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Synthesis and Evaluation Catalytic Efficiency of Perovskite-Type Oxide Nanopowders in Removal of Bromocresol Purple from Aqueous Solution

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Abstract. A₁₋₃A₃BO₃ belongs to the perovskite oxides of the ABO₃ structure. In this study, nanoparticles of LaₓCa₀.₅FeO₃ were fabricated by sol–gel citrate technique. A series of common analytical techniques were used to characterize the crystallinity, morphology, specific surface area, and grain size of the nanopowders. These properties were characterised by means of XRD, SEM, EDX and FTIR. The calculated particles size using the Scherrer's formula was about 20 nm. Moreover, the family of perovskite-type oxides could be considered as an adsorbent/catalyst material for the removal of dyes. This study has also investigated the efficiency of LaₓCa₀.₅FeO₃ as an adsorbent for removal of dye (Bromocresol Purple (BP)), from an aqueous solution. The adsorption studies were carried out at different pH values, various adsorbent dosages and contact time in a batch experiments. The kinetic studies indicate that the removal process obeys the Pseudo-first-order kinetic equation. Also, the isotherm evaluations reveal that the adsorption of BP by the nanoparticles follows the Langmuir model. In addition, this nanoparticle with good specific affinity towards dye molecules was a promising adsorbent for dye removal from natural water.

Keywords: Perovskite oxides, Sol–gel method, Nanopowders, dye removal, bromocresol purple

1. INTRODUCTION

The structure of the LaMO₃ perovskite oxide consists of MO₆ and LaO₁₂. A₁₋₃A₃BO₃₋₃ belongs to the group of perovskite oxides of the ABO₃ structure with a trivalent rare earth in the A position (La) and a trivalent metal ion in the B position (Co, Fe or Ni). When La⁺³ ions in LaMO₃ are replaced by earth alkaline ions such as Ca⁺² to form La₁₋₃Caₓ(Co, Fe, Ni)O₃₋₃ a positive charge can be generated. Since Fe⁺² cations have different oxidation states, the charge neutrality can be maintained by the formation of oxygen vacancies and a change in the valence state of the cations. Therefore, these structures have an oxygen deficiency, δ, due to the high oxygen vacancy concentration and can show the fine electric conductivity, catalytic, mechanical, and colossal magnetoresistance (CMR) properties which have attracted a lot of attention (Gao and Wang, 2010; Gao et al., 2006; Chi et al., 2010). Furthermore, perovskite oxide, La₁₋₃CaₓFeO₃₋₅ could be a mixed ionic and electronic conductor. It has been widely investigated for use in various high-temperature electrochemical devices such as solid oxide fuel cells (Zhen et al., 2006; Jiang, 2008) or oxygen permeation membranes (Van Hassel et al., 1993). Moreover, they have been proposed as alternative catalysts for oxidation of carbon monoxide and hydrocarbons (Hu, 2005; Hirano et al., 2007) and promising catalyst for multi component reactions (Sanaeishoar et al., 2014).

A number of approaches such as solid-state reactions (Zhou et al., 2006), mechanical-synthesis (Szabo et al., 2002), coprecipitation (Nakayama et al., 2003; Srdic et al., 2005), solution combustion or thermal decomposition (Bansal and Zhong, 2006; Berger et al., 2004; Berger et al., 2007) hydrothermal, and sol-gel technique (Pechini, 1967; Cizauskaite and Kareiva, 2008) have been used to synthesize LaMO₃-based perovskite powders. The sol-gel method is highly attractive because various metal ions are chelated to form metal complexes in solution and are uniformly distributed at the molecular level. In this method, citric, oxalic and fatty acids and EDTA (Ethylenediaminetetraacetic Acid) have been utilized as complexing agents, among which, citric acid is a good chelating agent for transition metal cations for synthesizing ultra-fine powders of complex oxide compositions (Raileanu et al., 2013).

Growing concern for public health and environmental quality has prompted a wide interest in developing and implementing various materials and methods for removing the toxic organic and inorganic
pollutants from water (Senthilnathan and Philip, 2010). Dyes from the effluent of textile, paper, printing, and leather industries are the major sources of water contamination. There are more than ten thousand types of commercially available dyes with over seven hundred tons of dyestuff produced annually worldwide and used extensively in industries (Banat et al., 1996; Spadaro et al., 1994; Robinson et al., 2001). It is estimated that about 10–15% of the dyes were lost in industrial effluents (Forgacs et al., 2004).

