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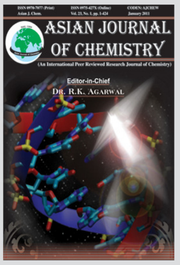

Synthesis, Characterization of Nanocrystalline $LaMnO_{3+\delta}$ and Its Application for the Removal of Chemical Oxygen Demand from Industrial Effluents

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Nanocrystalline $LaMnO_{3+\delta}$ has been synthesized by low temperature initiated, self propagating solution combustion process. It is an inexpensive synthesis and readily yields nanocrystalline product. It was characterized by powder XRD, FT-IR and SEM. The surface area of product is *ca.* 24 m^2/g. The SEM micrographs show that the product is voluminous, fluffy and porous. It is found that 60 mg of $LaMnO_{3+\delta}$ powder could remove 85 % of chemical oxygen demand from 100 mL of industrial effluent at pH 10.

Key Words: Nanocrystalline, $LaMnO_{3+\delta}$, COD, Removal.

INTRODUCTION

The development of large scale industries over the last few decades has led to a great increase in the production of industrial waste water with high toxicity that is now causing major environmental problems. Consequently, chemical, biochemical and solidification based methods have been employed to treat industrial waste water, but these processes have some limitation, including high costs and the possibility of producing secondary pollution. Therefore, development of an economical and convenient method for the treatment of industrial waste water is desirable. It is known that nanoparticles act as good catalysts. Since then, the application of nanomaterials to water treatment have been attempted to provide solutions to many environmental problems[1,2]. It has been shown that more than 3000 organic pollutants that are difficult to degrade using traditional methods can be broken down by treatment with a combination of nano TiO_2 or ZnO under UV light irradiation[3]. This method is especially effective when it is used to treat effluents that contain high levels of organic pollutants not easily degraded by other processes. For $LaMnO_{3+\delta}$, its physico-chemical properties are influenced by the synthesis conditions and micro structural features. Lanthanum manganites are commonly prepared by solid-state reaction of oxides or carbonates at high temperatures of about 1300 ºC. The solid-state reaction has the limitations of the need for high temperature, the low reactivity, large particle size of the product and poor homogeneity. On the other hand, the solution combustion method[4] enables us to obtain many oxide materials in a few minutes. Phase purity and homogeneity are achieved at a temperature as low as 300 ºC. In this paper, the synthesis of nanocrystalline $LaMnO_{3+\delta}$ by solution combustion method using oxalyl dihydrazide as a fuel and the corresponding metal nitrates as oxidizers is reported. The product is characterized by powder XRD, SEM, surface area and FT-IR. The use of nanocrystalline $LaMnO_{3+\delta}$ powder as adsorbent for the removal of chemical oxygen demand from the industrial effluents waste water is investigated.

EXPERIMENTAL

For the synthesis of $LaMnO_{3+\delta}$, AnalaR grade lanthanum nitrate $[La(NO_3)_3 \cdot 6H_2O]$, manganese nitrate $[Mn(NO_3)_2 \cdot 4H_2O]$ and oxalyl dihydrazide, $C_2H_6N_4O_2$ (ODH) in the mole ratio 1:1:1.25 were dissolved in double distilled water. The stoichiometry composition was calculated based on the total oxidizing and reducing valencies of the oxidizer and the fuel[4]. The resulting solution was transferred into a cylindrical petri dish of 250 mL capacity and evaporated over a hot plate to remove excess water. The dish containing wet powder was kept in a muffle furnace maintained at 300 ± 10 ºC. The reaction mixture undergoes dehydration and is ignited rapidly with the liberation of gaseous products such as CO_2 and oxides of nitrogen. The combustion propagates throughout the reaction mixture without further external heating as the heat of reaction released during combustion is more than the heat required for the decomposition of the redox mixture. 20 moles of gas is evolved per mole of $LaMnO_{3+\delta}$.

The formation of $LaMnO_{3+\delta}$ can be represented by the following reaction:

$$4\,La(NO_3)_3\,(aq) + 4\,Mn(NO_3)_2\,(aq) + 10\,C_2H_6N_4O_2\,(aq) + O_2\,(g) \rightarrow 4\,LaMnO_{3+\delta}\,(s) + 20\,CO_2\,(g) + 30\,H_2O\,(g) + 30\,N_2\,(g)$$

The phase purity and crystal structure were examined by Scintag X-ray diffractometer using CuK_α (λ = 1.5418 Å) radiation with a nickel filter. The surface morphology of the sample was examined on a JEOL (JSM-840 A) scanning electron microscope (SEM). The FTIR spectral studies were made using a Perkin-Elmer spectrometer (spectrum 1000) with KBr pellets. Quanta Chrome Corporation, NOVA 1000 gas sorption analyzer was used to determine the surface area of the powder samples. The chemical oxygen demand (COD) which is a measure of oxygen equivalent of organic matter of the sample that is susceptible to oxidation by a strong oxidizer was determined by open reflux method. The sample was refluxed in strong acid solution with a known excess of $K_2Cr_2O_7$. After digestion, the remaining untreated $K_2Cr_2O_7$ was titrated with standard ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter was calculated in terms of oxygen equivalent[5].

