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Characterization and evaluation catalytic efficiency of La_{0.5}Ca_{0.5}NiO₃ nanopowders in removal of reactive blue 5 from aqueous solution

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ABSTRACT

In the present study, nanoparticles of perovskite-type $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ (LCNO) were fabricated by sol-gel method in the presence of nitrate-metal-ethylene glycol (EG) polymerized complex. A series of analytical techniques were used to characterize the crystallinity, morphology, specific surface area and grain size of $La_{0.5}Ca_{0.5}NiO_3$ powders. Thermal decomposition process of the complex precursor was examined by means of differential thermal analysis-thermal gravimetric analysis (DTA/TGA). X-ray diffraction (XRD) results showed that single perovskite phase has been completely formed after calcination at 750 °C. In addition, transmission electron microscopy (TEM) images revealed that the average size of the particles is approximately 10-32 nm in diameter. The surface morphology and composition of these nanopowders were also investigated using scanning tunneling microscopy (STM), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX). LCNO nanoparticles showed the excellent adsorption efficiency towards reactive blue 5 (RB5) as a reactive dye in aqueous solution. The adsorption studies were carried out at different pH values, dye concentrations, various adsorbent dosages and contact time in a batch experiments. The dye removal efficiency was found to be decreased with increasing in initial pH of dye solution, and LCNO exhibited good dye removal efficiency at acidic pH specially pH 2. Experimental results indicated that the adsorption kinetic data follow a pseudo-second-order rate for tested dye. The isotherm evaluations revealed that the Langmuir model attained better fits to the experimental equilibrium data than the Freundlich model. Finally, the photocatalytic degradation of RB5 using LCNO under solar light and UV irradiation at pH 2 was also investigated. The results showed that the nanoparticles cannot act as pure photocatalyst and the degradation of RB5 dye follows only an adsorption process.

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1. Introduction

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. Dyes from the effluent of textile, paper, printing, and leather industries are the major sources of water contamination. The presence of dyes in water reduces light penetration and hinders photosynthesis in aquatic plants [1]. Some dyes and their degradation products in surface water are reported to be highly carcinogenic [2]. It is, therefore, essential to treat the dye effluents prior to their discharge into the receiving water.

Dyes are organic compounds consisting of two main groups of compounds, chromophores (responsible for color of the dye) and auxochromes (responsible for intensity of the color) [3]. Dyes are classified according to the chemical structure and type of application. Based on chromophores, 20–30 different groups of dyes can be discerned, with azo, anthraquinone, phthalocyanine and triarylmethane accounting for the most important groups. Azo (around 70%) and anthraquinone (around 15%) compose the largest classes of dyes.

Many processes are employed to remove dye molecules from colored effluents; in general, treatment methods can be divided into three categories: (i) physical methods such as adsorption [4–6], and membrane filtration [7]; (ii) chemical methods such as ionic exchange [8], chemical oxidation [9,10], electrochemical degradation [11], and ozonation [12]; and (iii) biological degradation [13].

Adsorption techniques for wastewater treatment have become more popular in recent years because of their efficiency in the removal of pollutants which are stable in biological degradation process. Adsorption can produce high quality water while also being a process that is economically feasible [14].

The physical characteristics of the adsorbents, 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 adsorbent materials with diverse compositions, properties and functionalities.

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The family of perovskite-type oxides generally formulated as ABO_3 (A is a rare earth metal with large ionic radius or alkali earth metals; B is a transition metal with a small ionic radius) could be considered as an adsorbent/catalyst material for the removal of dyes [15,16].

Though, several articles have investigated the effectiveness of spinel-type oxides as catalysts for photodegradation and removal of water-soluble dyes [17–19], to our knowledge, the confirmation and optimization of the efficiency of the perovskite oxides catalysts and the degradation pathway for the removal of azo dyes from aqueous solution have received little attention in the literature.

