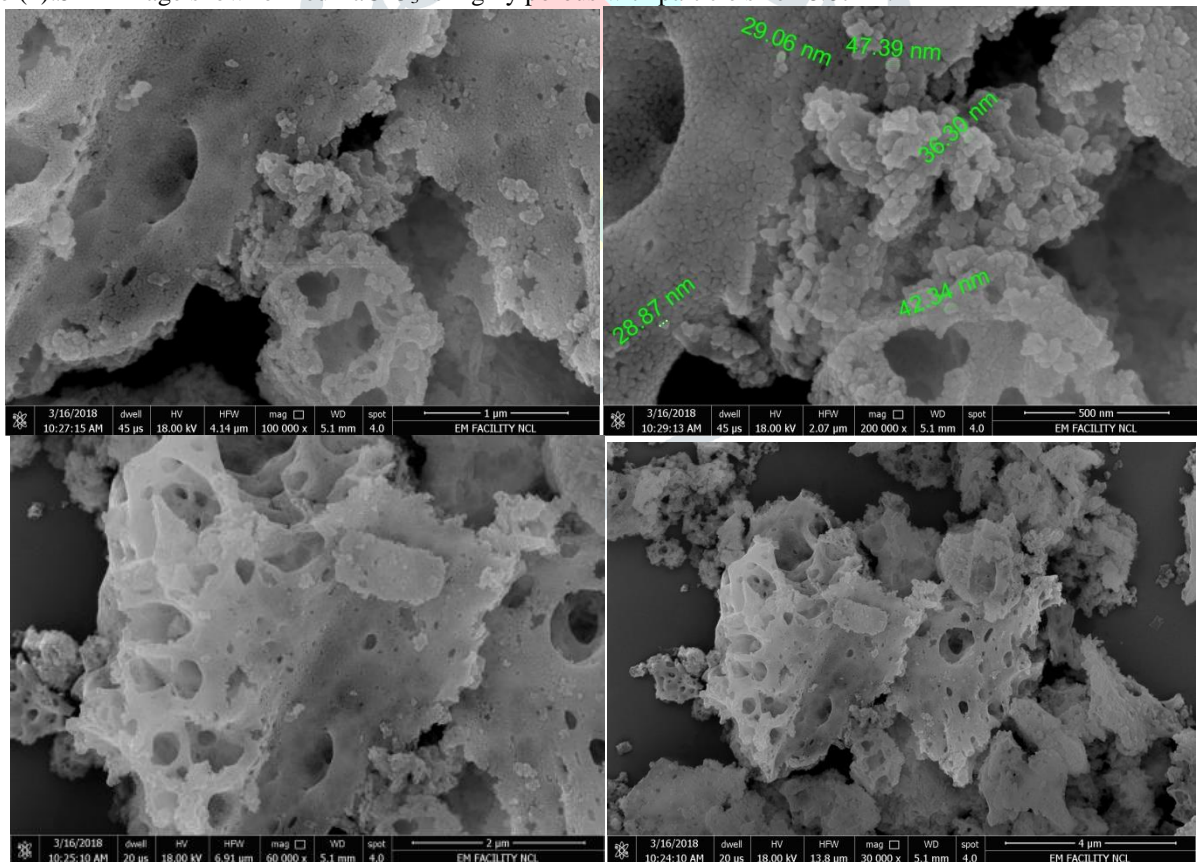

Figure 1. XRD result of $LaCrO_3$ as prepared .