RESULTS AND DISCUSSION

Fig. 1 shows powder X-ray diffraction pattern of $LaMnO_{3+\delta}$. It shows that $LaMnO_{3+\delta}$ is cubic. The broadness of powder-XRD peaks indicates the nanocrystalline nature of the product. The crystallite size of the as made and calcined powders were calculated from the broadening of the X-ray diffraction peaks using the Scherrer's formula[6] and it was found to be in the range 30-50 nm.

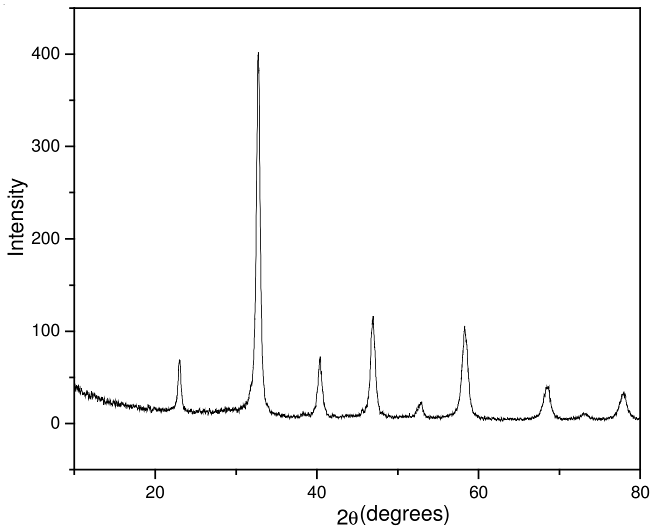

Fig. 1. Powder X-ray diffraction pattern of $LaMnO_{3+\delta}$

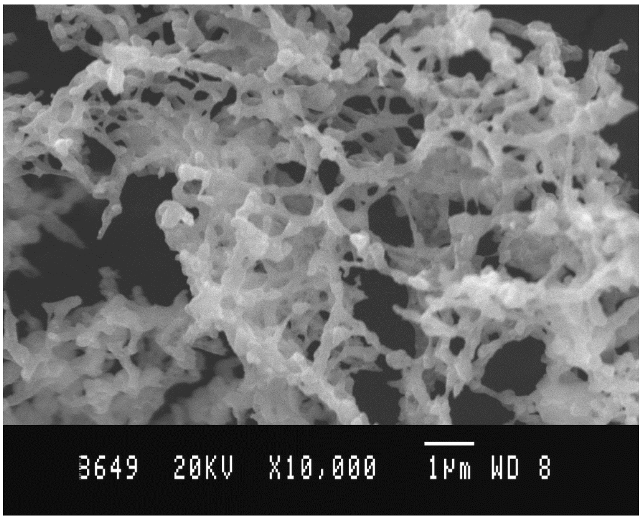

Fig. 2. SEM micrograph of $LaMnO_{3+\delta}$

The SEM micrograph of $LaMnO_{3+\delta}$ shown in Fig. 2, reveals that the particles are uniform in size and agglomerated with a grain size of 0.5-2.5 μm. The porous and voids in the micrographs can be attributed to the large amount of gas escaping from the reaction mixture during combustion. The surface area of the $LaMnO_{3+\delta}$ determined[7] by BET method using nitrogen as adsorbent gas is *ca.* 24 m^2/g.

Fig. 3 shows the infrared spectrum of $LaMnO_{3+\delta}$. Two characteristic bands are observed, one around 600 cm^{-1} which corresponds to the stretching mode of the Mn-O-Mn or Mn-O bond and another band *ca.* 400 cm^{-1} attributed to the bending mode which is sensitive to Mn-O-Mn bond angle.