This study has investigated the efficiency of perovskite-type oxide nanoparticles, $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ (LCNO), as an adsorbent for removal of azo dye, reactive blue 5 (RB5), from an aqueous solution. The effect of different variables including concentration of dye, different pH values, adsorbent doses and reaction time, for removal of RB5 on LCNO nanopowders has been evaluated and two kinetic models have also been analyzed. Furthermore, preparation of LCNO nanoparticles via sol–gel method and its characterization by different techniques such as DTA, TGA, XRD, STM, SEM-EDX and TEM have been reported.

2. Experimental

2.1. Reagents

 La_2O_3 (99.99% purity), CaCO_3 (99.99% purity), Ni(NO_3)_2.6H_2O (99.99% purity) were all obtained from Merck, Germany; citric acid (CA) (99.5% purity), ethylene glycol (EG) and nitric acid were purchased from Aldrich, USA. The commercial color index (CI) reactive dye (RB5, molecular weight = 774.16 g/mol) was generously provided by Arzoo Textile Mills, Faisalabad, Pakistan 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 of $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ nanopowder

 La_2O_3 and $CaCO_3$ weighed and dissolved in nitric acid (2 M) to form lanthanum nitrate and calcium nitrate. Then the aqueous solutions of metal nitrates with nominal atomic ratios La:Ca: Ni = 0.5:0.5:1 were mixed together in deionized water. Citric acid (CA) was proportionally added to the metal solution to have the same amounts of equivalents. The solution was concentrated by evaporation at approximately 50 °C with stirring for 1 h to convert



Fig. 1. Molecular structure of reactive blue 5 (RB5) dye.

it to stable (La, Ni)/CA complexes. Then ethylene glycol (EG) was added to this solution as a cross-linking agent. The solution while being stirred, was heated at approximately 75 °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 up to 110 °C and kept for 6 h in baking oven. The gel pieces were ground in an agate mortar to form fine powders. Finally, $La_{0.5}Ca_{0.5}NiO_{3-6}$ nanoparticles were obtained by thermal treatment of the precursors at two different temperatures 650 °C and 750 °C for 9 h in air. The annealing of the amorphous precursor allows removing most of the residual carbon and the hexagonal perovskite phase with the R-3m space group was obtained.

2.3. Characterization

Several techniques were employed to analyze and validate the synthesized powder. Thermal behavior (DTA and TGA) 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 650 °C and 750 °C XRD measurements were carried out in the region of $(2\theta = 20 \text{ to } 70^\circ)$ using CuK α radiation on a Rigaku D/MAX RB XRD diffractometer equipped with a curved graphite monochromator. The microstructure of powder was examined using LEO 912AB TEM under a working voltage of 120 kV, while the morphology and chemical analysis of the particles was investigated using SEM-EDX technique. The SEM of the type LEO 1450 VP (V = 30 kV) was equipped with an EDX spectrometer of the type Inca 400 (Oxford Instruments). The surface morphology was also studied using SS1 STM and all images were recorded in the constant-current mode at room temperature using a Remanium tip with a bias voltage of around 2 V in atmosphere. 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 (Agilent 8453 UV/VIS/NIR) was employed to monitor adsorption of dyes.

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 nanoparticle and contact time. A prepared solution of RB5 was distributed into different flasks (1 L capacity) and pH was adjusted with the help of the pH meter (Metrohm 620, Swiss 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 nanoparticles (catalyst dosage) 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 (50-250 mg/L), pH of solution (1-13), catalyst dosage (0.01, 0.02 and 0.03 g) and mixing time (1-36 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 nanoparticles was tested. After a preselected time of decolorization, samples were collected and absorbance of the solution at a λ_{max} equals to 599 nm (Agilent 8453) was measured to monitor the residual RB5 concentration.

2.5. Photocatalytic degradation experiment

The photocatalytic reaction for the degradation of 50 mg/L RB5 aqueous solution was carried out in a Pyrex glass vessel with constant magnetic stirring. A 300 W high-pressure mercury lamp with a

maximum emission at 365 nm was used for irradiation. The LCNO catalyst concentration in the RB5 aqueous solution was 0.02 g/10 mL. The absorption/degradation equilibrium of the suspensions was established under stirring at room temperature in a dark condition and the suspensions were then irradiated under the UV light. At given time intervals, about 5 mL aliquots were sampled and centrifuged to remove the catalyst particles. Then the centrifuged solution was analyzed by the UV-vis method using Agilent 8453 spectrometer. The concentration of RB5 in the samples was calculated using the calibration curve, and temperature of all the experiments was set to 25 °C by circulator.