3.2 SEM Image Of $LaCrO_3$

Surface morphology & size was studied by Scanning electron microscopy.SEM images of $LaCrO_3$ were studied using QUANTA 200 3D shown in fig no (2).SEM image show formed $LaCrO_3$ is highly porous with particle size 28.87nm.
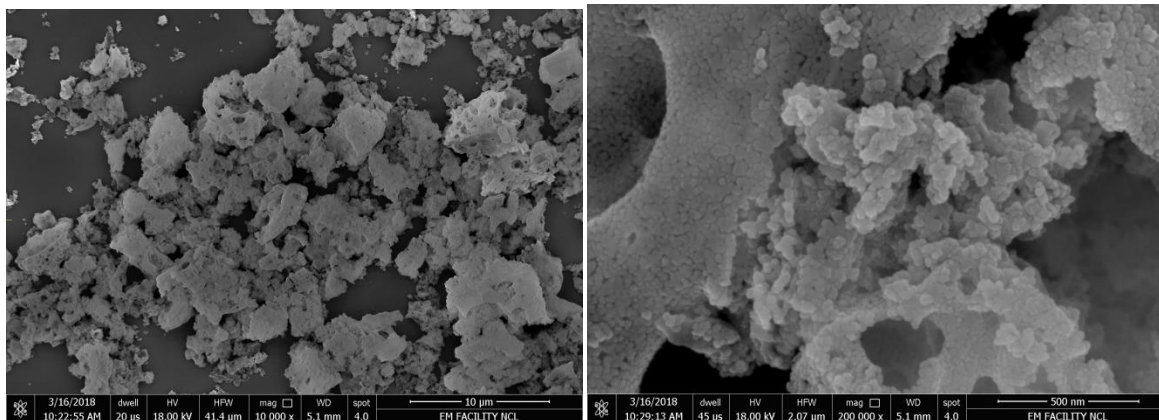
Fig 2SEM images of LaCrO₃ as prepared

3.3 TG/DTA Of LaCrO3

TG curve show little loss in weight might be due to loss of moisture,CO_2,nitrogen gas is shown in fig no (3).DTA is recorded in nitrogen gas by using Perkin and Elmer's STA 6000 is shown in fig no (4).This weight loss &weight gain was ignorable. This indicated that synthesized powder was stable from beginning.
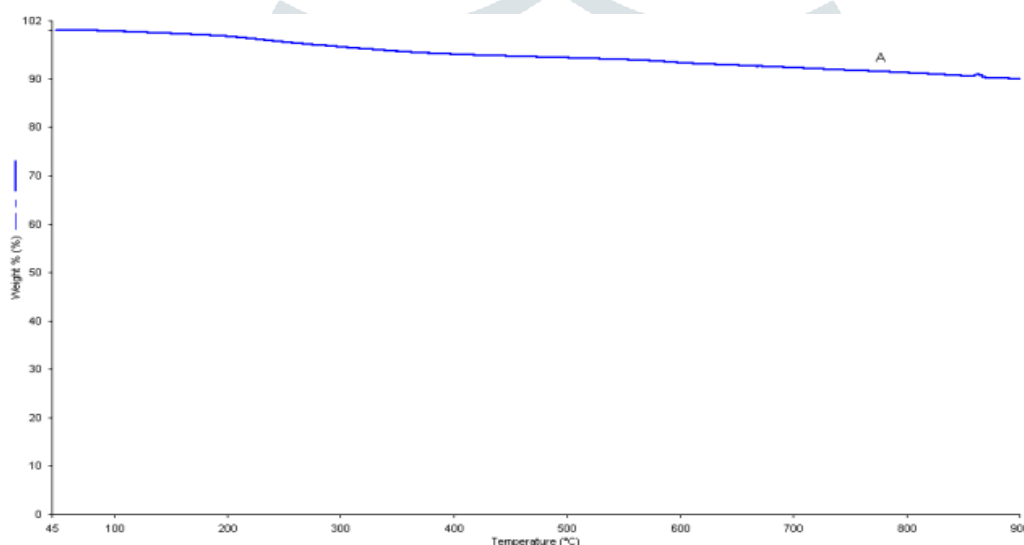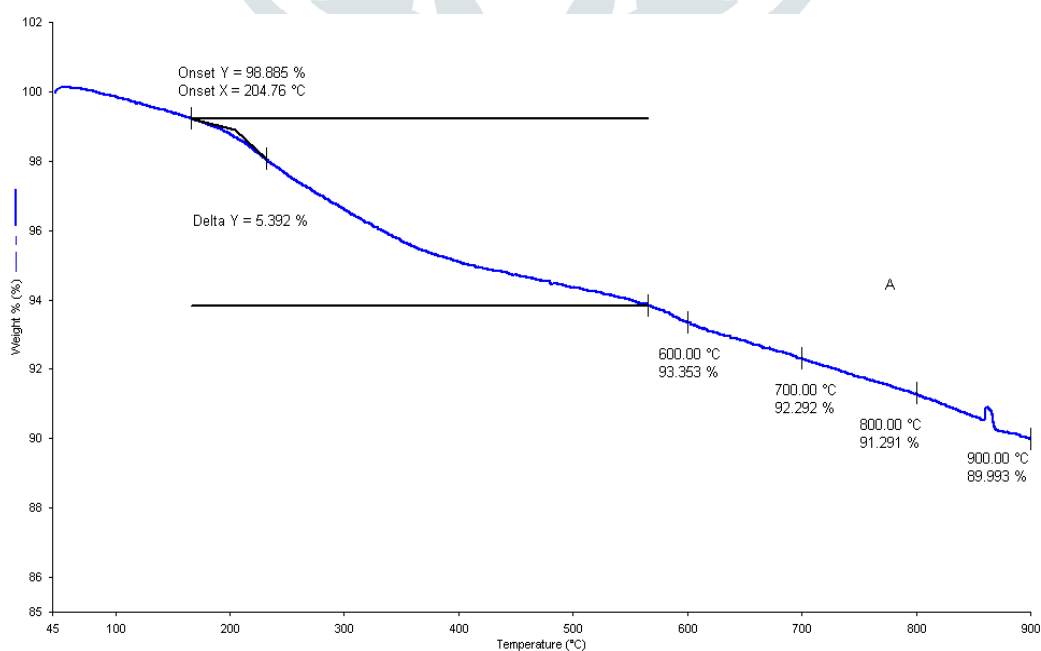

