

A Dissertation thesis entitled

**“Degradation efficiency of malachite green dye by
LaCO_{0.8}Cu_{0.2}O₃ perovskite oxide under natural and UV
condition”**

**Submitted in partial fulfillment of the requirements
for the award of the degree of**

Master of Science

**IN
INDUSTRIAL CHEMISTRY**

Submitted by

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2022-2023**

*Dedicated To My Parents
&
Department of industrial Chemistry*



*Without their love, support and constant
encouragement
this would not have been possible.*

DECLARATION

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled **“Degradation efficiency of malachite green dye by $\text{LaCO}_{0.8}\text{Cu}_{0.2}\text{O}_3$ perovskite oxide under natural and UV condition”** has been carried out by us at Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India, under the supervision and Guidance of **Er. Dhaval A. Tank, Assistant Professor, Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for the award of any degree either in this or any other form.

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ABSTRACT

Perovskite are the catalytic material having the general formula of ABO_3 and can be prepared by various synthetic methods such as Co-precipitation method, Citrate method, Ball mill method, Sol-gel method etc. They are being applied in many areas of current development because of their optical, magnetic, electronic and ferroelectric properties. General uses of Perovskite nano-particles have been in adsorbents for waste water treatment, fuel cells, drug delivery and air pollution controller. The ultimate goal of the wastewater treatment is to provide the protection of human health and environmental aspect. The interest in these catalysts has been revitalized in the past ten years by the introduction of the concept of catalyst generatability of Perovskite Catalyst, which is in principle well.

INTRODUCTION

Perovskites obtained their name from the calcium titanium oxide (CaTiO_3) structure which was first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after a Russian nobleman and mineralogist Count Lev Aleksevich von Perovski (1792–1856). The term perovskite and perovskite structure are often used interchangeably but while true perovskite is formed of calcium, titanium and oxygen in the form CaTiO_3 .

Generally, perovskites have the general formula ABO_3 where, A and B are two cations of very different sizes and X is an anion that bonds to both. O is often oxygen but also other large ions such as halides, sulfides and nitrides are possible. Also, both A-site and B-site ions can be partially replaced by other metal ions with similar radii and their crystal structure can remain unchanged. More importantly, the perovskite structure allows special introduction of desired metal ions into the B-site to improve catalytic efficiency. Because of the fluctuation of the cation radius, the crystal can deviate from the ideal structure within a certain extent. Besides, the high thermal and hydrothermal stability of the structure make it possible for perovskites to work stable over various conditions.

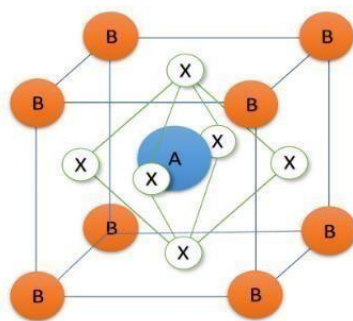


Fig.1 Structure of perovskite ABO_3 crystal

Perovskites are ceramic materials that belong to the class of mixed oxides. The perovskite structures are existing in different forms such as: ABO_3 - perovskite (ex: BaTiO_3 , CaTiO_3), A_2BO_4 -Layered perovskite (ex: Sr_2RuO_4 , K_2NiF_4), $\text{A}_2\text{BB}'\text{O}_6$ -Double perovskite (ex: $\text{Ba}_2\text{TiRuO}_6$) and $\text{A}_2\text{A}'\text{B}_2\text{B}'\text{O}_9$ -Triple perovskite (ex: $\text{La}_2\text{SrCO}_2\text{FeO}_9$), etc. At present, perovskites are mainly prepared by the sol-gel method, combustion method, co-precipitation method, chelating precursor method etc.

Literature survey

PEROVSKITE PROPERTIES:

A large number of perovskite type oxides have been studied because of their interesting properties including super conductivity, insulator-metal transition, ionic conduction characteristics, dielectric properties and Ferro-electricity. Perovskite structured ceramic materials with general chemical formula ABO_3 are value-added materials used for several applications such as capacitors, non-volatile memories, actuators and sensors, piezoelectric, ultrasonic and underwater devices, high temperature heating applications, frequency filters for wireless communications, etc.

Perovskite type structures have properties with functionality because of their non-stoichiometry of the cation and the anions, the distortion of the cation configuration, and the mixed valence and the valence mixture electronic structure.

(1) Super conductivity:

Super conductivity is a phenomenon of exactly zero electrical resistance and discharge of magnetic flux field so occurring in certain materials when cooled below a characteristic critical temperature. The oxide perovskites are a large family of materials with many important physical properties. Significantly, this perovskite structure type provides an excellent structural framework for the existence of super conductivity. Sodium, potassium, rubidium and cesium, tungsten, bronzes were found to be super conductors.

(2) Dielectric Properties:

Dielectric or electrical insulating materials are understood as the materials in which electrostatic fields can continue for a long time. The dielectric materials offer a very high resistance to the channel of electric current under the action of the applied DC-voltage and therefore sharply diverge in their basic electrical properties from conductive materials.

(3) Ferro-electricity:

Ferro-electricity is the phenomenon in which a spontaneous electric polarization occurs in some materials by the application of an external electric field.

(4) Optical properties:

Perovskite have emerged as a revolutionary class of materials having excellent optical properties. The optical properties of single domain crystals of BaTiO₃ at various temperatures. The refractive index of the crystal was nearly a constant value of ~2.4 from 20 to 90 and reached a maximum value of ~2.46 at 120. Lawless and De Varies also measured the index of refraction of BaTiO₃ at 5893 Å in the range 20 to 105 and above Curie point the index increased 1.3 % to 2.398 % and remained constant to 160. The single crystal of BaTiO₃, 0.25 mm thick, was found to transmit from 0.5μ to 6μ. The optical co-efficient was obtained from 0.20μ to 17μ in wavelength.

(5) Piezoelectric:

Piezoelectricity is the ability of some materials To generate an electric charge in response to Applied mechanical stress. The piezoelectric Effect was discovered in 1880 by the bothers Pierre Curie and Jacques Curie. They found That if certain crystals were subjected to mechanical strain, they became electrically polarized and the degree of polarization was proportional to the applied strain.