3. Results and discussion

3.1. Thermal study

Fig. 2 shows DTA curve (a) and TGA/DTG curves (b) of the thermal decomposition process of LCNO xerogel obtained at a heating rate of 5 °C/min in the air from room temperature to 1000 °C. The total weight loss of the xerogel was approximately 72% and the decomposition process can be divided into three distinct steps. The first weight loss occurs during the heating step from 50 °C to 250 °C, which is due to the dehydration and decomposition of nitrates. In this area, DTA curve shows two endothermic peaks at 120 °C and 240 °C accompanied by about 22% weight loss in the TG. A weight loss of about 45% is observed from 240 °C to about 580 °C in the TG curve, which corresponds to the oxidizing combustion of the organic compounds such as citric acid (forming carbonate and oxide with cation). The DTA curve reveals a strong and sharp exothermic peak with a vertex at 520 °C which is likely due to the oxidation or combustion of the



Fig. 2. (a) DTA and (b) TGA/DTG curves of the xerogel precursors obtained by the ethylene glycol-metal nitrate polymerized complex.

chelate complex which happen along with forming the metal oxides. Between 580 °C and 735 °C, the DTA curve shows an exothermic peak at 700 °C, accompanied by a slight continued weight loss (5%) may be attributed to the decomposition or solid state reaction of the carbonate intermediates [20]. No obvious change was observed above 735 °C. Hence, it is plausible to conclude that the optimum calcination temperature is about 750 °C.

3.2. X-ray structural analysis

XRD patterns of the synthesized powder which calcined at two different temperatures 650 °C and 750 °C for 9 h (heating rate: 3 °C/ min) are shown in Fig. 3. XRD results reveal the existence of a perovskite-type phase for sol-gel method at both temperatures. When the precursor was calcined at 650 °C for 9 h, several sharp peaks were observed attributed to the perovskite $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ by comparison with standard XRD spectra. As shown in Fig. 3, diffraction intensities of the pervoskite phase increased when the calcination temperature was increased from 650 °C to 750 °C, indicating that the $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ crystallinity improves by shifting to higher calcination temperature. The diffraction peaks at 2θ angels appeared in the order of 24.41°, 33.24°, 41.16°, 47.64°, 54.2°, 58.44°, and 69.76° can be assigned to scattering from the (1 0 1), (1 1 0), (1 1 4), (2 0 0), (1 1 6), (0 0 8) and (2 2 0) planes of the $La_{0.5}Ca_{0.5}NiO_{3-\delta}$ perovskite type crystal lattice, respectively. XRD data shows La_{0.5}Ca_{0.5}-NiO_{3- δ} crystallizes in a hexagonal phase with a = b = 4.866. c = 12.652 and space group R-3m(166). The crystallite sizes were calculated using XRD peak broadening of the (110) peak using the Scherer's formula:

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\,\cos\theta_{hkl}}\tag{1}$$

where D_{hkl} (nm) is the particle size perpendicular to the normal line of (hkl) plane, β_{hkl} is the full width at half maximum, θ_{hkl} (Rad) is the Bragg angle of (hkl) peak, and λ (nm) is the wavelength of Xray. The calculated particles size of LCNO nanoparticles calcinated at 750 °C was about 35 nm.



Fig. 3. XRD patterns of samples of the LCNO nanoparticles calcinated at two different temperatures of 650 $^\circ\text{C}$ and 750 $^\circ\text{C}.$

3.3. Microscopic and BET analyses

The surface morphology and size of the particles were investigated using microscopic methods.

The size of perovskite particles was evaluated and conformed by TEM. Fig. 4 shows representative TEM image of LCNO. The image of the sample which calcined at 750 °C consists of particles ranging in size of about 15 to 40 nm. It is clear that the nanoparticle perovskites consist of agglomerates smaller than 70 nm. As the TEM images show, the morphology of nanoparticles is homogeneous [21]. It can be seen that the obtained value (around 30 nm) is in agreement with the result achieved from XRD measurement.

