

Color Removal from Dye Wastewater using cost-effective $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst

*Femina Patel, Panchami Patel, Nirali Patel, Sanjay Patel

Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad-382481, INDIA

E-mail: femina.patel@nirmauni.ac.in, sanjay.patel@nirmauni.ac.in

Phone: (o) +91-02717-241911-15, Ext (523/103) (m) 9898538809, Fax: 91-02717-241917

Abstract- $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst was prepared by sol-gel (using distilled water and nitric acid) and co-precipitation method (using nitric acid) in the presence of nitrate-metal-ethylene glycol (EG) polymerised complex. The $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst showed excellent adsorption efficiency towards reactive black 5 (RB5) as a reactive dye in aqueous solution. The adsorption studies were carried out at different pH values, dye concentrations, various catalyst dosages and contact time in batch experiments. The dye removal efficiency was found about 99% at acidic pH specially 2 pH. The isotherm evaluation indicates that the Langmuir model fits the experimental data better than the Freundlich model. Experimental results indicated that the adsorption kinetic data follow a pseudo-second-order rate for the tested dye. COD and TOC reduction by catalyst is also tested with 60% reduction of COD. A systematic study on the structural, morphological of the $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst by various analytical techniques (XRD, DTA and BET) is to be done to characterize the crystallinity, morphology, specific surface area and grain size of $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst.

Keywords- Dyes, adsorption, perovskites, COD, TOC.

1. INTRODUCTION

Dyes are organic compounds consisting of two groups of compounds, chromophores (responsible for color of the dye) and auxochromes (responsible for intensity of the color) [1]. Dyes have a synthetic origin and complex aromatic molecular structures which make them more stable and difficult to biodegrade. Dyes can have both direct and indirect toxic effects on humans in the form of tumours, cancers and allergies [2]. The presence of dyes in water reduces light penetration and hinders photosynthesis in aquatic plants. Color removal in natural waters is needed because color is an indirect indicator of potential for trichloromethane formation during disinfection with chlorine. The color of water, polluted with organic colorants, reduces when the cleavage of the $-\text{C}=\text{C}-$ bonds, the $-\text{N}=\text{N}-$ bonds and heterocyclic and aromatic rings occurs. The absorption of light by the associated molecules shifts from the visible to the ultraviolet or infrared region of the electromagnetic spectrum [3].

Physicochemical methods involve physicochemical processes such as membrane filtration, flocculation, precipitation, adsorption, chemical reduction, oxidation, and advanced chemical oxidation. Biological processes include aerobic, anaerobic and combinations of the two [2, 3].

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [4]. The physical characteristics of the catalysts such as surface area, porosity, size distribution, density and surface charge have high influence in the adsorption process. As a result, there has been a great interest

in developing new catalyst materials with diverse compositions, properties and functionalities [1].

The structural family of perovskites is a large family of compounds having crystal structures normally as ABX_3 where X can be oxygen, F^- or Cl^- and A is a rare earth metal with large ionic radius or alkali earth metals, and B is a transition metal with a small ionic radius.

This kind of material can tolerate substitutions at both cation sites without modification of crystal structure. The substitution at A site with ions having lower valence can allow the formation of structural defects such as cationic or anionic vacancies and/or change in the oxidation state of the transition metal cation to maintain the electronegativity of the compound when the oxidation state of B cation increases, the redox process generates larger amounts of available oxygen at low temperatures & overall oxidation efficiency is increased. The oxygen vacancies favour the catalytic activity in oxidation reactions because they increase the lattice oxygen mobility. The preparation method of perovskites is important both in defining suitable textural characteristics and in achieving phase of greater purity. The literature describes numerous synthesis methods, which allow the incorporation of cations into functional perovskite structure due to the high calcinations temperature used. The most commonly used method to overcome the problem of purity is the sol-gel citratemethod. This develops catalysts with high surface areas but it has the drawbacks of sintering at high temperatures [5].