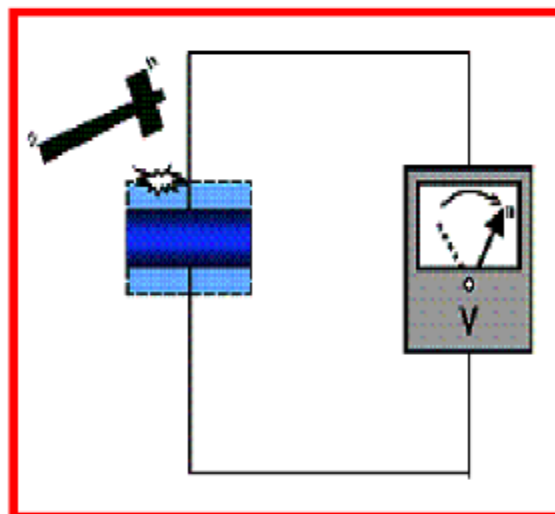


Fig.2 Piezoelectric effect

Catalyst Characterization Technique

X-ray Powder Diffraction (XRD):

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, standardized, and average bulk composition is determined.

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

Principles of Operation:

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, parallel to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

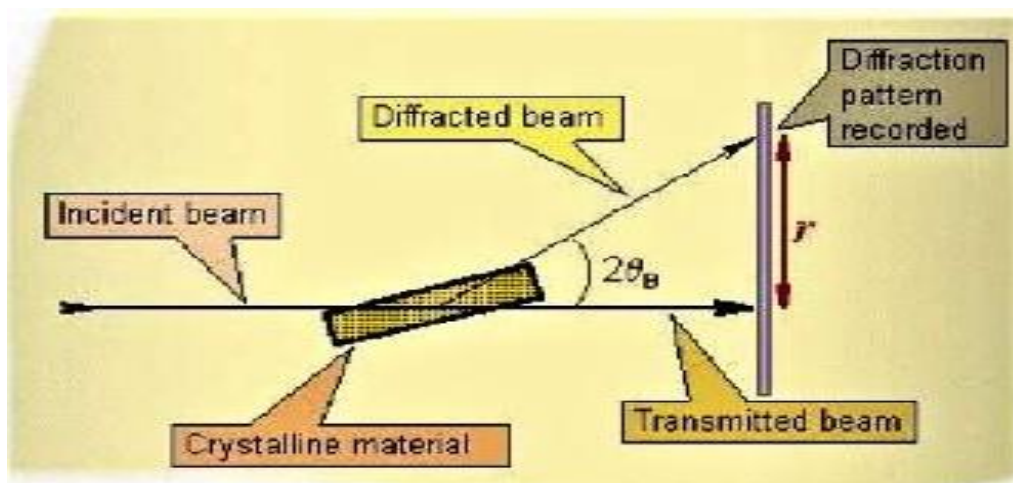
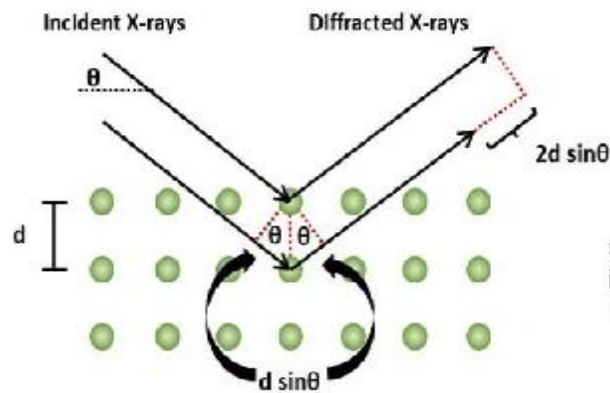


Fig.3 Process of XRD

Applications:

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include:

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- Determination of unit cell dimensions
- Measurement of sample purity
- Determine crystal structures using Rietveld refinement method
- Determine of modal amounts of minerals (quantitative analysis)

SYNTHESIS METHOD FOR PEROVSKITE

Lanthanum ortho ferrites (LaFeO_3) are an active perovskite-type oxide with a general elemental composition formula of ABO_3 , where A is a rare earth metal while B is a transition metal. LaFeO_3 have gained interest for advanced applications such as fuel cell, sensor, electrodes, and catalyst. In the past decades, LaFeO_3 was proposed to be a significant material in the field of photo catalysis because it exhibits several attention-grabbing properties such as narrow band gap (Eg; 51.86_2.36 eV), high stability, and also environmentally friendly. Furthermore, it can be activated under visible light irradiation, which enables the PC to be activated under sunlight without the requirement of additional irradiation source. For synthesis of these PCs, no much advancement has been achieved to determine the best synthesis method for LaFeO_3 .

CITRIC ACID SOL-GEL METHOD

Perovskite catalysts are prepared by a citrate sol-gel method as follows: the reagents (nitrate salts of desired oxides) first dissolve in distilled water in stoichiometric amounts. A given amount of citric acid dissolved in deionized water is added in above solution as a ligand. The solution is adjusted to pH 7.5–8.0 with aqueous ammonia or acetic acid, stirring and heating to a temperature of 60–80 °C for 4 hour, syrup obtained is then heated to 100°C for 24 hr in air, followed by calcination at 450°C for 2 hr, and then temperature is raised to 600 in 4 hr. Black samples are obtained. This method is the most effective route to create high surface area catalysts. A typical example of $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ prepared by the sol-gel method is given by Wang et al. Analytical grade $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, KNO_3 and $\text{Co}(\text{NO}_2)_2 \cdot 6\text{H}_2\text{O}$ are weighed according to the stoichiometric ratio, and then dissolved in distilled water. Some citric acid is added with the same mole fraction as for the metallic ions. The mixture is stirred for 3 h while ammonia is added to adjust the pH value to be 8–9. The mixture is placed in a water bath at 80–90 °C to be dehydrated. The sample slowly becomes sol, and then gel. After being heat-treated at 120°C for 2 hr, the sample is put into an oven at a temperature of 300–400°C for 4 hr, and the sample becomes powder. The powder is kept at 500°C for 2 hr after being further ground. Then it is calcined at 800°C for 12–24 hr, thus the $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ perovskite composite oxide is obtained.