Scanning electron microscopy (SEM) of perovskite oxide (LCNO) prepared by the sol-gel method and calcined at 750 °C is shown in Fig. 5. Based on the SEM images, porosity of the surface is evident and it seems that the particles have not grown with uniform size. The particles size of LCNO that were propagated on the surface seems to be in the range of 50–200 nm. The surface looks rough and nearly fully covered with the particles grown on it. Further, it can also be seen from the SEM result that in addition to the larger particles (50–200 nm), the surface contains also rather smaller particles as down to 20 nm or less. However, appearance of bigger particles on the surface looks to be dominant. The aggregation of the smaller particles (in the nm range) may result in bigger LCNO particles on the surface.

Fig. 6 shows the scanning tunneling microscopy (STM) images $(500 \text{ nm} \times 500 \text{ nm})$ of LCNO nanoparticles which can be used to determine the particles size and height. In Fig. 6a, the bright spots are higher than the dark ones and particles distribution on the surface is mapped obviously. Three particles were selected for quantitative measurements and results showed that their average size and height were obtained around 25 nm and 5 nm, respectively (Fig. 6b).

The EDX analysis was performed to further confirmation of the obtained product composition. Fig. 7 shows EDX spectrum which indicates the existence of La, Ca, Ni and O elements in this nanoparticle.

The specific surface area of the catalyst was measured by means of conventional BET method. Results showed that the average specific surface area of LCNO nanoparticle was 60.91 m²/g. This value may be attributed to the enhanced crystalline grain size calcined at 750 °C.



Fig. 4. TEM micrograph of the LCNO nanoparticles.



Fig. 5. SEM images of LCNO nanoparticles.

3.4. Adsorption of dyestuff on the LCNO nanoparticles surface

The efficiency of the prepared and characterized LCNO nanoparticles as an adsorbent for removal of RB5 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 RB5 by LCNO particles was evaluated at different pH values, ranging from 1 to 13, with a stirring time of 10 min. The initial concentrations of dye and adsorbent dosage were set at 50 mg/L and 0.02 g, respectively. The percentage of dye removal is defined as:

Removal rate % =
$$\frac{C_o - C}{C_o} \times 100$$
 (2)

where C_o and C are the initial and residual concentrations of RB5, respectively.

As shown in Fig. 8, the dye removal was much higher in acidic pH (pH 1 and 2), and decreased when the pH was increased from 3 to 13. Since the removal of RB5 increased to its maximum value at pH 2 (the removal of RB5 above 91% was achieved), probably the electrostatic attraction between the dye molecules (negatively charged) and LCNO surface (positively charged) might be the predominant adsorption mechanism [22]. Therefore, to have the optimized condition to

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M. Yazdanbakhsh et al. / Desalination 281 (2011) 388-395



Fig. 6. (a) STM images of LCNO for the area of $500 \text{ nm} \times 500 \text{ nm}$. (b) Height profile along the white line.

remove RB5, acidic pH should be applied and pH 2 seems to lead to the best result; so this pH was selected to run further experiments.

3.4.2. Effect of contact time and adsorbent dosage

To further assessing of dye removal, the effects of contact time and adsorbent concentration on the removal of RB5 by LCNO nanoparticles were examined. For all batch experiments, Initial dye concentrations and solution pH were fixed as 50 mg/L and 2, respectively.

Results are shown in Fig. 9. As indicated, increasing of contact time in different dosages of adsorbent led to decreasing in the residual concentration of RB5. This behavior was also observed when catalyst dosage increased from 0.01 to 0.03 g. This decreasing in the



Fig. 7. Energy dispersive X-ray (EDX) spectrum of the LCNO nanoparticles.

