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Efficient and sustainable adsorbents with perovskite structure for removal of pollutants from aqueous media

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Abstract

Mixed oxides with perovskite structure are materials which has recently been highlighted as promising adsorbents for removing pollutants from aqueous media. Factors such as metal selection and doping significantly influence achieving the desired phase and application of materials. Materials like LF-9C ($LaFeO_3$), L3C7F-9C ($La_{0.3}Ca_{0.7}FeO_3$) and L7C3F-9C ($La_{0.7}Ca_{0.3}FeO_3$) were synthesized using a modified proteic method with collagen as a complexing agent, followed by heat treatment at 350 °C and calcination at 900 °C. The materials were characterized by X-ray diffraction, determination of the specific surface area and of the point of zero charge. The results of the adsorption studies show that the materials are efficient adsorbents for the removal of a blue turquoise dye in aqueous media, with efficiency ranging between 36 and 98%, with kinetic fitting with for Pseudo Second Order (PSO) model. The materials were applied in reuse studies and maintained the efficiencies, highlighting the better performance presented by the material without doping. Tested with wastewater from a textile factory, the efficiency (Er) of adsorbents for removal the blue dye present were: LF-9C (Er =12%) L3C7F-9C (Er =13%), L7C3F-9C (Er = 11%), and compared with the silica gel (Er = 11%) and activated carbon (Er = 25%) materials, but only the mixed oxides prepared showed outstanding potential for reuse with maintenance of efficiency, indicating that they are very promising materials.

Keywords: Perovskite; $LaFeO_3$; adsorption of contaminants; materials reuse.

1. Introduction

In the industrial sector, managing waste and contaminants, particularly from textile dyes, is essential due to potential environmental and health risks [1-2]. Turquoise blue compound, with molecular formula $C_{32}H_{16}CuN_8Na_2O_6S_2$, is often used as a dye in the textile industry, and it is classified as anionic and its chromophore group is phthalocyanine. It is non-biodegradable, highly toxic, and poses environmental and potential carcinogenic risks [3-4]. Various studies concentrate on efficient, cost-effective, and environmentally responsible techniques for treating textile effluents. Among several processes for removing pollutants from aqueous media is the adsorption process, which can be highly efficient for treating different types of contaminants from aqueous media [3-5].

The mixed oxides show promise in diverse applications like catalysis, electrocatalysis, and more recently in adsorption in aqueous media [4,6-7]. The perovskite structure combines metallic and non-metallic elements [4-8], where its ABO_3 structure features A sites occupied by large cations (alkali metals, alkaline earth metals, or lanthanides), B sites by smaller metal cations (*d*-block transition elements), and oxygen [8].

The efficiency of a material of oxide mixed type with perovskite structure for a specific application may be related to the metal selection and doping, but its use as an adsorbent requires also that the material is not only efficient but also that it can be recovered, regenerated and reused in several cycles so that secondary pollution is not generated after the adsorption process.

Based on the above, mixed oxides with perovskite structure were synthesized to studying them as potential adsorbents of environmental contaminants, including a possible reuse of the materials prepared in a new process, producing efficient and sustainable adsorbents.

Experimental

For the synthesis process were used the reactants: $Fe(NO_3)_3 \cdot 9H_2O$, $La(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ and after the procedure, the material was pre-calcined at 350°C for 2 hours, followed by calcination at 900°C for 2 hours. The synthesis procedure was based on previous research by the group [4, 6]. The resulting powders were named LF-9C, L3C7F-9C and L7C3F-9C.

The crystalline phases of the materials were analyzed using a Panalytical EMPYREAN diffractometer with CuKα (λ = 1.540562 Å), scanning from 10° to 60° (2θ) at a rate of $5°min^{-1}$. The crystallite size determined via the Scherrer equation based on the three main peaks of the perovskite phase. Specific surface area was determined by the BET method using Quantachrome NOVA 1200e equipment. The zero charge point (ZCP) was determined using an equilibrium method in a batch system, following adapted and previous methodologies [4,6]. The adsorption studies were conducted in a Dubnoff bath with Tecnal stirring and heating control, with a temperature of 30°C using erlenmeyer flasks containing 20 mL of the turquoise blue (TB) solution at natural pH (at 30 ppm) and 20 mg of the adsorbent material and the adsorbent was previously dried at 60 °C for 30 minutes. The systems were subjected to magnetic stirring during contact times from 10 to 150 minutes. At the end of the time, the solution was subjected to the centrifugation process for 8 minutes and 4000 rpm. The supernatant solution was analyzed by Shimadzu UV-Vis absorption spectroscopy, model UV-1800. And the procedure was repeated changing the temperatures to 40 and 50 °C. The entire study was carried out in triplicate.