Fig 3   TG Curve of LaCrO₃ as prepared

Fig 4 DTA Curve of LaCrO₃as prepared

3.4 EDS of LaCrO₃

To study EDS, ELITE PLUS model is used.From EDSit is clear that in $LaCrO_3$ percentage of oxygen is 88.04%,percentage of lanthanum is 9.16% & percentage of chromium is 2.80%.as shown in table no.1
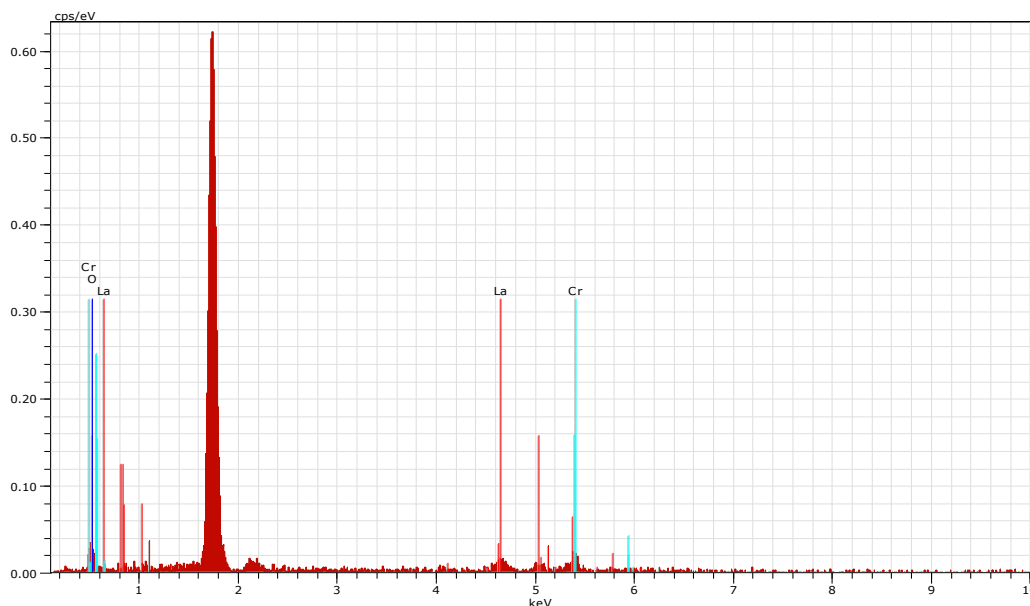