2. EXPERIMENTAL

2.1 Reagents

La(NO₃)₃·6H₂O (99.0% purity), Ca(NO₃)₂·4H₂O (99.99% purity), Ni(NO₃)₂·6H₂O (98.00% purity), citric acid (CA) (99.7% purity), ethylene glycol (EG) and nitric acid were all obtained from Piyush Chemicals, Ahmedabad. The reactive dye (RB5, molecular weight=774.16 g/mol) was obtained from Evergreen Industries, Ahmedabad. Distil water was used throughout the experiments.

2.2 Preparation

Preparation of La_{0.5}Ca_{0.5}NiO₃ catalyst was done by Sol-Gel (S-G) method using Distil Water (DW), Sol-Gel method using Nitric Acid (NA) and Co-Precipitation (CP) method using Nitric Acid (NA). The aqueous solutions of metal nitrates with nominal atomic ratios La:Ca:Ni=0.5:0.5:1 were mixed together in DW in the case of Sol-Gel method using DW and were mixed together in NA in the case of Sol-Gel method using NA. Citric Acid (CA) was proportionally added to the metal solution to have the same amount of equivalency. The solution was concentrated by evaporation at approximately 80°C for 30 min to convert it to stable (La,Ni)/CA complexes. Then ethylene glycol (EG) was added to the solution as a cross-linking agent. The solution while being stirred, was heated at approximately 80°C to remove excess water and subsequently to accelerate polyesterification reactions between CA and EG. Then, the dry gel was obtained by letting the sol into an oven and heated slowly upto 110°C and kept for 6 hr in baking oven. The gel pieces were ground in an agate mortar to form fine powders. Finally, La_{0.5}Ca_{0.5}NiO₃ catalyst was obtained by thermal treatment of precursors at 750°C temperature for 9 hr in air. The Co-precipitation method follows the same method as Sol-Gel but instead of adding CA and EG, 1 M Sodium Carbonate is added till the pH of the solution was 10 and then the solution was washed using DW till the pH of the solution was around 7. The catalyst was then heated in the air oven and calcined in the same way as in Sol-Gel method.

2.3 Characterization

Thermal behaviour (DTA) of the gel precursor dried at 110 °C was studied using NETZSCH-402EP thermoanalyzer in the temperature range from 20 to 1000 °C (5 °C/min) within a dynamic air atmosphere. For structural investigation of calcined powder at 750 °C XRD measurements were carried out in the region of (2θ=20 to 70°) using CuKα radiation on a Rigaku D/MAX RB XRD diffractometer equipped with a curved

graphite monochromator. The specific surface area (SSA) of the catalyst was calculated using BET method from the nitrogen adsorption isotherms obtained at 77 K on samples outgassed at 250 °C with the use of a Micromeritics Accusorb 2100E apparatus. A UV-vis spectrophotometer (Shimadzu UV-1800) was employed to monitor adsorption of dyes. COD was analysed using HACH DRB 200 and TOC by Shimadzu V_{CSH}.

2.4 Dye Removal Experiments

Batch experiments were performed to evaluate the effect of the following parameters on the removal of RB5 by LCNO particles: initial solution pH, initial dye concentration, different doses of catalyst and contact time. A prepared solution of RB5 was distributed into different flasks (1 L capacity) and pH was adjusted with the help of a pH meter (VSI 07, Indian made). The initial pH value of the dye solution was adjusted to the desired levels, using either HCl (0.5 M) or NaOH (0.5 M). A known mass of LCNO was then added to 10 mL of the RB5 aqueous solution, and the obtained suspension was immediately stirred for a predefined time. All experiments were done at the room temperature. The investigated ranges of the experimental variables were as follows: dye concentration (50–150 mg/L), pH of solution (1–13), LCNO dosage (0.01, 0.02 and 0.03 g) and mixing time (1–30 min). The initial RB5 concentration for all experiments was adjusted to 50 mg/L, except for the experiments in which the effect of the initial RB5 concentration in the removal of RB5 by LCNO catalyst was tested. After a preselected time of decolorization, samples were collected and absorbance of the solution at a λ_{max} equals to 599 nm (Shimadzu UV-1800) was measured to monitor the residual RB5 concentration.