The traditional physical, chemical and biologic means of wastewater treatment often have little degradation effect on this kind of pollutants. On the contrary, the technology of nanoparticulate photodegradation has been proved to be effective to them. Compared with the other conventional wastewater treatment means, this technology has such advantages as: 1) wide application, especially to the molecule-structure complexed contaminants which cannot be easily degraded by the traditional methods; 2) the nanoparticles itself has no toxicity to the health of our human lives and 3) it demonstrates a strong destructive power to the pollutants and can mineralize the pollutants into CO2 and H2O. Due to the excellent features of this technology, it appears promising and has drawn the attention of researchers of at home and abroad (Tavakkoli et al., 2013; Yazdanbakhsh et al., 2011; Carbajo et al., 2006).

In the present study, La0.5Ca0.5FeO3 (LCFO) component with perovskite structure was prepared via the sol-gel method and characterized by different techniques such as XRD, FTIR, SEM and EDX. Moreover, its efficiency as an adsorbent for removal of dye, bromocresol purple (BP), from an aqueous solution was evaluated. The effect of different variables including concentration of dye, different pH values, adsorbent doses and reaction time, for removal of BP on LCFO nanopowders has been investigated and two kinetic models have also been analyzed.

2. MATERIALS AND METHODS

2.1. Reagents

La(NO3)3.9H2O (99.99% purity), Ca(NO3)2.4H2O (99.99% purity), Fe(NO3)3.9H2O (99.99% purity) were all obtained from Merck, Germany; citric acid (CA) (99.5% purity), was purchased from Aldrich, USA. The commercial color index (CI) dye (BP, molecular weight = 540.22 g/mol) was generously provided by Sigma company, T8154-20mL USA which was used without further purification (Fig. 1). All the reagents were of analytical grade and thus used as received. Deionized water was used throughout the experiments.

2.2. Preparation and characterization of La0.5Ca0.5FeO3

For the preparation of the nanoperoxskite in this work, Proportional amounts of, La(NO3)3.9H2O, Ca(NO3)2.4H2O and Fe(NO3)3.9H2O, were dissolved in 20 ml of deionized water. Citric acid (CA) was proportionally added to the metal solution by stirring at room temperature. The solution was concentrated by evaporation at approximately 75°C to remove excess water. Then, the dry gel was obtained by letting the sol into an oven and heated slowly up to 110°C and kept for 10 h in baking oven. Then, it was ground in agate mortar and turned into powder and calcinated at 750°C in air for 9 h. The annealing of the amorphous precursor allows removing most of the residual carbon and the orthorhombic perovskite phase was obtained.

The complex polymeric gel and derived powders have been analyzed by Fourier transform infrared (FTIR) spectroscopy on Perkin Elmer BX II FTIR spectrometer. The crystallization and microstructure of the oxide powders have been characterized with an X-ray diffractometer employing a scanning rate of 0.02 S⁻¹ in a 2θ range from 20 to 70°, using a X pert, 200, Equinox 3000, France, equipped with CuKα radiation. The data have been analyzed using JCPDS standards. The microstructure and elemental distribution on the surface were investigated using KYKY EM3200 (V=30kV) scanning electron microscope and energy dispersive X-ray spectroscopy (EDX, Inca 400, Oxford Instruments). A UV–Vis spectrophotometer (Perkin Elmer lambda 35) was employed to monitor adsorption of dyes.

2.3. Dye removal experiments

A prepared solution of BP was distributed into different flasks (1 L capacity) and pH was adjusted with the help of the pH meter (HORIBA F 11 E, Japan 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 nano-LCFO powder (catalyst dosage) was then added to 10 mL of the BP 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 (50–250 mg/L), pH of solution (1–13), catalyst dosage (0.005, 0.01, 0.02 and 0.03 g) and mixing time (1–40 min). After a preselected time of decolorization, samples were collected and absorbance of the solution at a λmax = 450 nm for pH = 1 to 5 and λmax = 530 nm for pH = 6 to 13 was measured to monitor the residual BP concentration.
3. RESULTS AND DISCUSSIONS