392

M. Yazdanbakhsh et al. / Desalination 281 (2011) 388-395



Fig. 8. Effect of initial pH of dye solution on removal of RB5 (LCNO dosage = 0.02 g, initial dye concentration = 50 mg/L, stirring time = 10 min).

concentration is due to the adsorption of RB5 on LCNO nanoparticles and the greater number of adsorption sites for dye molecules are available at greater LCNO dosages [23,24]. The removal efficiency of RB5 at the initial dosage of 0.01 g, increased from 60% at the second minute of contact to 92% at time equals to 36 min by keeping constant stirring, however, with increasing LCNO dosage to 0.03 g, obtained removal efficiency in the second minute of stirring was 96%, and complete removal (100%) was attained after 10 min. The catalyst dosage obtained in this study for complete removal of RB5 on to LCNO nanoparticles is less than most of the reported values in the literatures for dye removal using other adsorbents [25–28].

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 RB5 concentration on dye removal efficiency by LCNO particles was studied by varying the initial dye concentration from 50 to 250 mg/L at pH 2, a catalyst dosage of 0.03 g and contact time of 10 min, as shown in Fig. 10. Results show that removal of textile dye RB5 decreases with increasing initial concentration. As it is obvious, the percentage removal of RB5 decreased from around 100% at a concentration of 50 mg/L to 42% when the concentration was increased to 250 mg/L. This behavior reveals the dependency of adsorption to initial concentration of RB5.

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 [29,30].



Fig. 9. Effect of stirring time on removal of RB5 in different doses (♦) 0.01 g, (■) 0.02 g, (▲) 0.03 g of LCNO (initial dye concentration = 50 mg/L, initial pH 2).



Fig. 10. Effect of initial dye concentration on removal of RB5 (LCNO dosage = 0.03 g, initial pH 2, stirring time = 10 min).

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

Pseudo – first – orderequation : $lnC(t) = lnC_o - k_1 t$ (3)

Pseudo – second – orderequation :
$$\frac{1}{C(t)} = k_2 t + \frac{1}{C_o}$$
 (4)

where k_1 and k_2 are the first-order and second-order rate constant, respectively; C_o stands for the initial RB5 concentration and C(t) is the concentration of RB5 at time t. Higher value of \mathbb{R}^2 were obtained for pseudo-second-order (0.99) than for pseudo-first-order (0.91) adsorption rate models, indicating that the adsorption rates of RB5 on to the LCNO nanoparticles can be more appropriately described using the pseudo-second-order rate rather than pseudo-first-order rate.

The values of the rate constant, k_1 and k_2 are 0.0437 and 0.0054 $(M^{-1} min^{-1})$, 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 [31].

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

$$q_e = \frac{V(C_o - C_e)}{m} \tag{5}$$

where q_e is equilibrium dye concentration on adsorbent (mg/g), *V* is the volume of the dye solution (L), C_o and C_e (mg/L) are the initial and equilibrium dye concentrations, respectively, and *m* (g) is the mass of LCNO nanoparticles. Fig. 11 shows the changes of q_e versus C_e which describes the interactive behavior between adsorbate and adsorbent.

Various isotherm models, such as Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich are used to describe the nonlinear equilibrium relationship between the solute adsorbed onto the adsorbent and that left in the solution [6,18]. The more common models used to investigate the adsorption isotherm are Langmuir and Freundlich. The Langmuir model equation, assuming monolayer adsorption on a homogeneous adsorbent surface, can be presented as follows [32]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

M. Yazdanbakhsh et al. / Desalination 281 (2011) 388-395



Fig. 11. Plots of q_e vs. C_e for removal of RB5 (LCNO dosage = 0.03 g, initial dye concentration, 50, 100, 150, 200 and 250 mg/L, volume of dye solution = 10 mL, stirring time = 10 min, initial pH 2).

where the q_{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_{max} and b can be determined from the linear regression plot of (C_e/q_e) versus C_e . The parameters of the Langmuir equation in this work, namely q_{max} and b are 36.23 (mg/ g) and 0.16 L/mg, respectively. The linearized form of the Freundlich isotherm is expressed as follows [33]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

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 $log q_e$ versus $log C_e$ gives the K_F and n values that leads to obtained values 16.21 and 36.76, respectively.