3. RESULTS AND DISCUSSIONS

3.1 Adsorption of Dyestuff on the La_{0.5}Ca_{0.5}NiO₃ Catalyst Surface

3.1.1 Effect of pH:

The effect of the initial solution pH on the dye removal efficiency of RB5 on LCNO catalyst was evaluated at different pH values, ranging from 1 to 13 with a stirring time of 10 min (as shown in Fig. 1(a) and (b) and Fig. 2). The initial concentrations of dye and catalyst dosage were set as 50 mg/L and 0.01 g respectively. The percentage of dye removal is defined as:

$$\text{Removal Rate (\%)} = \frac{C_0 - C}{C_0} \times 100$$

Where, C₀ and C are initial and residual concentrations of RB5 respectively.

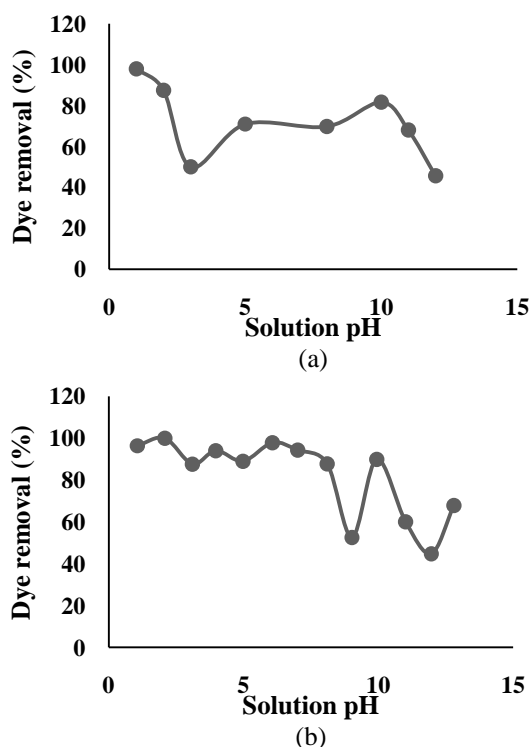


Fig. 1. (a) Effect of initial pH of dye solution on removal of RB5 (catalyst prepared by S-G using DW) and (b) effect of initial pH of dye solution on removal of RB 5 (catalyst prepared by S-G using NA)

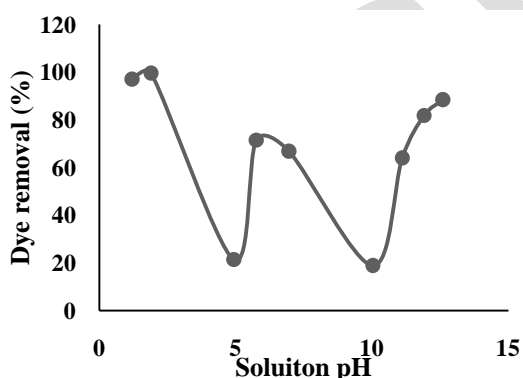


Fig. 2. Effect of pH on % removal of RB 5 (catalyst prepared by CP using NA)

The dye removal efficiency was found to be decreased with increase in initial pH of dye solution, and $La_{0.5}Ca_{0.5}NiO_3$ catalyst exhibited 100% dye removal efficiency at 2 pH. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. At low pH solution, the percentage of dye removal for anionic dyes will increase. Higher uptakes are obtained at lower pH which may be due to the electrostatic attractions between negatively charged functional groups located on the reactive dye and positively charged catalyst surface. Hydrogen ion also acts as a bridging ligand between the catalyst wall and the dye molecule [5].