3.1. X-ray Diffraction

XRD patterns of the synthesized nanopowder which calcined at 700°C for 9 h (heating rate: 3°C/min) is shown in Fig. 2. XRD results reveal the existence of a perovskite-type phase for sol-gel method at this temperature. When the precursor was calcined at 700°C for 9 hours, several sharp peaks were observed attributed to the perovskite \( \text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3 \) by comparison with standard XRD spectra. The diffraction peaks at 20 angles appeared in the order of 22.65°, 32.30°, 39.85°, 46.36°, 57.65°, and 67.66° can be assigned to scattering from the (0 2 0), (2 0 0), (2 2 0), (2 0 2), (3 2 1), and (4 0 0) planes of the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3 \) perovskite type crystal lattice, respectively. XRD data also shows \( \text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3 \) crystallizes in an orthorhombic phase with \( a = 5.5408 \), \( b = 7.843 \), \( c = 5.544 \) Å. The crystallite sizes were calculated using XRD peak broadening of the (2 0 0) peak using the Scherer’s formula (1):

\[
D_{hkl} = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta_{hkl}}
\]

where \( D_{hkl} \) is the particle size perpendicular to the normal line of (hkl) plane, \( \beta_{hkl} \) is the full width at half maximum, \( \theta_{hkl} \) is the Bragg angle of (hkl) peak, and \( \lambda \) is the wavelength of X-ray. The particle sizes of LCFO nanoparticles calcinated at 700°C is about 20 nm.

3.2. SEM and EDX Analysis

The surface and textural morphology of LCFO nanopowder by SEM image is illustrated in Fig. 3. According to the SEM image, the size of LCFO particles was found to range between 20 to 50 nm. The surface looks scaly and nearly fully covered with the particles that have grown on it. Moreover, the porosity of the surface is evident and it seems that the particles have grown with uniform size. The pores size varied from 0.1 to 0.3 μm. It must be mentioned that pores with large geometric dimensions are more suitable for water treatment. Also, the existence of these meso-pores facilitates the sorption of hazardous chemicals to the surface. This phenomenon improved the efficiency and workability of LCFO as a promising adsorbent.

The surface looks scaly and nearly fully covered with the particles grown on it. Further, it can also be seen from the SEM image that in addition to the larger particles, the surface contains also rather smaller particles. Nonetheless, the dominant particles on the surface were the larger ones. When smaller particles (in the nm range) aggregate, this may lead to the formation of bigger LPMO NPs on the surface.

The EDX analysis was performed to further confirmation of the obtained product composition. Fig. 4 shows EDX spectrum which indicates the existence of La, Ca, Fe and O elements in this nanoparticle.
Fig. 2: XRD pattern of La$_{0.5}$Ca$_{0.5}$FeO$_3$ nanopowder

Fig. 3: SEM images of LCFO nanopowders.

Fig. 4: Energy dispersive X-ray (EDX) spectrum of the LCNO nanoparticles.
3.3. FT-IR Spectroscopy

The FT-IR spectra of the LCFO fresh xerogel and calcinated xerogel in the range of 500-4000 cm\(^{-1}\) were shown in Fig. 5 (a,b). The dried gel of the sample shows the characteristic bands at about 1725, 1617 and 1385 cm\(^{-1}\) corresponds to the symmetric and anti-symmetric stretching mode of carboxylate group (Kuznetsov et al., 2002; Kim and Honma, 2004). The band at about 1230 cm\(^{-1}\) assigned to the NO\(_3\) stretching vibration (Lui et al., 2007). The absorption band around 1080 cm\(^{-1}\) is attributed to C–O bond (Nakamoto, 1978). As can be seen in Fig. 5 b, the bands correspond to O–H group, NO\(_3\), and carboxylate ligand disappear as the gel was calcinated at 700 C.

The FTIR spectra of calcined sample shows the vanishing of bands related to organic and hydroxyl groups. Two bands are observed at 400-650 cm\(^{-1}\) in the FTIR spectrum of sample, one of them is strong at ~ 617 cm\(^{-1}\) and other weak peaks at 431 cm\(^{-1}\). These peaks are characteristics of perovskite oxides and can be attributed to \(\nu\) M–O stretching and \(\delta\) O–M–O bending mode of vibrations, respectively.