CO-PRECIPIATION METHOD:

Co-precipitation method is an excellent option to produce high purity nano-particles, which involves better stoichiometry of reaction. Schematic diagram of the synthesis process for nano-sized ESB powder via reverse strike co-precipitation is well illustrated. The process occurs when two low soluble salts were mixed to form metal hydroxides. The precipitation usually starts within an acidic solution and subsequently added with alkaline solution to attain a neutralized precipitate. Commonly, ammonia or sodium bicarbonate is used as a precipitating agent. These precipitates are then calcined at appropriate temperatures to yield the final powder. For the synthesizing route, the optimization of operating conditions such as concentration of solution, pH, temperature, and stirring speed of the mixture is required in order to obtain the final product with required properties. Recently, co-precipitation method has been introduced to synthesize perovskite lanthanum ortho ferrite nano-particles. Nakayama first attempted to synthesize LaFeO_3 using $\text{La}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ as hydrate precursor. The hydrate precursor was obtained by titration of ammonia water into a 1:1 solution of La and Fe in which La_2O_3 and Fe_2O_3 were dissolved by nitric acid. Subsequently, the hydrated precursor was calcined at different temperatures starting from 400°C up until 1300°C . As shown in the report, the highest BET surface area of LaFeO_3 ($38.7 \text{ m}^2 \text{ g}^{-1}$) was obtained at a calcination temperature of 600°C . However, the homogeneity of nano-particles improved at a calcination temperature of 1300°C . Somehow, nano-particles synthesized via co-precipitation method usually form agglomerated particles, which would affect the photocatalytic performance. In order to prevent this, higher calcination temperature is required but this leads to low surface area.

GEL COMBUSTION METHOD:

Gel-combustion method has sparked great interest for synthesizing various nano-particles including LaFeO_3 to produce homogenous nano-particles of high purity, large-scalable synthesis, and high removal efficiency of pollutants. Schematic description of three steps is illustrated. First, substance that acts as a chelating agent in the process or as an organic fuel in a combustion reaction is used to accelerate high-intensity reaction of mixing reagents. The chemical energy released from the exothermic reaction develops into an instantaneous self-combustion. The nano-particles obtained in this method exhibited high purity and large specific surface area at calcination temperatures that are much lower than those required for conventional co-precipitation reaction methods. The morphology also portrayed better homogeneity. Many attempts have been made to synthesize LaFeO_3 using this method. Idrees et al. prepared LaFeO_3 nano-particles via combustion of nitrate and citrate precursors and produced nano-particles of increased crystallinity when calcined at higher calcinations temperatures. On the other hand, Hao and Zhang successfully synthesized LaFeO_3 via a simple gel-combustion method at calcination temperatures of 200°C - 400°C . Interestingly, the study has revealed that the synthesized LaFeO_3 at 200°C had a porous nano-structure with a large surface area. Which could have the potential to be utilized for degradation of wide arrays of organic contaminants. Despite the advantages of method, a great understanding of combustion behavior is needed to obtain the final desired products. The usage of better ligand or chelating agents is one of the criteria that is required to attain desired products. It can be used to eliminate the occurrence of unbound metal cations, thus ensuring the complexation of all metal cations to give homogenous precursors. Typically, glucose, citric acid (CA), ethylene diamine tetra acetic acid (EDTA), and urea are used to chelate the metal cations.

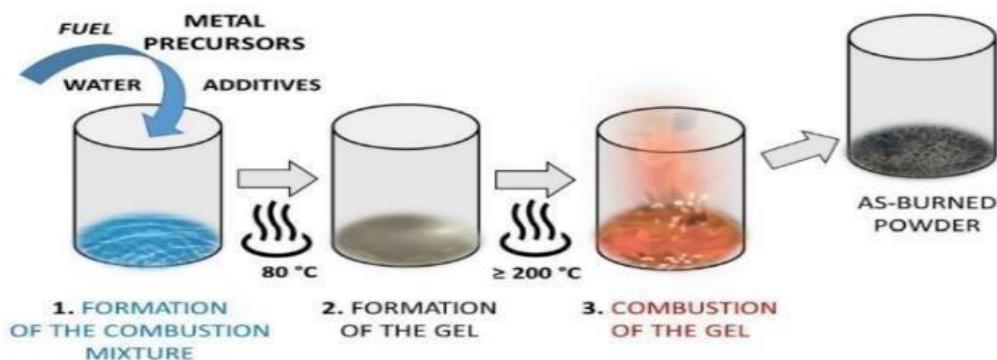


Fig.4 Schematic diagram description of the three main steps in gel combustion synthesis.

Application of Perovskite

Perovskite-phase metal oxides exhibit a variety of interesting physical properties which include ferroelectric, dielectric, pyroelectric, piezoelectric, superconductivity, multiferroic, Proton conducting, Colossal Magneto Resistance (CMR), Giant Magneto Resistance (GMR), Mixed conduction, catalyst behavior, etc. Depending on these distinct properties's perovskite are useful for several various applications such as:

- Waste Water Treatment
- Non-volatile memories
- Photo electrochemical cell
- Recording application
- Laser application
- Perovskite Solar Cell
- High temperature heating application
- Air Pollution Controller
- Dye degradation

Experimental Work

1) Experiment No.-1

Preparation of Catalyst $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ by Citrate method

Apparatus: - Beaker, Measuring Cylinder, Funnel, Glass Rod, Filter Paper, Water Bath, Evaporating Disk, Thermometer, Muffle Furnace, Oven, Weight Balance.

Chemicals: - Lanthanum Nitrate, Cobalt Nitrate, Copper Nitrate.