3.1.2 Effect of contact time and catalyst dosage:

Results shown in Fig. 3 indicate increase in contact time and increase in catalyst dosage leads to decrease in residual contact concentration of RB5; this may be due to the increase in number of adsorption sites for dye molecules at greater LCNO dosages.

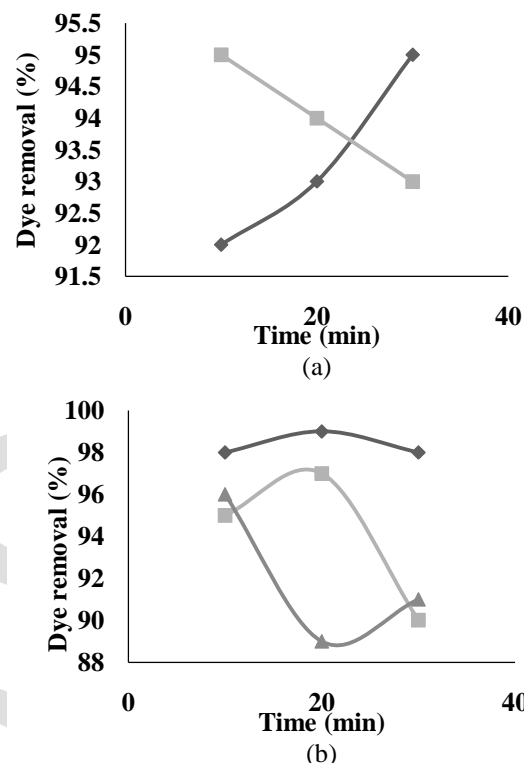


Fig. 3.(a) Effect of stirring time on removal of RB5 in different dosage (♦) 0.02 gm (■) 0.03 gm of LCNO prepared by S-G using DW (dye concentration = 50 mg/L, pH = 1) and (b) Effect of stirring time on removal of RB5 in different dosage (♦) 0.01 gm (■) 0.02 gm (▲) 0.03 gm of LCNO prepared by S-G using DW (dye concentration = 100 mg/L, pH = 1)

There is a decline in decolorization rates when catalyst dosage is increased which can be attributed to increasing formation of aggregates between particles of catalyst which results in decrease of surface area.

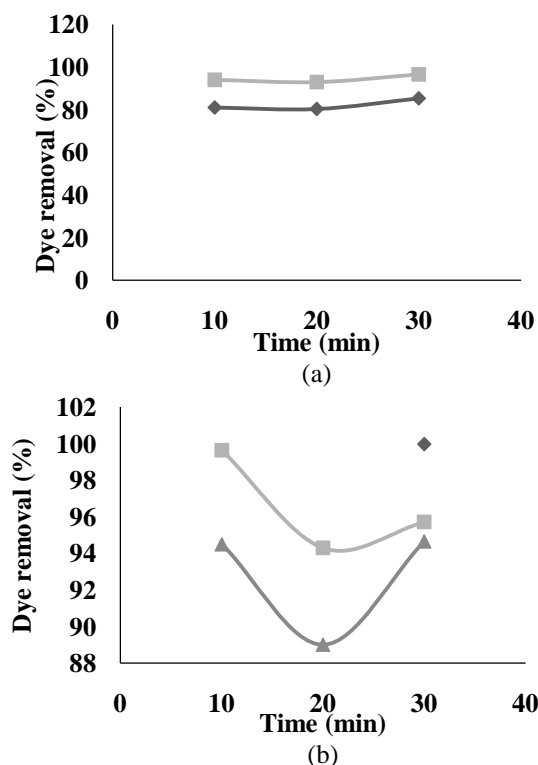


Fig. 4. (a) Effect of stirring time on removal of RB5 in different dosage (♦) 0.02 gm (■) 0.03 gm of Catalyst prepared by S-G using NA (dye concentration = 50 mg/L, pH = 2) and (b) Effect of stirring time on removal of RB5 in different dosage (♦) 0.01 gm (■) 0.02 gm (▲) 0.03 gm of catalyst prepared by S-G using NA (dye concentration = 100 mg/L, pH = 2)