Fig 5   EDS image of LaCrO₃as prepared

Table No 1: Percentage Composition Of Element

Element	Atomic No.	Series	Unn.[wt.%]
O	8	K	88.04
La	57	L	9.16
Cr	24	K	2.80
Total			100.00%

3.5 IR Of LaCrO₃

IR pattern of formed oxide wasstudied using FTIR λ 7600 as shown in fig no (6) which show absorbance from frequency 401.12 to 620.97 corresponds to La-O and Cr-O bond.
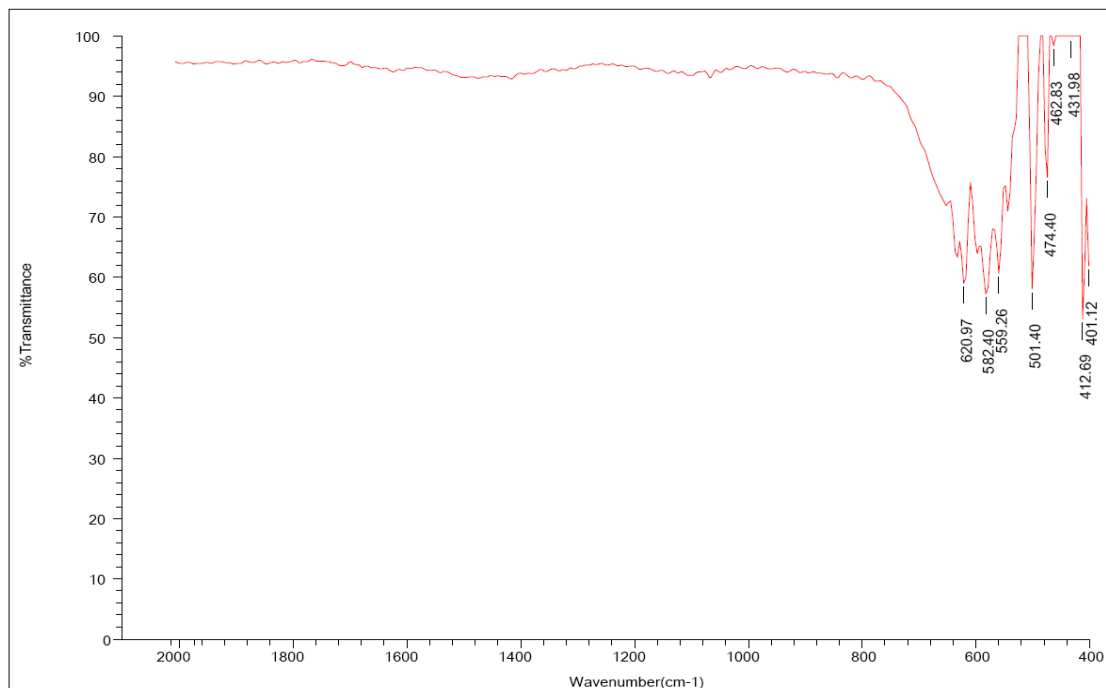