![Fig. 5: FT-IR spectra of LCFO precursor (a), and the calcinated powders at 700 °C (b).](image)

3.4. Adsorption experiment

The efficiency of the prepared and characterized LCFO nanoparticle as an adsorbent for removal of BP from liquid solutions was investigated using a batch equilibrium technique placing different amount of adsorbent in a glass bottle containing 10 ml of a dye solution at 50 mg/L concentrations. The adsorption studies were carried out for different pH values, contact time, catalyst dosage and dye solution concentrations and results are presented in the following sections.
3.4.1. Effect of pH

Solution pH is an important parameter that affects adsorption of dye molecules. The effect of the initial solution pH on the dye removal efficiency of BP by LCFO nanoparticles was evaluated at different pH values, ranging from 0.5 to 13, with a stirring time of 30 min. The initial concentrations of dye and adsorbent dosage were set at 50 mg/L and 0.01 g, respectively. The percentage of dye removal is defined as (2):

$$\text{Removal rate } % = \frac{C_0 - C(t)}{C_0} \times 100$$  \hspace{1cm} (2)

where $C_0$ and $C(t)$ are the initial concentration and concentration of BP at time $t$, respectively.

As shown in Fig. 6, the dye removal was much higher in acidic pH and decreased when the pH was increased from 3 to 13. Since the removal of BP increased to its maximum value at pH 1 (the removal of BP above 97% was achieved) the electrostatic attraction between the dye molecules (negatively charged) and LCFO surface (positively charged) might be the predominant adsorption mechanism [Al-Degs et al., 2008]. Therefore, to have the optimized condition to remove BP, acidic pH should be applied and pH 1 seems to lead to the best result; so this pH was selected to run further experiments.

![Fig. 6: Effect of initial pH of dye solution on removal of BP (LCFO dosage = 0.01 g, initial dye concentration = 50 mg/L, stirring time = 30 min).](image)

3.4.2. Effect of contact time and adsorbent dosage

To further assessing of dye removal, the effects of mixing time and adsorbent concentration on the removal of BP by LCFO nanoparticles were examined. Initial dye concentrations and pH of the solutions were fixed at 50 mg/L and 1, respectively, for all the batch experiments.

Results are shown in Fig. 7. As indicated, increasing of mixing time in different dosages of adsorbent led to decrease in the concentration of BP. This behavior was also observed when catalyst dosage increased from 0.005 to 0.03 g. This decreasing in the concentration is due to the adsorption of BP on LCFO nanoparticles and the greater number of adsorption sites for dye molecules made available at greater LCFO dosages (Erdem et al., 2005; Wang et al., 2008). The removal efficiency of BP at the initial dosage of 0.01 g, increased from 77% at the second minute of contact to 95% at time equals to 30 min by keeping constant stirring, however, with rising LCFO dosage to 0.03 g the percentage of removal obtained in the second minute of stirring was 88%, and the most percent of removal (98%) was attained when the stirring was continued till time equals to 15 min. The adsorbent dosage obtained in this study for complete removal of BP on to LCFO nanopowder is less than most of the reported values in the literatures for dye adsorption using other adsorbents (Moussavi and Mahmoudi, 2009; Song et al., 2008; Kong et al., 2009; Zhang et al., 2006).
3.4.3. Effect of dye concentration

The initial dye concentration is another important variable that can affect the adsorption process. The effect of initial BP concentration on dye removal efficiency by LCFO particles was studied by varying the initial dye concentration from 50 to 300 mg/L at pH 1, a catalyst dosage of 0.01 g and contact time of 30 min, as shown in Fig. 8. Results show that removal of textile dye BP decreases with increasing initial concentration. As it is obvious, the percentage removal of BP decreased from around 95% at a concentration of 50 mg/L to 50% when the concentration was increased to 300 mg/L. This behavior reveals the dependency of adsorption to initial concentration of BP.

3.5. Adsorption kinetic studies

To find the suitable chemical removal model for describing the experimental kinetic data, the obtained data were evaluated using pseudo-first and pseudo-second-order reaction rate models (Santos et al., 2008; Ho and McKay, 1999).

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

first-order equation: \[ \ln C(t) = \ln C_0 - k_1 t \] (3)

second-order equation: \[ \frac{1}{C(t)} = k_2 t + \frac{1}{C_0} \] (4)

where \( k_1 \) and \( k_2 \) are the first-order and second-order rate constant, respectively; \( C_0 \) stands for the initial BP concentration and \( C(t) \) is the concentration of BP at time \( t \). Higher value of \( R^2 \) were obtained for first-order (0.98) than for second-order (0.92) adsorption rate models, indicating that the adsorption rates of BP on to the LCFO nanoparticles can be more appropriately described using the first-order rate rather than second-order rate. The values of the rate constant, \( k_1 \) and \( k_2 \) are 0.055 and 0.014 (M\(^{-1}\) min\(^{-1}\)), respectively.
3.6. Adsorption isotherms studies

The equilibrium isotherm of a specific adsorbent represents its adsorptive characteristics and analysis of isotherm data is so important to predict the adsorption capacity of the adsorbent, which is one of the main parameters required for designing the adsorption processes (Afkhami and Moosavi, 2010). The amount of dye adsorbed onto LCFO nanoparticles has been calculated based on the following mass balance equation:

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

(5)

where \( q_e \) is equilibrium dye concentration on adsorbent (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, respectively, and \( m \) (g) is the mass of LCFO nanoparticles.