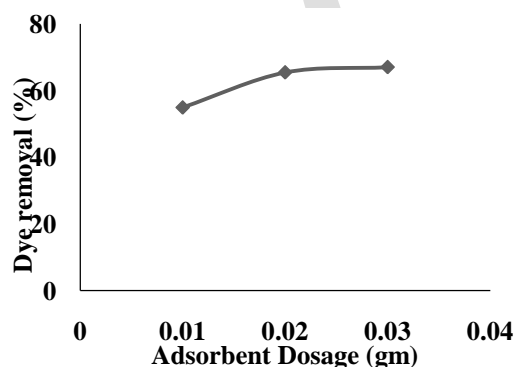


Fig. 5. Effect of Catalyst dosage on % removal with stirring time = 10 min at 2 pH using catalyst prepared by S-G using NA for dye concentration = 150 ppm

3.1.3 Effect of initial Dye Concentration:

The effect of initial RB5 concentration on dye removal efficiency by LCNO particles was studied by varying the initial dye concentration from 50 to 150 mg/L at pH 2, catalyst dosage of 0.03 g and contact time of 10 min.

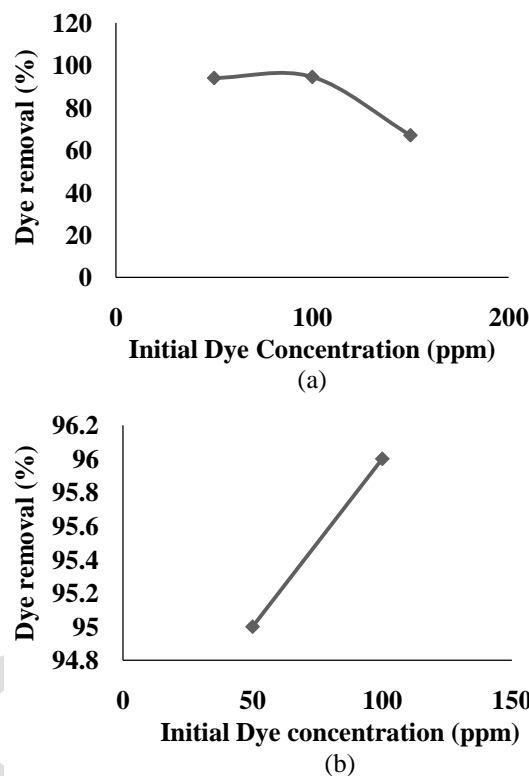


Fig. 6. (a) Effect of initial dye concentration on removal of RB5 using LCNO prepared by S-G using DW for initial dye concentrations = 50, 100 mg/L (b) Effect of Initial dye Concentration on removal of RB5 using LCNO prepared by S-G using NA

Results show that removal of dye RB5 decreases with increasing initial concentration. The percentage removal of RB5 decreased from around 98% to 60% for increase in initial dye concentration from 50 to 150 mg/L. The removal of dye RB5 decreases with increasing the initial concentration is because the number of dye molecules is more than the number of available sites on the LCNO catalyst.

3.1.4 Comparison of Catalyst $La_{0.5}Ca_{0.5}NiO_3$ prepared by Sol-Gel method (using NA and DW):

Percentage removal by LCNO catalyst prepared by various methods i.e. SG method using DW (at 1 pH) and S-G method using NA (at 2 pH) was studied with catalyst dosage of 0.03 g and contact time of 10 min.