Fig 6 IR image of LaCrO₃as prepared
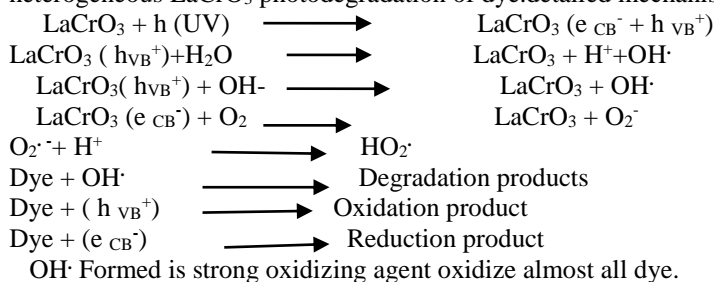
3.6 BET surface area Of LaCrO₃

BET surface area of $LaCrO_3$ by flow BET nitrogen adsorption method was found to be 22.7 m^2/gm.It is determined using ISO S4652/ASTM D-3037/USP846/EP 2.926 METHOD.

PHOTOCATALYTIC DEGRADATION MECHANISM

4.1 Photocatalytic Oxidation

When aqueous $LaCrO_3$ suspension is irradiated to light energy which is greater than band gap energy, photogeneration of conduction band electron and valence band hole take place. Electron reduces dye to superoxide radical anion O_2^- using oxygen of $LaCrO_3$ or dissolved in water. Holes show oxidation of dye to form R^+ or react with OH^-. Hydrogen peroxide is highly oxidant species plays important role in heterogeneous $LaCrO_3$ photodegradation of dye. detalied mechanism is explained [30-32] as

$$LaCrO_3 + h\ (UV) \longrightarrow LaCrO_3\ (e_{CB}^- + h_{VB}^+)$$
$$LaCrO_3\ (h_{VB}^+) + H_2O \longrightarrow LaCrO_3 + H^+ + OH^\cdot$$
$$LaCrO_3(h_{VB}^+) + OH^- \longrightarrow LaCrO_3 + OH^\cdot$$
$$LaCrO_3\ (e_{CB}^-) + O_2 \longrightarrow LaCrO_3 + O_2^-$$
$$O_2^{\cdot-} + H^+ \longrightarrow HO_2^\cdot$$
$$Dye + OH^\cdot \longrightarrow Degradation\ products$$
$$Dye + (h_{VB}^+) \longrightarrow Oxidation\ product$$
$$Dye + (e_{CB}^-) \longrightarrow Reduction\ product$$

$OH^\cdot$ Formed is strong oxidizing agent oxidize almost all dye.

4.2 Photosensitized Oxidation

In this excitation of adsorbed dye takeplace by visible light to singlet or triplet state. After that electron transferred from exiated dye to conduction band of $LaCrO3$. Dye is converted to cationic dye radical as follow[33-35]
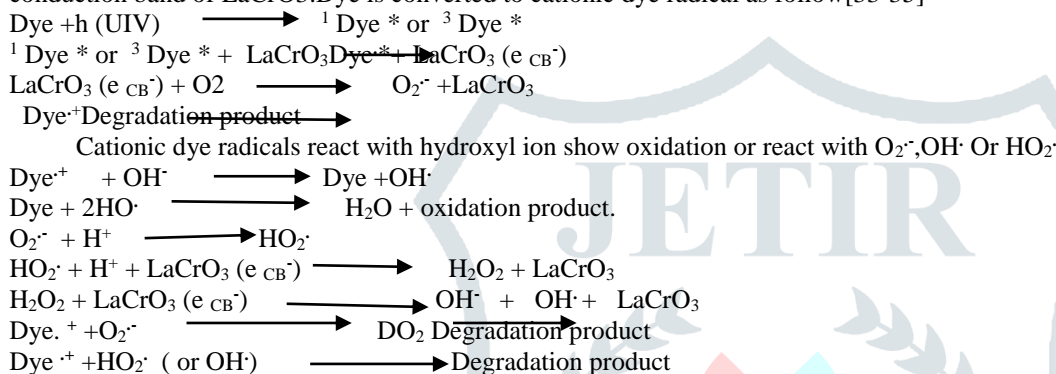
$$Dye + h\ (UIV) \longrightarrow {}^1Dye^* \text{ or } {}^3Dye^*$$
$${}^1Dye^* \text{ or } {}^3Dye^* + LaCrO_3 \longrightarrow Dye^{\cdot+} LaCrO_3\ (e_{CB}^-)$$
$$LaCrO_3\ (e_{CB}^-) + O2 \longrightarrow O_2^{\cdot-} + LaCrO_3$$
$$Dye^{\cdot+} \longrightarrow Degradation\ product$$