The turquoise blue removal efficiency of the water and the amount of adsorbed turquoise blue was calculated using the equations related in [4,6]. The kinetic models applied were pseudo first-order, pseudo second-order, and variable constants analyze experimental data.

The adsorbents prepared were also were applied in tests using textile effluent collected from a textile industry located in Sergipe/Brazil. The tests were carried out under the same conditions as the kinetic study presented previously, but at temperature of 30°C, time 150 minutes and using also commercial adsorbents, such as active carbon (CA) and silica gel (SG).

The adsorption study using adsorbents recovered was conducted using 20 mL of the turquoise blue solution (at 30 ppm), 30°C, time of 150 minutes and in triplicate. The adsorbent reuse study was developed using the recovered masses of the adsorbent used in the adsorption test related previously. The mass of adsorbent recovered after cycle 0 of adsorption tests (using virgin adsorbent) is subjected to calcination. This regenerated adsorbent is subjected to a new solution of the contaminant, producing test cycle 1. This procedure is repeated two more times.

Similar study was made using textile effluents.

Results and Discussion

Figure 1 shows X-ray diffractograms of the calcined materials LF-9C, L7C3F-9C and L3C7F-9C. The materials display peaks similar to standard chart ICSD-7794, with a prominent peak at 2θ = 32.21° attributed to the $LaFeO_3$ phase. Additional peaks associated with this phase are evident at 22.66°, 39.76°, 46.23°, and 57.45°, consistent with literature [9]. Peaks corresponding to the Fe_2O_3 phase (ICSD-7797) are also observed at 2θ = 35.60° for L7C3F-9C and at 2θ = 24.00° and 33.34° for L3C7F-9C.

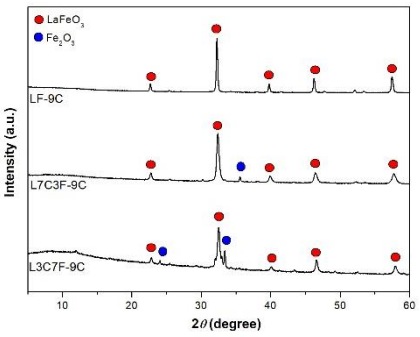

Fig 1. X-ray diffraction pattern of the materials.

Table 1 shows the results of the crystallite size (D), specific surface area (SSA), pH at point of zero charge (pHpzc) of materials. Crystallite sizes ranged from 20 to 50 nm, and are in accordance with the literature. The pHpzc can be useful in adsorption studies in the liquid phase, as it provides indications of conditions that could facilitate the interaction between adsorbate-adsorbent. The pH at the point of zero charge is 3.7 for LF-9C, 6.3 for L7C3F-9C and 7.3 for L3C7F-9C. Below these values, the adsorption of anionic

compounds is favored, as in reported [4]. The presence of calcium in the composition of adsorbent typically increases the pHpzc, a characteristic seen in mixed oxides containing this metal in their structure [10]. This pH increase may result from calcium partly substituting lanthanum, creating anionic sites within the structure. Specific surface area (SSA) measurements were 12 $m^2\ g^{-1}$ for LF-9C, 26 $m^2\ g^{-1}$ for L3C7F-9C and 19 $m^2\ g^{-1}$ for L7C3F-9C. The area values of these oxides are low due to the high temperatures involved in synthesis and calcination, but a slightly higher area value than typically reported in the literature for materials with these structures [4,6,10].

Table 1. Specific surface area, point of zero charge and crystallite size of materials.

Adsorbent	SSA (m^2g^{-1})	pHpzc	Crystallite size (nm)
L3C7F-9C	26	7.3	27
L7C3F-9C	19	6.6	20
LF-9C	12	3.7	50

Table 2 shows that the three adsorbent materials were efficient in removing TB compound from the aqueous medium, with efficiency values ranging from 36 to 98%. The results indicate that the highest removal efficiency values are found in materials without doping. Temperature variations had a subtle impact on adsorption of TB compound on the adsorbents. An increase in temperature from 30 °C to 40 °C practically does not affect the efficiency of the adsorbents to remove the TB compound from the medium, however an increase from 40 °C to 50°C generally produces a small decrease in efficiency.

Table 2. Removal efficiency (E%) of TB and adsorbed quantity (q) at different temperatures test.

Adsorbent	30°C		40°C		50°C	
	E (%)	q (mg/g)	E (%)	q (mg/g)	E (%)	q (mg/g)
L3C7F-9	36	11	35	11	31	9
L7C3F-9	46	14	47	14	38	12
LF-9C	98	29	98	29	96	29

The results show that the type and amount of metal that makes up site A of the structure significantly influences the adsorption capacity of TB, as the material ($LaFeO_3$) with the lowest SSA and pHpzc and largest crystallite size was the one with very high Er, close to 100%.