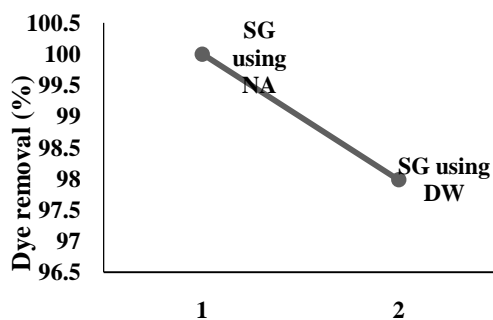


Fig. 7. Effect of pH on % removal of dye on La_{0.5}Ca_{0.5}NiO₃ Catalysts prepared by S-G method (using NA and DW)

3.2 ADSORPTION KINETIC STUDIES

Catalyst La_{0.5}Ca_{0.5}NiO₃ prepared by S-G method (using NA):

For the pseudo-first and pseudo-second order kinetic model, the experimental data have been fitted with the following equations:

Pseudo first order equation: $\ln C(t) = \ln C_0 - k_1 t$

Pseudo second order equation: $\frac{1}{C(t)} = k_2 t + \frac{1}{C_0}$

Where, k_1 and k_2 are the first-order and second-order rate constant; C_0 stands for the initial RB5 concentration and $C(t)$ is the concentration of RB5 at time t .

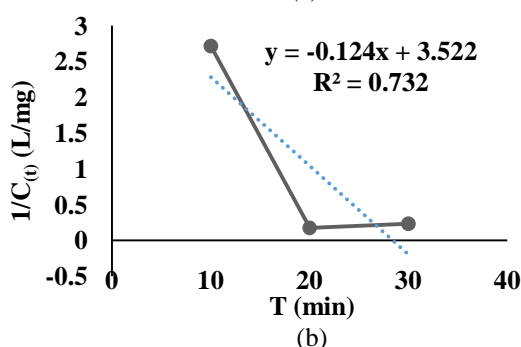
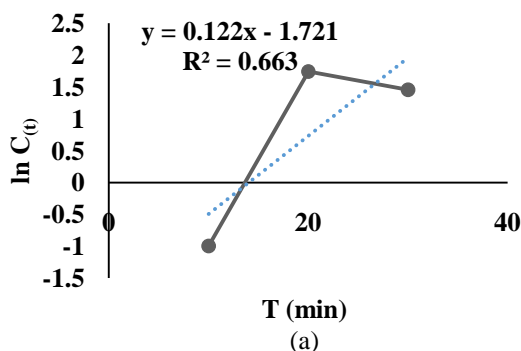


Fig. 8 (a) Plot for pseudo-first order equation and (b) Plot for pseudo-second order equation

Higher value of R^2 were obtained for pseudo-second-order (0.7325) than for pseudo-first-order (0.6636) adsorption rate models, indicating that the adsorption rates of RB5 on catalyst La_{0.5}Ca_{0.5}NiO₃ to the can be more appropriately described using

the pseudo-second-order rate. The values of the rate constant, k_1 and k_2 are 0.1227 and -0.1241 ($M^{-1} min^{-1}$).

3.3 ADSORPTION ISOTHERMS STUDIES

The amount of dye adsorbed onto catalyst has been calculated based on the following mass balance equation:

$$q_e = \frac{V(C_0 - C_e)}{m}$$

where, q_e is equilibrium dye concentration on catalyst (mg/g), V is the volume of the dye solution (L), C_0 and C_e (mg/L) are the initial and equilibrium dye concentrations, and m (g) is the mass of Catalyst La_{0.5}Ca_{0.5}NiO₃.

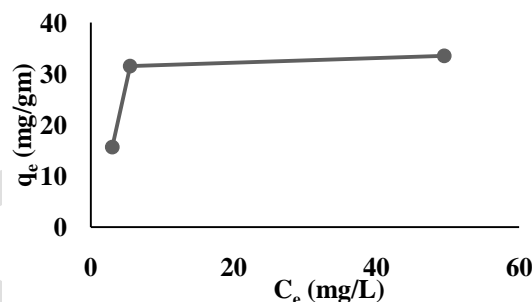


Fig. 9. Plot of q_e vs. C_e for removal of RB5 (Catalyst dosage=0.03 g, initial dye concentration = 50, 100, 150mg/L, volume of dye solution=10 mL, stirring time=10 min, initial pH 2)

The Langmuir model equation, assuming monolayer adsorption on a homogeneous catalyst surface, can be presented as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$$

Where, the q_{max} (mg/g) is the maximum value of q_e . The values of q_{max} as 35.087 (mg/g) and b as 0.452 L/mg can be determined from the linear regression plot of (C_e/q_e) versus C_e .