Cationic dye radicals react with hydroxyl ion show oxidation or react with $O_2^{\cdot-}, OH^\cdot$ Or $HO_2^\cdot$

$$Dye^{\cdot+} + OH^- \longrightarrow Dye + OH^\cdot$$
$$Dye + 2HO^\cdot \longrightarrow H_2O + oxidation\ product.$$
$$O_2^{\cdot-} + H^+ \longrightarrow HO_2^\cdot$$
$$HO_2^\cdot + H^+ + LaCrO_3\ (e_{CB}^-) \longrightarrow H_2O_2 + LaCrO_3$$
$$H_2O_2 + LaCrO_3\ (e_{CB}^-) \longrightarrow OH^- + OH^\cdot + LaCrO_3$$
$$Dye^{\cdot+} + O_2^{\cdot-} \longrightarrow DO_2\ Degradation\ product$$
$$Dye^{\cdot+} + HO_2^\cdot\ (or\ OH^\cdot) \longrightarrow Degradation\ product$$

Photo oxidation or photosensitizing mechanism take place, as reaction take place in sunlight.

4.3 Primary Substrate Disappearance

By using Langmuir-Hinshelwood kinetic model destruction rate of photo catalytic oxidation of dye using $LaCrO_3$ was studied [36,37]

$$r = DC/dt = kKC/1 + KC$$

Where r is oxidation rate of reactant, t is time, C is concentration of reactant is adsorption coefficient, k is reaction rate constant. Colour removal of Eriochrome Black T was determined by UV-Visible spectrum in 200-800 nm region using spectrophotometer.

4.4 Effect of initial dye concentration

As rate of degradation depend on formation of OH radical, initialy it increase with increase in concentration but further decrease with high dye concentration which reduce generation of OH radical. [38, 39]

$250\ cm^3$ Eriochrome Black T + 0.025 gm $LaCrO_3$ catalyst +1 ml ($6\%\ H_2O_2$)

4.5 Effect of oxidant

OH radical plays duel role as strong oxidant and strong scavengers, hence small quantity of H_2O_2 increase rate of photodegradation of Eriochrome Black T [40]

4.6 Effect of pH

pH affect rate of photodegradation of Eriochrome Black T. When we studied it at different pH range (2.1-13). Rate of degradation is high at 8.2 pH value. In the absence of H_2O_2 rate of decomposition decrease at pH 12.4 because increase in concentration of OH^- blocked active site of catalyst.[41] Without catalyst solution show absorbance at 500 nm. 10 ppm solution of Eriochrome Black T decolorized within 40 minutes in presence of $LaCrO_3 \backslash H_2O_2$ at 8.2 pH.

4.7 Separation and reuse of photocatalyst

After photodegradation, catalyst is recovered by centrifugation and reused. Release of degraded intermediates from surface of catalyst prevents blocking and poisoning of catalyst.

After first run catalyst was separated by centrifugation and added in same concentration of Eriochrome Black T for degradation .Rate of decomposition is as same in first time. Five run of degradation of Eriochrome Black T show no significant loss of photoactivity.

CONCLUSION

We are successfully prepared catalyst in short time with high surface area, using simple equipments, procedure, in good yield and reactivity. Catalyst is applicable to photodegradation of Eriochrome Black T. After degradation it can reuse up to five run reveal green nature of catalyst.

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