Calculation: -

- Molecular weight of Lanthanum (La) : $138.91 \text{ g/mol} = 139 \text{ g/mol}$
- Molecular weight of Cobalt (Co) : $58.93 \text{ g/mol} = 59 \text{ g/mol}$
- Molecular weight of Copper (Cu) : $63.54 \text{ g/mol} = 64 \text{ g/mol}$
- Molecular weight of : $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$
 $= 139 + 59(0.8) + 64(0.2) + 48$
 $= 247 \text{ g/mol}$

- Molecular weight of Lanthanum Nitrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$]:
 $= 138.91 + 42 + 144 + 12 + 96$
 $= 432.91 \text{ g/mol}$
 $\approx 433 \text{ g/mol}$

- Molecular weight of Cobalt Nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] :
 $= 58.93 + 28 + 96 + 12 + 96$
 $= 290.93 \text{ g/mol}$
 $\approx 291 \text{ g/mol}$

- Molecular weight of Copper Nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$]:
 $= 63.54 + 28 + 96 + 6 + 48$
 $= 241.54$
 $\approx 242 \text{ g/mol}$

Preparation of Catalyst:- 15 g

Calculation of Lanthanum (La) and Lanthanum Nitrate [La (NO₃)₃·6H₂O]

$$247 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 = 139 \text{ g Lanthanum (La)}$$

$$\begin{aligned} 15 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 &= ? \\ &= 15 \times 139 / 247 \\ &= 8.4412 \text{ g Lanthanum (La)} \end{aligned}$$

$$139 \text{ g Lanthanum (La)} = 433 \text{ g Lanthanum Nitrate [La(NO}_3)_3 \cdot 6\text{H}_2\text{O]}$$

$$\begin{aligned} 8.475 \text{ g lanthanum(La)} &= ? \\ &= 8.4412 \times 433 / 139 \\ &= 26.29 \text{ g Lanthanum Nitrate [La(NO}_3)_3 \cdot 6\text{H}_2\text{O}] \end{aligned}$$

Calculation of Cobalt(Co) and Cobalt Nitrate[Co(NO₃)₂·6H₂O]

$$247 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 = 47.2 \text{ g Cobalt (Co)}$$

$$\begin{aligned} 15 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 &= ? \\ &= 15 \times 47.2 / 247 \\ &= 2.8663 \text{ g Cobalt (Co)} \end{aligned}$$

$$59 \text{ g Cobalt (Co)} = 291 \text{ g Cobalt Nitrate [Co(NO}_3)_2 \cdot 6\text{H}_2\text{O]}$$

$$\begin{aligned} 2.8663 \text{ g Cobalt (Co)} &= ? \\ &= 2.8663 \times 297 / 59 \\ &= 14.1417 \text{ g Cobalt Nitrate [Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}] \end{aligned}$$

Calculation of Copper(Cu) and Copper Nitrate[Cu(NO₃)₂·3H₂O]

$$247 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 = 12.8 \text{ g Copper (Cu)}$$

$$\begin{aligned} 15 \text{ g LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3 &= ? \\ &= 15 \times 12.8 / 247 \\ &= 0.7773 \text{ g Copper (Cu)} \end{aligned}$$

$$64 \text{ g Copper (Cu)} = 242 \text{ g Copper Nitrate [Cu (NO}_3)_2 \cdot 3\text{H}_2\text{O]}$$

$$\begin{aligned} 0.7773 \text{ g Copper (Cu)} &= ? \\ &= 0.7773 \times 242 / 64 \\ &= 2.94 \text{ g Copper Nitrate [Cu (NO}_3)_2 \cdot 3\text{H}_2\text{O}] \end{aligned}$$

Calculation of Citric Acid:

Molecular weight of CA (C₆H₈O₇): 192.13 g/mol

$$\text{Citric acid} = \left(\frac{g \text{ of } La}{M.W. \text{ of } LA} + \frac{g \text{ of } Co}{M.W. \text{ of } Co} + \frac{g \text{ of } Cu}{M.W. \text{ of } Cu} \right) \times \text{M.W. of citric acid}$$

$$= \left(\frac{8.4412}{139} + \frac{2.8663}{59} + \frac{0.7773}{63.5} \right) \times 192.13$$

$$= (0.06072 + 0.04858 + 0.01224) \times 192.13$$

$$= 0.1215 \times 192.13$$

$$= 23.35 \text{ g}$$

10 % excess = 25.90 g Citric Acid

Diagram 1. $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ by Citrate method