The experimental results of this study were fitted to the aforementioned models. The linearized form plot of the Langmuir isotherm is shown in Fig. 12. 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 LCNO nanoparticles is better described by the Langmuir model than the Freundlich model and generally it has been found better suited for characterizing monolayer adsorption process onto the homogeneous adsorbent surface.



Fig. 12. Langmuir isotherm plot of RB5 adsorption onto LCNO nanoparticles: LCNO dosage = 0.03 g, initial pH 2, stirring time = 10 min, initial dye concentration = 50, 100, 150, 200, 250 mg/L.

3.7. Photocatalytic activity measurement

To confirm the photocatalytic activity of LCNO for the degradation of RB5 under light, a series of comparative experiments were carried out; firstly, in the presence of LCNO catalyst and UV irradiation; secondly, in the presence of LCNO catalyst under solar light; thirdly, in the presence of LCNO catalyst in the dark and finally, in the absence of LCNO catalyst under UV irradiation. The experiments were evaluated by the photocatalytic degradation of 50 mg/L concentration RB5 and 0.02 g catalyst dosage. Since some dyes are degraded by direct UV irradiation, it should be examined to what extent RB5 is photolyzed if no catalyst was used [34]. The plot of experimentally derived values of degradation versus time for LCNO nanoparticles is depicted in Fig. 13. The degradation rates of RB5 in the absence of the catalyst under UV irradiation were very low which was only up to 11% in 18 min. In the presence of LCNO in the dark, the dye concentration decreases quickly at the starting point (66% at 2 min), and then reaches a saturation value which is due to the adsorption of dye molecule on the catalyst surface. Finally, as can be seen, the simultaneous utilization of UV irradiation or solar light with LCNO nanoparticles could increase the removal rate of RB5, as 71% and 82% of RB5 is removed under UV irradiation and solar light, respectively, within 2 min. It suggests that this sample exhibits higher catalytic performance under solar light in comparison to UV irradiation. Hence, LCNO nanoparticles cannot act as photocatalyst for the degradation of RB5 in an aqueous solution. The degradation follows merely an adsorption process, though UV and solar light somewhat are effective in dye removal process.

4. Conclusions

In summary, nanocrystalline $La_{0.5}Ca_{0.5}NiO_3$ powders were synthesized by the sol–gel method using citric acid and ethylene glycol and subsequent calcination process. A systematic study on the structural, morphological and removal dye efficiency of LCNO nanoparticles was carried out by means of various analytical techniques. XRD and microscopic analysis reveal that the LCNO nanoparticles, prepared by calcinating the gel precursor at 750 °C for 9 h, have good crystallinity with hexagonal perovskite structure. In addition, the present investigation has shown that the synthesized LCNO oxide can be a promising surface material to remove azo dye from water over a wide range of dye concentrations. The processing parameters such as dosage of catalyst, contact time, initial dye concentration and pH value can all affect the adsorption process significantly. The results show that the prepared powders could effectively remove high concentrations of RB5 dye molecules. Also the percentage of removal obtained in the



Fig. 13. The degradation of RB5 at different irradiation time for: (\blacksquare) solar light with LCNO nanocatalyst; (\triangle) UV irradiation with LCNO nanocatalyst; (\triangle) UV on nanocatalyst; (\triangle) UV irradiation with LCNO nanocatalyst; (\triangle) LCNO nanocatalyst in dark condition (LCNO dosage = 0.02 g, initial pH 2, initial dye concentration = 50 mg/L).

M. Yazdanbakhsh et al. / Desalination 281 (2011) 388-395

10th minute of stirring was 100% using 0.03 g catalyst at pH 2. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of RB5 dye on to the LCNO as compared to the Freundlich model. The kinetic data for the removal of RB5 tend to follow pseudo-second-order kinetic equation. In general, experimental results of the photocatalytic activity reveal that dye removal can be achieved by the adsorption process and LCNO nanocatalyst indicates favorable adsorption behavior in a dark condition for removal RB5 dye. However, it should be emphasized that catalytic performance under solar light leads to better results than UV irradiation and in a dark ambient.

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