LaMnO₃/ZnO/NGP composite: synthesis, characterization and its application for wastewater treatment

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Abstract. A series of LaMnO₃/ZnO/NGP samples was successfully synthesized using co-precipitation method in 3 weight percentage of nanographene platelets (NGP) on LaMnO₃/ZnO (3, 5, 10 wt.%). The structure of the sample was studied by X-ray diffraction (XRD) and Raman spectroscopy. The morphology and element structure of the sample was studied by Transmission electron microscopy (TEM) and Energy dispersive x-ray (EDX) spectroscopy, respectively. The thermal stability of the sample was characterized by thermogravimetric analysis (TGA). The XRD pattern confirmed the following structures: orthorhombic for LaMnO₃ nanoparticles, hexagonal wurzite for ZnO nanoparticles and graphitic like for NGP. The samples were tested for methylene blue (MB) removal and they show successful results in wastewater treatment through the adsorption test. The removal of MB was investigated by changing experimental variables such as the LaMnO₃/ZnO/NGP dosage, the weight percentage of NGP on LaMnO₃/ZnO and initial MB concentration. The experimental analysis of adsorption kinetics was best fit using pseudo second-order and Langmuir kinetic model. The increasing weight ratio of NGP shows higher adsorption of MB. Among the three different synthesized weight ratio of NGP in LaMnO₃/ZnO (3, 5, 10 wt.%), 10 wt.% of NGP on LaMnO₃/ZnO shows the maximum adsorption capacity than others.

1. Introduction

Dyes that are usually used in textile industries to color cotton, polyamide fibers and wooden are discharged into the environment without any treatment could cause health hazards to flora and fauna as well as to human [1–3]. Different strategies have been put in place to address the toxicity of these organic dyes by processing contaminated effluents. Methylene blue (MB) is a well-known dye and common strategies to proceed it are: adsorption, coagulation, sedimentation, and ion flotation [4].

Metal and metal oxide nanomaterials have been widely found to be excellent adsorbents for environmental remediation [5–6]. Many studies have been devoted to the use of metal and metal oxide alone or as a composite system (such as TiO, ZnO, NiO, Fe₂O₃, SnO₂, CuO, ZnO/TiO₂, ZnO/SnO₂, etc.) in the removal of methylene blue from wastewater. Oxide zinc (ZnO) is earth abundant making it of low cost, in addition to its chemical properties, this material is a good choice for mass scale applications [7]. ZnO nanoparticles (ZnO NPs) have been reported to have applications for the removal of organic pollutants. Khoshhesab et al. [8] and Farrokhi et al. [9] determined for ZnO NPs a removal capacity of 27.6 and 22.1 mg g⁻¹ for reactive black 2 and 5, respectively. Nanographene platelet (NGP) is a multilayer graphene that has become an interesting carbon-based materials as an adsorbent because of its high adsorption capacity. We still did not find an experimental satisfactory adsorption using LaMnO₃ nanoparticles, this material being a p-type semiconductor which is known as a good catalyst in the visible light spectra. This research evaluates LaMnO₃/ZnO/NGP as a composite
material for the removal of aqueous methylene blue. This research includes the effect of dosage; weight ratio of NGP; initial MB concentration in the adsorption kinetics of MB.

2. Experimental details

2.1. Chemicals
All the chemicals were of analytical grade and were used without further purification. For the co-precipitation synthesis the following chemicals and reagents were used: lanthanum (III) chloride hexahydrate (LaCl\textsubscript{3}·6H\textsubscript{2}O, Merck, 99%), manganese (II) chloride tetrahydrate (MnCl\textsubscript{2}·4H\textsubscript{2}O, Merck, 99%), sodium hydroxide (NaOH, Merck, 99%), zinc sulfate heptahydrate (ZnSO\textsubscript{4}·7H\textsubscript{2}O), and nanoplatelets.