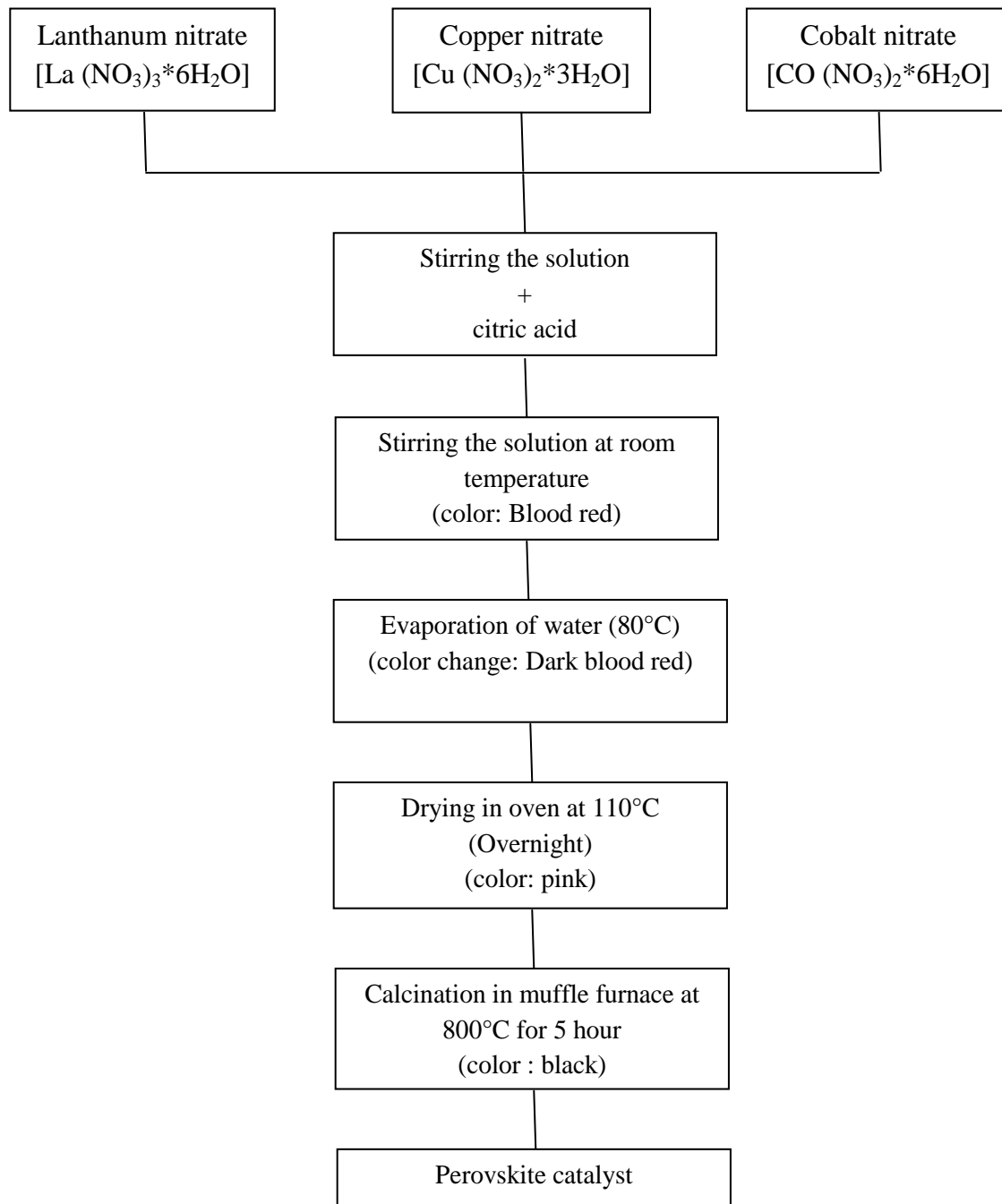




Fig. 5 Mixture of four solution stirred for 30 minutes of lanthanum nitrate + cobalt nitrate + copper nitrate and citric acid



**Fig. 6 Evaporation of water
(80°C)
(color change: Dark blood red)**



**Fig. 7 Drying in oven at 110°C
(Overnight)
(color: pink)**



Fig. 8 Calcination in muffle furnace at 800°C for 5 hours (color: black)



Fig. 9 powder of catalyst

2) Experiment No.-2

Preparation of Catalyst LaFeO₃ by Sol-Gel Method:

Apparatus: - Beaker, Measuring Cylinder, Funnel, Glass Rod, Filter Paper, Water bath, Evaporating Dish, Thermometer, Muffle Furnace, Oven, Weight Balance.

Chemicals: - Lanthanum Nitrate, Iron Nitrate, Glycine, Distilled water.

Calculation:

- Molecular weight of Lanthanum (La) = 138.91 g.
- Molecular weight of Iron (Fe) = 55.84 g.
- Molecular weight of Oxygen (O) = 16 g.

- Molecular weight of Lanthanum Nitrate [La(NO₃)₃.6H₂O]:
= 138.91 + 42 + 144 + 12 + 96
= 432.91 g/mol
≈ 433 g/mol
- Molecular weight of Iron Nitrate [Fe(NO₃)₃.6H₂O]:
= 55.84 + 42 + 144 + 18 + 96
= 349.84 g/mol
≈ 350 g/mol
- Molecular weight of Glycine [C₂H₅NO₂]:
= 24 + 5 + 14 + 32
= 75 g/mol

Preparation of catalyst: 15 g

Prepared by 0.05 M La(NO₃)₃.6H₂O Solution:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{liter of solvent}}$$

$$0.05 = \frac{\text{Moles of solute}}{1}$$

$$\text{Moles of solute} = 0.1 \times 0.05$$

$$\text{Moles of solute} = 0.005$$

$$\begin{aligned}\text{Weight of Solute} &= \text{Moles of solute} \times \text{Molecular weight of Solute} \\ &= 0.005 \times 433 \\ &= 2.165 \text{ g.}\end{aligned}$$

Prepared by 0.05 M Fe(NO₃)₃·6H₂O Solution:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{liter of solvent}}$$

$$0.05 = \frac{\text{Moles of solute}}{1}$$

$$\text{Moles of solute} = 0.1 \times 0.05$$

$$\text{Moles of solute} = 0.005$$

$$\begin{aligned}\text{Weight of Solute} &= \text{Moles of solute} \times \text{Molecular weight of Solute} \\ &= 0.005 \times 350 \\ &= 1.75 \text{ g.}\end{aligned}$$

Prepared by 0.4 M Glycine Solution:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{liter of solvent}}$$

$$0.4 = \frac{\text{Moles of solute}}{1}$$

$$\text{Moles of solute} = 0.1 \times 0.4$$

$$\text{Moles of solute} = 0.04$$

$$\begin{aligned}\text{Weight of Solute} &= \text{Moles of solute} \times \text{Molecular weight of Solute} \\ &= 0.04 \times 75 \\ &= 3\text{g.}\end{aligned}$$