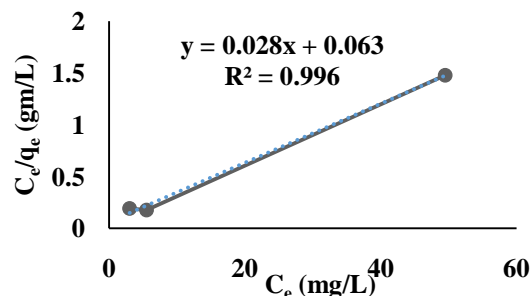


Fig. 10. Langmuir isotherm plot of RB5 adsorption onto Catalyst La_{0.5}Ca_{0.5}NiO₃: Catalyst dosage=0.03 g, initial pH 2, stirring time=10 min, initial dye concentration=50, 100, 150 ppm

The linearized form of the Freundlich isotherm is expressed as follows

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where constant K_F represents the capacity of the catalyst for the adsorbate and n is related to the adsorption distribution. A linear regression plot of $\log q_e$ versus $\log C_e$ gives the K_F and n values as 16.07 and 4.854.

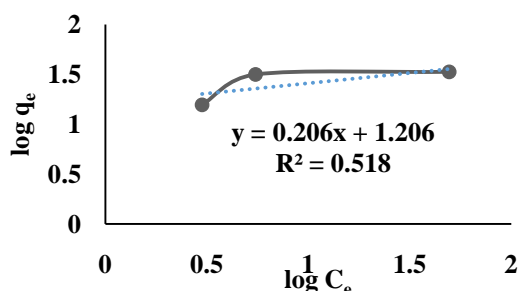


Fig. 11. Freundlich isotherm plot of RB5 adsorption onto Catalyst $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$: Catalyst dosage=0.03 g, initial pH 2, stirring time=10 min, initial dye concentration=50, 100, 150 ppm

The value of correlation coefficient (R^2) for Langmuir isotherm is greater than that of the Freundlich isotherm for the adsorption of investigated dye. This indicates that the adsorption of RB5 on Catalyst $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ is better described by the Langmuir model.

Performance Evaluation:

The adsorption capacity varies and it depends on the characteristics of the individual catalyst and the initial concentration of the adsorbate. The maximum adsorption capacities of catalysts are listed in the table 1. It shows that the q_{\max} of RB5 on $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ prepared by both distilled water and nitric acid is high so it can be concluded that $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ is a catalyst with good adsorption capacity.

Table 1: Adsorption Capacities of organic dyes on various catalysts

Catalyst	q_{\max} (mg/g)	Reference
ZnCr_2O_4	41.32	[7]
$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$	36.23	[3]
$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (DW)		Present study
$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (NA)	35.087	Present study
$\text{LiCo}_{0.5}\text{Fe}_{0.5}\text{O}_2$	76.92	[8]

The cost of 15 gm of LCNO catalyst by Sol-Gel method is approx. Rs.824.83 so for 10 mL of dye wastewater treatment the catalyst cost is Rs. 0.5498 (0.01 g LCNO for 10 mL) compared to Rs.2.5325 of activated carbon (2.5 gm for 10mL). This concludes that LCNO is a catalyst with low cost and good adsorption capacity.