2.2. Catalyst preparation
In a previous publication of ours [10], the co-precipitation method to synthesize LaMnO\textsubscript{3} nanoparticles was discussed. We have employed the same method to make LaMnO\textsubscript{3}/ZnO/LaMnO\textsubscript{3} nanocomposites. Two 0.00125 moles in 31 mL of water solutions of ZnSO\textsubscript{4}·7H\textsubscript{2}O and LaMnO\textsubscript{3} (solution A and B, respectively) were made. A 0.0025 moles in 62 mL of water solution of NaOH was added drop wise to adjust the pH of the solution A in a magnetically stirrer set up at 80 °C. The solution B was added to the pH adjusted solution A at stirred at 80 °C for a period of time of 2 h. The precipitate was collected by centrifuging the solution, and it was washed repeatedly by miliQ water and ethanol. The LaMnO\textsubscript{3}/ZnO nanocomposite (the precipitate) was dried under vacuum at 120°C.

LaMnO\textsubscript{3}/ZnO/NGP was synthesized by keeping a constant LaMnO\textsubscript{3}/ZnO molar ratio of 1:0.5. LaMnO\textsubscript{3}/ZnO was dispersed on the surface of NGP by the co-precipitation method. A colloidal solution of nanoplatelets, miliQ water and ethanol was made by dissolving it in 80 mL water and 40 mL ethanol. This colloidal solution was sonicated for 2 h. The next step was to keep the colloid at 120 °C for 3 h to bind the LaMnO\textsubscript{3}/ZnO nanocomposite on nanoplatelets sheets. The final composite was separated from the colloid by centrifuge and 12 h drying in vacuum. Different NGPs by weight percentage in the LaMnO\textsubscript{3}/ZnO/NGP nanocomposite were synthesized.

2.3. Characterization
A Rigaku miniflex 600 X-ray Diffraction (XRD) instrument with a monochromatic beam Cu-K\textsubscript{α} (\(\lambda = 1.54060 \text{ Å}\) was operated in 40 kV and 20 mA to determine the diffraction patterns of the samples. The FEI Tecnai G2 SuperTwin Transmission Electron Microscopy (TEM) instrument with morphology and elemental testing capacity was employed for further characterisation. A Rigaku Thermo Plus EVO2 TG-8121 Thermogravimetric analysis (TGA) instrument was used for thermal gravimetric analysis of the samples with alumina as the reference and Raman Spectroscopy to identify the presence of graphene in nanocomposites.

2.4. Adsorption experiments
A methylene blue (i.e. dye) solution with a concentration of 20 mg/L was prepared by mixing the dye with miliQ water. This solution was pH adjusted with NaOH, LaMnO\textsubscript{3}/ZnO/NGP samples (i.e. removal agent) of different NGP concentration (3, 5, 10 wt.%) were added into the MB solution to conduct kinetic analysis of MB adsorption. Solutions of different MB initial concentration were tested to determine optimal adsorption efficiencies. To determine the MB concentration as a function of time, conductivity of MB was employed to determine the concentration of MB in the solution after having performed a MB concentration vs UV adsorption calibration curve.

\[ q_e = \frac{(c_0 - c_f) v}{w} \]

where \( q_e \) : equilibrium concentration of dye in the adsorbent (mg/g); \( c_0 \) and \( c_f \) are the initial and equilibrium concentration of the MB solutions (mg/L), respectively. \( v \) is the volume of MB solution (L); and \( w \) is the weight of the removal agent used in this adsorption test.

3. Results and discussion
Figure 1 shows the XRD spectra of the LaMnO\textsubscript{3}/ZnO/NGP samples where the NGP concentration was varied. The peaks at 20 of 22.13°, 22.97°, 25.07°, 31.09°, 32.22°, 33.21°, 38.95°, 40.06°, 45.41°,
Table 1. Lattice parameters of the LaMnO₃, LaMnO₃/ZnO and LaMnO₃/ZnO/NGP composites

| Samples            | Lattice parameter LaMnO₃ | ZnO | <D> LaMnO₃ (nm) | <D> ZnO (nm) |
|-------------------|-------------------------|-----|----------------|--------------|
| LaMnO₃            | 5.731                    | 7.721 | 5.540          | -            |
| LaMnO₃/ZnO        | 5.534                    | 7.704 | 5.479          | 5.214        |
| LaMnO₃/ZnO/3wt%   | 5.531                    | 7.682 | 5.731          | 5.192        |
| LaMnO₃/ZnO/5wt%   | 5.528                    | 7.681 | 5.730          | 5.190        |
| LaMnO₃/ZnO/10wt%  | 5.525                    | 7.679 | 5.738          | 5.191        |

Figure 1. XRD pattern of LaMnO₃ nanoparticles, ZnO nanoparticles, nanographene platelet (NGP) and LaMnO₃/ZnO/NGP composite.