Diagram 2. LaFeO₃ by Sol-Gel Method

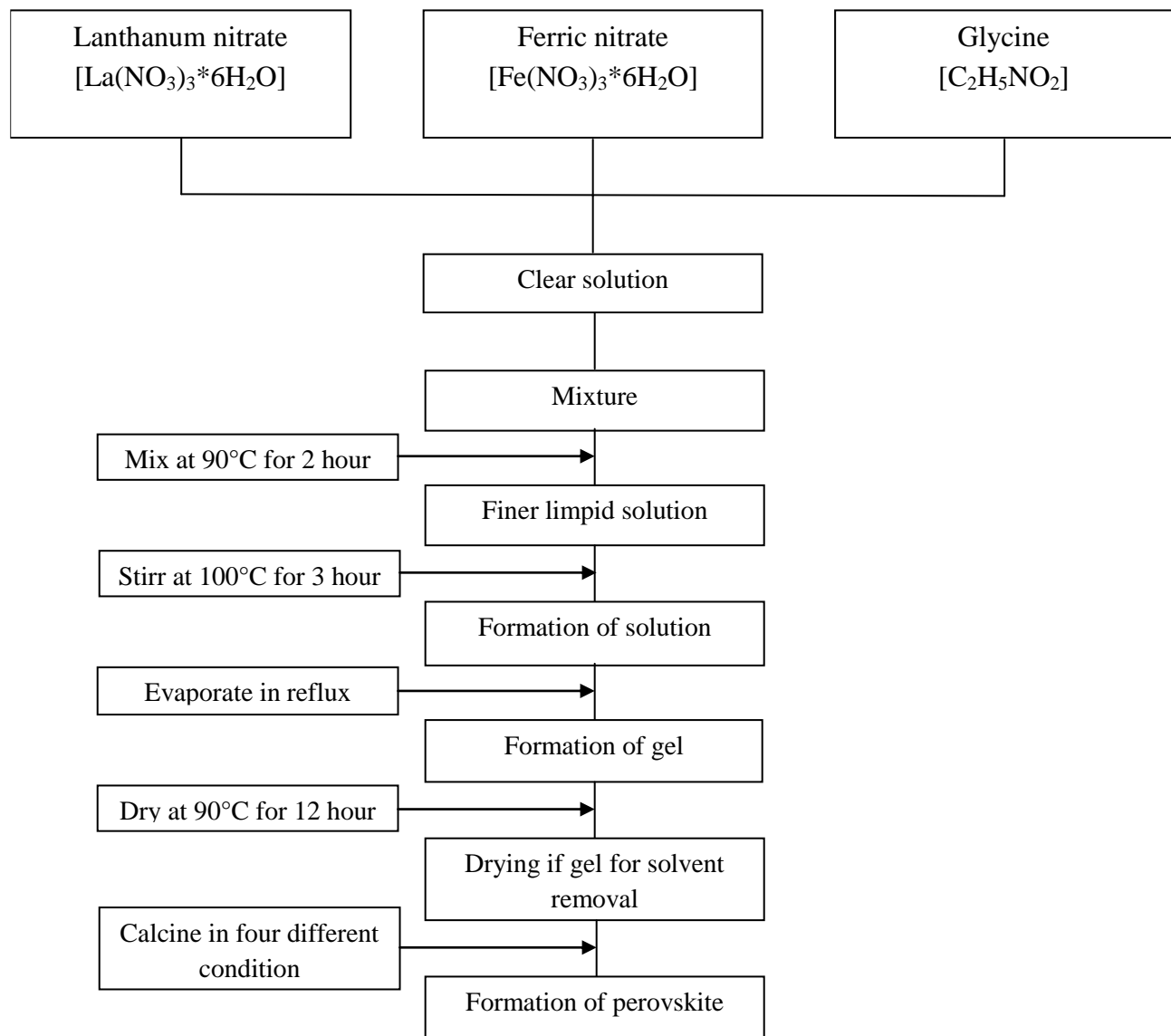




Fig. 10 Mixture of four solution stirred for 30 minutes of lanthanum nitrate + ferric nitrate and glycine



Fig. 11 Mix at 90°C for 2 hours



Fig. 12 (Formation of solution)



Fig. 13 Formation of gel



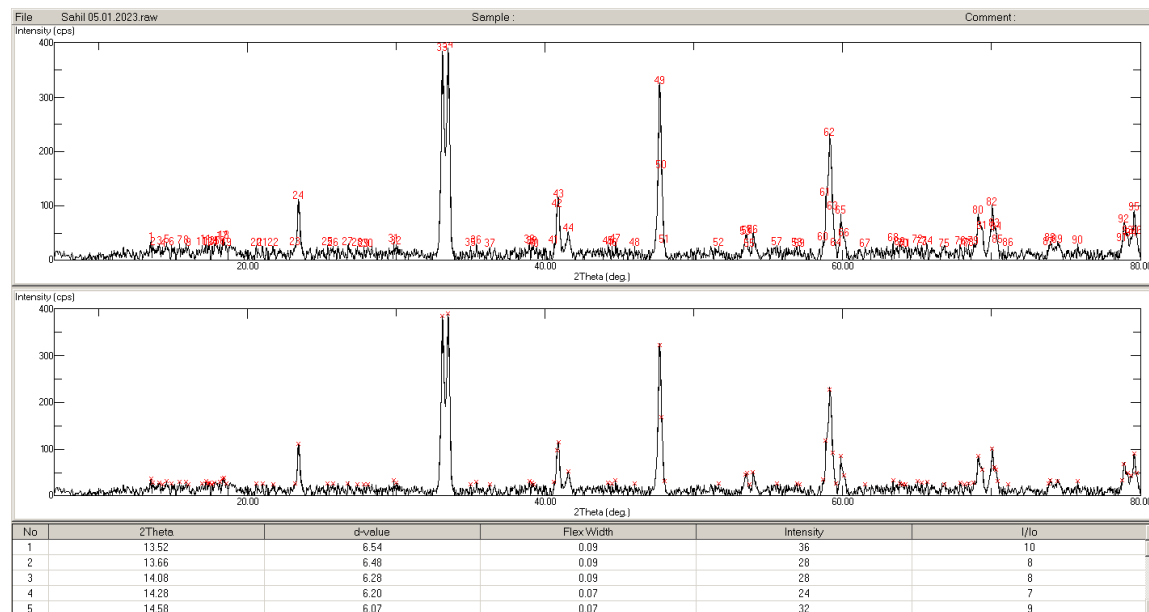
Fig. 14 Drying of gel for solvent removal



Fig. 15 Formation of perovskite

Result And Discussion

RESULT OF XRD (CITRATE METHOD)



Graph -1. XRD Graph $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ Catalyst Prepared by Citrate Method

Table 1. Results of XRD

No.	2 Theta	d-value	Flex width	intensity	I/I0
1	23.4	3.79	0.16	112	29
2	13.12	2.70	0.19	384	99
3	33.50	2.67	0.16	389	100
4	40.80	2.21	0.09	97	26
5	40.90	2.20	0.12	115	30
6	41.56	2.17	0.07	52	14
7	47.70	1.91	0.19	323	83
8	47.82	1.90	0.07	169	44
9	53.46	1.71	0.12	46	12
10	53.98	1.70	0.09	50	13
11	58.86	1.57	0.07	118	31
12	59.14	1.56	0.21	227	59
13	59.34	1.56	0.07	93	24
14	59.88	1.54	0.12	84	22
15	69.10	1.36	0.12	85	22
16	70.06	1.34	0.12	101	26
17	70.30	1.34	0.07	55	15
18	79.58	1.20	0.12	90	24

The crystal size of the samples based on the half-width of a diffraction peak using Scherrer formula.