3.4 COD RESULTS

COD is an effective method of analysing the amount of organic (biologically oxidizable and biologically inert) compounds present in wastewater. It gives the amount of organic compounds that can be oxidised by action of strong oxidising agent under acid condition. The catalyst for testing TOC was $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (NA) and $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (DW) (0.01 gm for 10 mL 50 ppm dye wastewater sample).

$$\text{COD (mg/L)} = \frac{8000 \times (\text{blank titr.} - \text{sample titr.})}{\text{mL Sample} \times (\text{Normality of } \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2)}$$

Blank Sample Titration Reading = 1.9 mL.

Table 2: COD Test Results

Catalyst		Titration Reading	COD	% Reduction	COD	% Color Removal
$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (DW)	Before Treatment	1.6	64	66.667		99.5
	After Treatment	1.8	32			
$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (NA)	Before Treatment	1.7	96	50		99.64
	After Treatment	1.8	32			

3.5 TOC RESULTS

TOC gives the amount of Total Organic Carbon in wastewater. The catalyst for testing TOC was $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ (NA) (0.06 g for 20 mL 50 ppm dye wastewater sample).

Table 3: TOC Test Results

Before Treatment TOC	After Treatment TOC	%TOC reduction	% Color Removal
21.764	16.339	24.92	95.068

4. CONCLUSION

$\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst were synthesized by the Sol-Gel Method (using distilled water and nitric acid) and Co-Precipitation Method (using nitric acid) using citric acid and ethylene glycol and the subsequent calcinations process. A systematic study on the structural, morphological of the $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst by various analytical techniques (XRD and microscopic analysis) is yet to be done. Dye removal efficiency of the $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst was investigated by carrying

out various experiments. The processing parameters such as catalyst dosage, stirring time, initial dye concentration and pH value were modified and dye removal efficiency was measured. The results show that the $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst could efficiently remove high concentrations of RB5 molecules. The percentage of removal obtained in the 10th minute of stirring was 99.63 % using 0.02 g catalyst at 2 pH. These studies have shown that the $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ catalyst can be a promising material to remove azo dyes from water over a wide range of dye concentrations.

5. REFERENCES

- [1] Mohammad Yazdanbakhsha, Haman Tavakkolia, Seyed Mohammad Hosseini, "Characterization and evaluation catalytic efficiency of $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ nanopowders in removal of reactive blue 5 from aqueous solution", *Desalination* 281 (2011) 388–395.
- [2] Thai Anh Nguyen, Ruey-Shin Juang, "Treatment of waters and wastewaters containing sulfur dyes: A review", *Chemical Engineering Journal* 219 (2013) 109–117.
- [3] M. Slokar & A. Majcen Le Marechal, "Methods of Decoloration of Textile Wastewaters", *Dyes and Pigments*, Vol. 37, No. 4 (1998) 335-356.
- [4] Esther Forgacs, Tibor Cserhatia, Gyula Oros, "Removal of synthetic dyes from wastewaters: a review", *Environment International* 30 (2004) 953–971.
- [5] C.A. Orge, J.J.M Orfao, M.F.R Pereira, B.P. Barbero, L.E.Cadus, "Lanthanum-based perovskite for the ozonation of selected organic compounds", *Applied Catalysis B: Environmental* 140-141 (2013) 426-432.
- [6] K. S. Bharathi, S. T. Ramesh, "Removal of dyes using agricultural waste as low-cost adsorbents: a review", *Appl Water Sci*, DOI 10.1007/s13201-013-0117-y.
- [7] M.Yazdandanbaksh, I. Khosravi, E.K. Goharshadi, A. Youssefi, *J. Hazard. Mater.* 184 (2010) 684-689.
- [8] Iman Khosravi, Mohammad Yazdanbaksh, Melika Eftekhari, Zohreh Haddadi, "Fabrication of nano Delafossite $\text{LiCo}_{0.5}\text{Fe}_{0.5}\text{O}_2$ as the new adsorbent in efficient removal of reactive blue 5 from aqueous solutions", *Material Research Bulletin* 48 (2013) 2213-2219.