The kinetic study was applied using pseudo first order (PFO), pseudo second order (PSO), and variable constant (VC) models. The R^2 values were close to 1 for all models, indicating their effectiveness in the test study. However, the experimental data exhibited the best fit with the pseudo-second-order model, Table 3.

Table 3. Parameters obtained from the PSO model for adsorption of TB using the adsorbent materials.

Adsorbent	k (min^{-1})	q_2 (mg/g)	R^2	Chi^2
L3C7F-9C	0.00764	10.71	0.9231	0.92906
L7C3F-9C	0.00128	17.07	0.9287	1.70692
LF-9C	0.00402	30.19	0.9841	1.5576

The study also investigated removal efficiency (E%) of TB compound during the reuse of the materials, employing calcination for recovery and regeneration of the adsorbent and the results is in Figure 2. Results showed excelent behavior over all reuse cycles studied, with efficiency values practically constant, although with median values for the adsorbents L3C7F-9C and L7C3F-9C. Therefore, there is a possibility that the TB compound used has degraded.

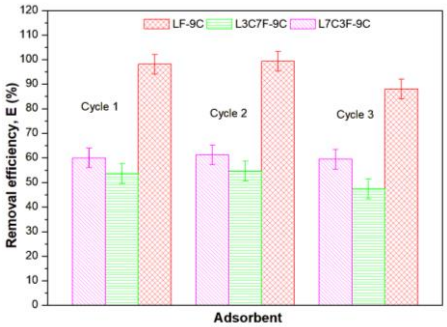

Fig. 2. TB removal efficiency during reuse cycles of the adsorbent materials.

The adsorbents synthesized alongside commercially used active carbon (CA) and silica gel (SG), were assessed for removing a textile dye from industrial effluent and the results is in Figure 3. LF-9C, L3C7F-9C and L7C3F-9C showed removal efficiencies of 12%, 13% and 11% respectively, similar to SG (11%) but lower than CA (25%).

It is worth noting that the pH of the solution collected in the textile effluent was 7.0, which is not the most favorable pH to obtain better results with adsorbents. Despite having lower values than commercial ones, the results are promising as there is the possibility of reusing the adsorbents.

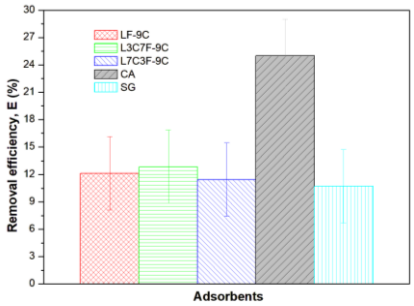

Fig. 3. Efficiency of removing dye from textile effluent using LF-9C, L3C7F-9C and L7C3F-9C and commercial (CA and SG) adsorbents.

Despite their lower efficiencies, the potential for reusing LF-9C, L3C7F-9C and L7C3F-9C is highlighted (Figure 4) and the cycles for both synthesized and commercial adsorbents, revealed a decrease in efficiency with each cycle. SG's efficiency notably decreased after the first cycle, while CA degradation during calcination rendered it unable for study.

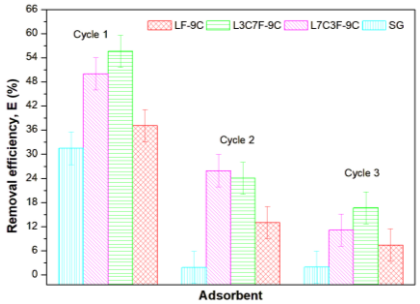

Fig. 4. Efficiency of removing dye from textile effluent during reuse cycles of adsorbent materials.

Conclusion

Mixed oxides of $LaFeO_3$, $La_{0.7}Ca_{0.3}FeO_3$ and $La_{0.3}Ca_{0.7}FeO_3$ with a perovskite structure were synthesized with success using the methodology used. The specific surface area and zero charge point values of the calcined materials ranged from 3.7 to 7.3 and the SSA ranged from 12 to 26 $m^2\ g^{-1}$. The materials obtained proved to be effective in Turquoise Blue removal studies from the water, with efficiency values ranging between 36% and 98%, values that are affected by the type and amount of metal in site A of the structure. The synthesized materials showed excellent results in the cycle reuse study, highlighting the $LaFeO_3$ material (E_R > 95%) that maintained the TB removal efficiency during all cycles. They are efficient and sustainable materials to remove contaminants from the synthetic solution and industrial effluent, because are regenerate and reuse.

Acknowledgements

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