From this XRD data, we can calculate diameter of LaCo_{0.8}Cu_{0.2}O₃ particles as follows:

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

Where, λ = wave length of X-Ray being used for XRD,

B = FWHM (Full Width Half Maximum),

θ = Angle of diffraction

$$[1] D = \frac{k\lambda}{\beta \cos\theta}$$

$k = 0.9$, $\lambda = 1.5 \text{ \AA}$, $2\theta = 70.13$, so $\theta = 35.065$, $\cos \theta = 0.8185$, $\beta = 0.07 = 0.00122 \text{ radian}$

$D = [(0.9 \times 1.5) / (0.00122 \times 0.8185)] = 1332.7 \text{ Angstrom} = \mathbf{133.27 \text{ nm}}$

$$[2] D = \frac{k\lambda}{\beta \cos\theta}$$

$k = 0.9$, $\lambda = 1.5 \text{ \AA}$, $2\theta = 23.4$, so $\theta = 11.7$, $\cos \theta = 0.9791$, $\beta = 0.16 = 0.00279 \text{ radian}$

$D = [(0.9 \times 1.5) / (0.00279 \times 0.9791)] = 4943.2 \text{ Angstrom} = \mathbf{494.32 \text{ nm}}$

$$[3] D = \frac{k\lambda}{\beta \cos\theta}$$

$k = 0.9$, $\lambda = 1.5 \text{ \AA}$, $2\theta = 40.90$, so $\theta = 20.45$, $\cos \theta = 0.936$, $\beta = 0.12 = 0.00209 \text{ radian}$

$D = [(0.9 \times 1.5) / (0.00209 \times 0.936)] = 6923 \text{ Angstrom} = \mathbf{692.30 \text{ nm}}$

$$[4] D = \frac{k\lambda}{\beta \cos\theta}$$

$k = 0.9$, $\lambda = 1.5 \text{ \AA}$, $2\theta = 40.80$, so $\theta = 20.20$, $\cos \theta = 0.937$, $\beta = 0.09 = 0.00157 \text{ radian}$

$D = [(0.9 \times 1.5) / (0.00157 \times 0.937)] = 9183.6 \text{ Angstrom} = \mathbf{918.36 \text{ nm}}$

$$[5] D = \frac{k\lambda}{\beta \cos\theta}$$

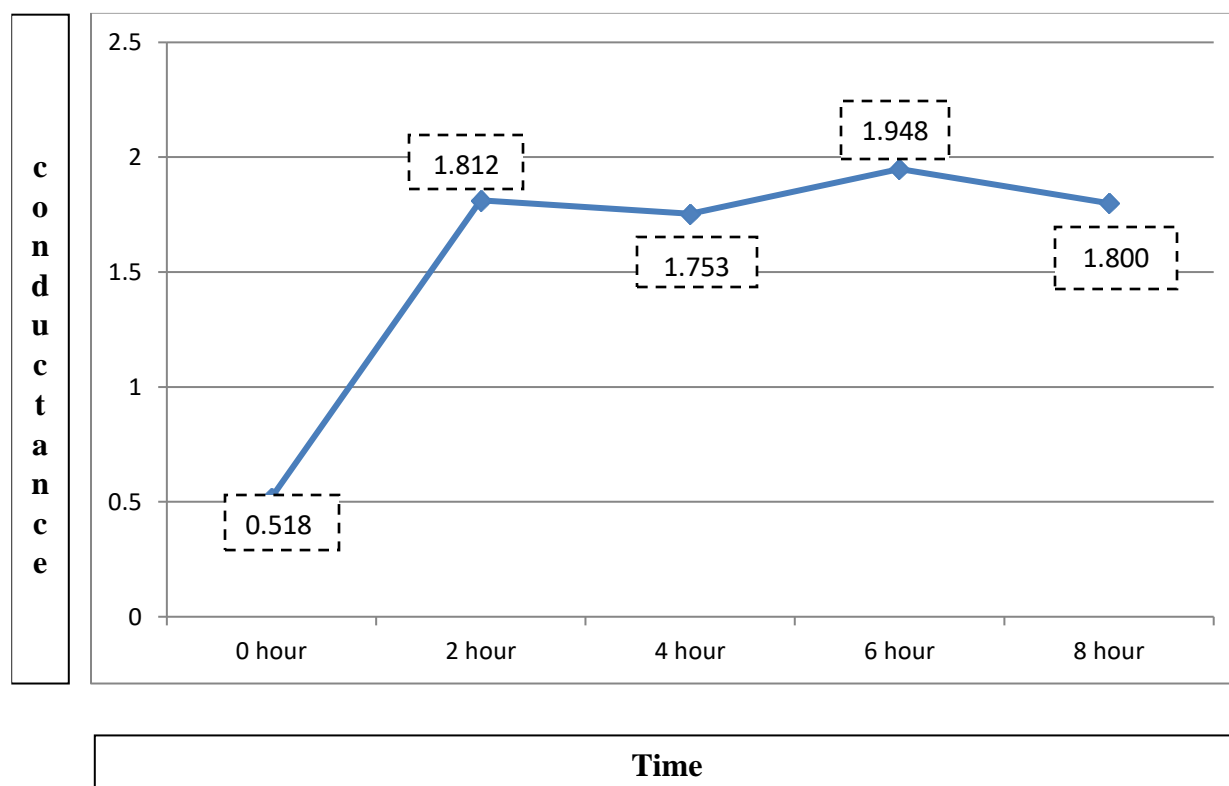
$k = 0.9$, $\lambda = 1.5 \text{ \AA}$, $2\theta = 59.34$, so $\theta = 29.67$, $\cos \theta = 0.8688$, $\beta = 0.07 = 0.00122 \text{ radian}$

$D = [(0.9 \times 1.5) / (0.00122 \times 0.8688)] = 12747.8 \text{ Angstrom} = \mathbf{1274.78 \text{ nm}}$

ACTIVITY OF CATALYST

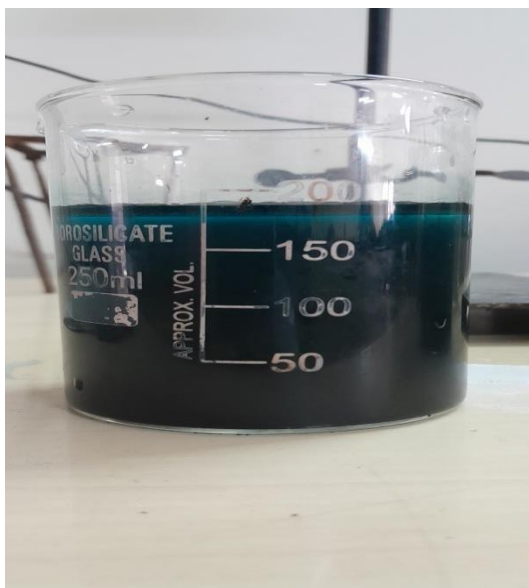
Catalytic activity of perovskite catalyst $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ in different types of dye water like malachite green and mixture of methylene blue and malachite green under different conditions such as placing dye water along with perovskite catalyst inside UV chamber or placing under direct sun light.