47.08°, 56.20°, 57.61°, 58.57°, 67.69°, and 75.69° match the reflection of the (110), (020), (111), (020), (002), (210), (220), (022), (202), (040), (222), (321), (123), (004) and (412) crystal planes. These results substantiate the expected orthorhombic structure of the LaMnO₃ nanoparticles [11-12].

The peaks at 20 of 31.73°, 34.35°, 36.22°, 47.52°, 56.51°, 62.82°, 66.42°, 67.89°, and 69.04° which correspond to the reflection of the (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes, this was expected and interpreted to be a hexagonal wurtzite structure for the ZnO nanoparticles. The peak of NGP was expected at 20 = 26.4° which correspond to the reflection of the NGP graphitic structure. There was no additional peak of interest in the diffraction pattern of the LaMnO₃/ZnO/NGP composite. The lattice parameters of LaMnO₃, LaMnO₃/ZnO and LaMnO₃/ZnO/NGP composite are listed in table 1.

The HRTEM image and EDX spectra is shown at figure 2a and figure 2b, respectively. The space lattices of the crystalline plane are 0.28 nm and 0.26 nm, which correspond to the (002) plane of LaMnO₃ and (100) plane of ZnO nanoparticle. The EDX spectrum of LaMnO₃/ZnO/NGP shows the relative abundance of the constituent elements of the sample. The EDX spectrum confirmed the presence of atomic Zn from the ZnO nanoparticles and atomic C from the nanographene platelets.

Thermogravimetric analysis of LaMnO₃/ZnO/NGP with 3, 5 and 10 wt.% of NGP are illustrated in figure 3a. The first weight loss observed at the temperature range between 25 to 120 °C is due to aqueous solution loss, which can be attributed to the dehydration process of water molecules and residual solvent in all the composite samples [13]. The addition weight loss is attributed to the combustion of the carbon in the nanographene platelets. The Raman spectroscopy of LaMnO₃/ZnO/NGP samples is displayed in figure 3b. The Raman spectroscopy of LaMnO₃/ZnO/NGP shows three expected bands, these bands are related to the nanographene platelets (NGP). They are D band, G band and 2D band. The D band structure is found at 1350 cm⁻¹, this band was used to investigate the disorder of the carbon structure in NGP. The G band structure is found at 1583 cm⁻¹, this band was used to investigate the characteristic of carbon in NGP while the 2D band structure was used to determine the number of graphene layer of NGP in LaMnO₃/ZnO/NGP.
MB adsorption on the removal agent was evaluated by changing the dye concentration with increment 20 mg/L dye concentration. Other studied variable was the dosage of the removal agent, which was evaluated in the 0.1–0.4 g/L. The best removal of MB by adsorption was found for the concentrate ion of the removal agent of 0.4 g/L. Figure 4a shows that better kinetics in the adsorption rate is found by increasing the dosage concentration of the removal agent, this result is interpreted to be related to a higher concentration of active sites that would adsorb more MB molecules [14]. Figure 4b shows the adsorption of LaMnO3/ZnO/NGP with different weight ratio of NGP in LaMnO3/ZnO. The results show that the increasing weight ratio of NGP could increase the removal agent adsorption rate to remove MB due to a higher surface area provided by NGP.

To understand the mechanism of adsorption, a kinetic model was used. The proposed kinetic model was a pseudo first order and pseudo second order as shown in equation (2) and equation (3), respectively.

\[
ln(q_e - q_t) = ln q_e - K_1 t
\]  

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]
Table 2. Pseudo-first and second order kinetics results on the adsorption of LaMnO$_3$/ZnO/NGP with different wt.% of NGP content.

| Samples                  | Exp. $q_e$ (mg/g) | Pseudo first order rate | Pseudo second-order rate |
|--------------------------|-------------------|-------------------------|--------------------------|
|                          | $q_1e$ (mg/g)     | $K_1$ (min$^{-1}$) | $R_1$ | $q_2e$ (mg/g) | $K_2$ (g/(mg min)) | $R_2$ |
| LaMnO$_3$/ZnO            | 11.896            | 5.882                   | 0.0120                   | 0.7089 | 12.479       | 0.0054       | 0.99 |
| LaMnO$_3$/ZnO/3wt% NGP   | 13.082            | 5.717                   | 0.0118                   | 0.6983 | 13.570       | 0.0628       | 0.99 |
| LaMnO$_3$/ZnO/5wt% NGP   | 14.269            | 5.855                   | 0.0118                   | 0.6981 | 14.718       | 0.0661       | 0.99 |
| LaMnO$_3$/ZnO/10wt% NGP  | 15.452            | 5.649                   | 0.0117                   | 0.6742 | 15.830       | 0.0074       | 0.99 |

Figure 4. The effects of (a) dosage and (b) different weight ratio of NGP on LaMnO$_3$/ZnO in the adsorption of MB.