Various isotherm models, such as Langmuir, Freundlich, and Temkin were applied to describe the nonlinear equilibrium relationship between the solute adsorbed onto the adsorbent and that left in the solution. An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent. The Langmuir model equation, assuming monolayer adsorption on a homogeneous adsorbent surface, can be presented as follows (Langmuir, 1918):

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \]  

(6)

where the \( q_{\text{max}} \) (mg/g) is the surface concentration at monolayer coverage which illustrates the maximum value of \( q_e \) and it can be attained as \( C_e \) is increased. The values of \( q_{\text{max}} \) and \( K_L \) can be determined from the linear regression plot of \((C_e/q_e) \) versus \( C_e \).

The linearized form of the Freundlich isotherm is expressed as follows [Freundlich, 1906]:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(7)

where \( K_F \) and \( n \) are constants of the Freundlich equation. The constant \( K_F \) represents the capacity of the adsorbent for the adsorbate and \( n \) is related to the adsorption distribution. A linear regression plot of \( q_e \) versus \( \log C_e \) gives the \( K_F \) and \( n \) values.

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm is as following

\[ q_e = A + B \ln C_e \]  

(8)

where \( A \) and \( B \) are isotherm constants (Fu et al., 1994).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Temkin model</th>
</tr>
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<tbody>
<tr>
<td>La0.5Ca0.5FeO3</td>
<td>( q_{\text{max}} ) (mg g(^{-1}))</td>
<td>( b ) (L mg(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.074</td>
<td>0.991</td>
</tr>
</tbody>
</table>

The experimental results of this study were fitted to the aforementioned models. The calculated adsorption parameters and correlation coefficient (\( R^2 \)) for the three isotherm models by linear regression are listed in Table 1. The value of correlation coefficient (\( R^2 \)) for Langmuir isotherm is greater than that of the Freundlich and Temkin isotherm for the adsorption of investigated dye. This indicates that the adsorption of BP on LCFO nanoparticles is better described by the Langmuir model than the others and generally it has been found better suited for characterizing monolayer adsorption process onto the homogeneous adsorbent surface. The linearized form plot of the Langmuir isotherm is shown in Fig. 9.
4. CONCLUSION

In present study, a nanoparticle La$_{0.5}$Ca$_{0.5}$FeO$_3$ powder was produced and tested as a novel adsorbent for the removal of dye. A systematic study on the structural, morphological and adsorption properties of La$_{0.5}$Ca$_{0.5}$FeO$_3$ samples has been carried out by means of various analytical techniques. The effects of LCFO dosage, initial pH, contact time and initial dye concentration on the removal of BP was investigated through batch experiments. Results indicated that the synthesized powder could effectively remove high concentrations of dye in a short contact time. The optimum dosage, pH and contact time were obtained to be 0.01 g, pH 1 and 30 min, respectively. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of BP dye onto the LCFO as compared to other models.

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REFERENCES


Bansal NP, Zhong Z (2006). Combustion synthesis of Sm$_0.5$Sr$_0.5$CoO$_3$–x and La$_0.6$Sr$_0.4$CoO$_3$–x nanopowders for solid oxide fuel cell cathodes. J. Power Sources., 158: 148-153.


Chi QG, Li WL, Zhao Y, Fei WD (2010). Low temperature preparation and electric properties of highly (100)-oriented Pb$_0.8$La$_0.1$Ca$_0.1$Ti$_0.975$O$_3$ thin films prepared by a sol–gel route. J. Sol-gel Sci. Tech., 54: 286-291.


Lui S, Qian X, Xiaoj J (2007). Synthesis and characterization of La0.8Sr0.2CoO3.5Fe0.5O3±δ nanopowders by microwave assisted sol–gel route. J. Sol-gel Sci. Tech., 44: 187-193.


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