*NOTE : ALL THE EXPERIMENTS WERE CARRIED OUT AT NORMAL TEMPERATURE AND PRESSURE



Graph. 2 Malachite green dye water placed inside UV chamber along with perovskite catalyst prepared by citrate method

When malachite green dye water containing perovskite catalyst which was prepared by citrate method when placed inside UV chamber having short UV range the initial conductance was observed to be 0.518 and has shown significant degradation of dye mean while the conductance was seen to be increasing till 2 hours and then it started decreasing and conductance was observed as 1.800 at the end of 8 hours mean while, the colour of the methylene blue dye water was less concentrated then the intital solution which clearly indicats the adsorption of dye on the surface of catalyst.



16 (a) Initial dye water solution

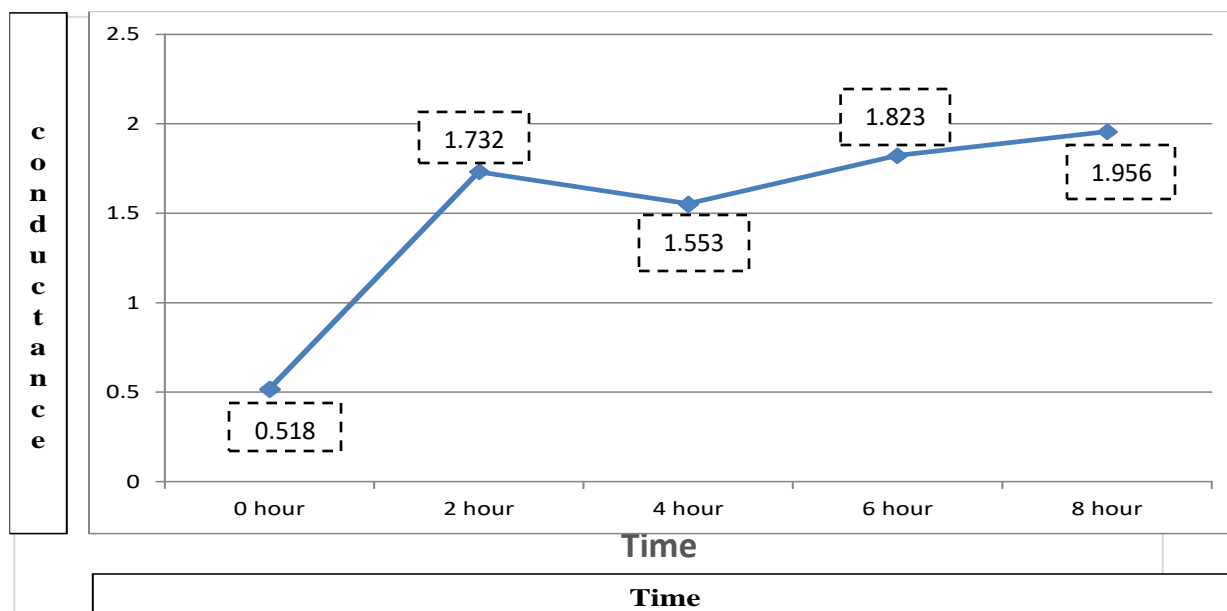


16 (b) Final dye water solution

Fig. 16 Malachite green dye water placed inside UV chamber along with perovskite catalyst prepared by citrate method

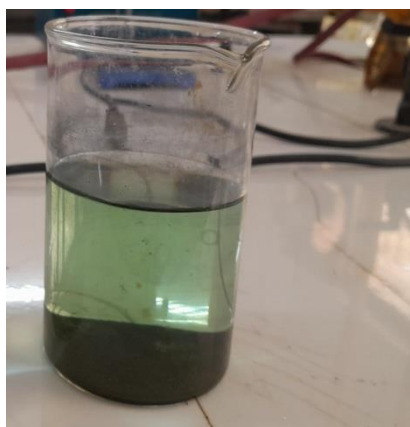
Above Fig. 16(a) shows the initial dark colour of dye water consisting of malachite green dye and the initial conductance of the solution was measured as 0.518. In that solution perovskite type catalyst ($\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$) prepared by citrate method is added to it which is responsible for the removal of malachite green dye by adsorption phenomenon when placed under UV chamber.

Meanwhile, Fig. 16(b) represents the final dye solution colour which is almost colourless and less concentrated than the initial colour and conductance of the dye solution was observed as 1.800 after 8 hours placed inside UV chamber under short UV range. Thus, we can conclude that there is significant adsorption of malachite green dye over the surface of perovskite catalyst by adsorption.



Graph.3 Malachite green dye placed in direct sunlight along with perovskite catalyst prepared by citrate method

When malachite green dye water containing perovskite catalyst which was prepared by citrate method when placed in direct sunlight has initial conductance of 0.518 and has shown significant degradation of dye meanwhile the conductance was seen to be increasing gradually and at the end of the 8 hours conductance was observed at 1.956 and the colour of the malachite green dye water was less concentrated than the initial solution which clearly indicates the adsorption of dye on the surface of catalyst.



17 (a) Initial dye water solution



17 (b) Final dye water solution

Fig. 17 Malachite green placed inside direct sunlight along with perovskite catalyst prepared by citrate method

Conclusion

In this dissertation, we have reported several aspects of perovskite catalyst. Here, we have mainly focused on the properties, synthesis method (prepared $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ citrate method and LaFeO_3 by sol gel method), its characterization and potential application of perovskite catalyst as adsorbents of dye from dye wastewater treatment for malachite green dye from both condition of sun light and UV light chamber. Perovskite proved to be very good in removing dyes, so their application needs to be expanded so that they can cover other water and wastewater contaminants. Considering the current engineering trend of practice-reduce, reuse and recycle; materials with properties of perovskite may garner more research attention and owing to their potentials become the next uprising materials of the future.

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