Figure 5. (a) Pseudo first order and (b) second order of adsorption LaMnO$_3$/ZnO/NGP.

where: $q_e$ and $q_t$: adsorption capacities at equilibrium and time t, respectively, and $K_1$: pseudo-first order kinetic constant (min$^{-1}$), and $K_2$: pseudo-second order constant (g/(mg min)). The result from the kinetic models were plotted in figure 5a and figure 5b. The experimental results are better fitted considering the pseudo second-order kinetic model, as the other model fails to accurately correlate the data. Kinetic parameters were determined by the pseudo second-order kinetic model from the experimental data in figure 5b and it is listed at table 2. It is concluded that the adsorption process of LaMnO$_3$/ZnO/NGP is best fitted using pseudo second-order kinetic model with a high correlation coefficient.
Figure 6 shows the kinetic behaviour of MB adsorption as a function of its initial concentration in the range of 20–150 mg/L. It can be seen from figure 6 that by increasing the initial concentration of MB, the adsorbent (removal agent) becomes less efficient. Figure 6a shows that a decrease of 14.07% to 6.56% in the adsorption because as the concentration of the MB becomes higher, the surface of the adsorbent becomes saturated and less efficient in removing MB from the solution. Figure 6b shows the adsorption kinetics of LaMnO/ZnO/NGP with different initial MB concentration. It can be seen that the kinetics of the adsorption is faster as a function of the initial conditions and higher adsorption capacities are obtained. Higher concentration of MB will improve the diffusion driving force and final equilibrium conditions of the adsorbent and the MB [15]. It was determined from figure 6b that the maximum adsorption capacity reaches its maximum when the initial MB concentration is 150 mg/L. The adsorption isotherm model for MB adsorption of LaMnO/ZnO/NGP were investigated using equation (4) (Langmuir isotherm model) and equation (5) (Freundlich isotherm model) as follow:

\[
\frac{C_e}{q_t} = \frac{C_e}{q_m} = \frac{1}{q_m K_L}
\]

\[
\log q_e = n \log C_e - \log k_f
\]

where, \(C_e\): the equilibrium concentration of MB in the solution (mg/L), \(q_t\): amount of MB adsorbed per unit weight of solid at equilibrium (mg/g), \(q_m\): maximum adsorption capacity (mg/g), \(K_L\): constant related to the heat of adsorption, \(k_f\): adsorption capacity (mg·L/g), and \(n\): degree of dependence of the adsorption at the equilibrium concentration.

It was proposed the Langmuir and Freundlich isotherm models to correlate the experimental results and develop a mechanism to explain the adsorption of MB on LaMnO/ZnO/NGP composites. Figure 7a and figure 7b show how these models fit the experimental results. The quantity of adsorbed MB of the removal agent was determined by the Langmuir isotherm. The Freundlich isotherm model includes non-ideal behaviour as it considers a heterogenous surface adsorption and multilayer adsorption. Figure 7 data reveals a better fit by the Langmuir model, this supports that the mechanism of MB adsorption is monolayer [16].
4. Conclusions
The co-precipitation method is effective to synthesize LaMnO$_3$/ZnO/NGP composites. XRD patterns support the expected structures for LaMnO$_3$, ZnO and NGP as orthorhombic, hexagonal wurtzite, and graphitic, respectively. The adsorption kinetics and performance of MB by LaMnO$_3$/ZnO/NGP composites of different composition were evaluated and the best sample in terms of adsorption capacity is the LaMnO$_3$/ZnO/NGP with a weight ratio 10 wt.%. Adsorption kinetics results are accurately modeled by pseudo second-order kinetics and the mechanism of adsorption fits the Langmuir isotherm model.

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