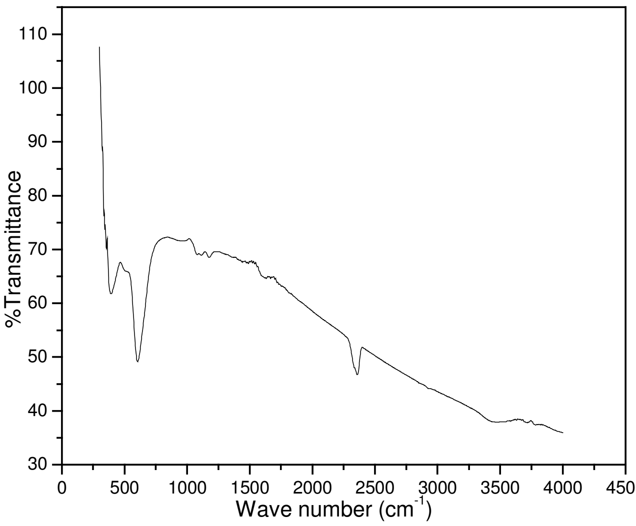

Fig. 3. FTIR spectrum of $LaMnO_{3+\delta}$

Effect of $LaMnO_{3+\delta}$ loading: Experiments were carried out by taking different quantities (10-120 mg) of $LaMnO_{3+\delta}$ powder separately in 100 mL of the effluent solutions and kept for stirring. Thereafter, the analysis of residual chemical oxygen demand in the treated effluent was performed and a relationship between removal of chemical oxygen demand (percentage) and adsorbent quantity was determined (Fig. 4). It was found that a maximum (75 %) removal of chemical oxygen demand occurs in the presence of 60 mg of $LaMnO_{3+\delta}$ powder. After this, the removal rate becomes almost constant with increase of adsorbent quantity and therefore 60 mg appears to be the optimum quantity.

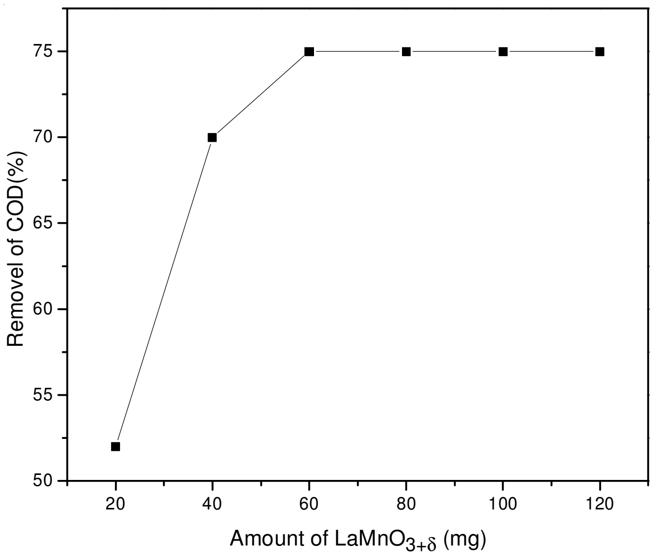

Fig. 4. Removal of chemical oxygen demand (COD) (%) *versus* adsorbent quantity

Effect of stirring: The rate of chemical oxygen demand removal by the adsorbent was determined using optimum dosage (60 mg) of $LaMnO_{3+\delta}$. The experiments were conducted for different intervals of stirring time taking 100 mL of effluent at neutral condition. After every 10 min of stirring, the residual chemical oxygen demand was analyzed. The chemical oxygen demand removal gradually increased with time and attained constant value above 1 h stirring (Fig. 5) and this duration seems to be the optimum time for a maximum (85 %) removal of chemical oxygen demand.

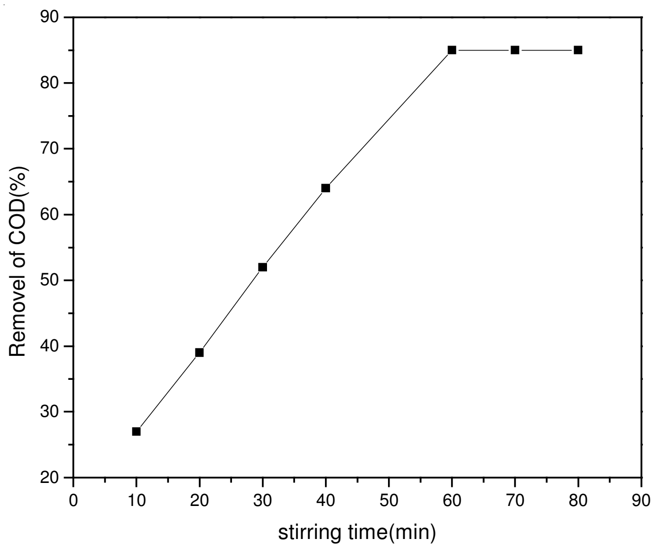

Fig. 5. Removal of chemical oxygen demand (COD) (%) *versus* stirring time

Effect of sedimentation: The effect of sedimentation time on the rate of chemical oxygen demand removal by the adsorbent was determined by using optimum dosage, 60 mg of $LaMnO_{3+\delta}$ powder with a stirring for 1 h at neutral condition. After every 10 min of sedimentation time, the residual chemical oxygen demand in the effluent was analyzed. The removal of chemical oxygen demand gradually increased with time and attained a constant value above 1 h sedimentation (Fig. 6) and this interval is considered as the optimum time for the maximum removal of chemical oxygen demand (85 %).

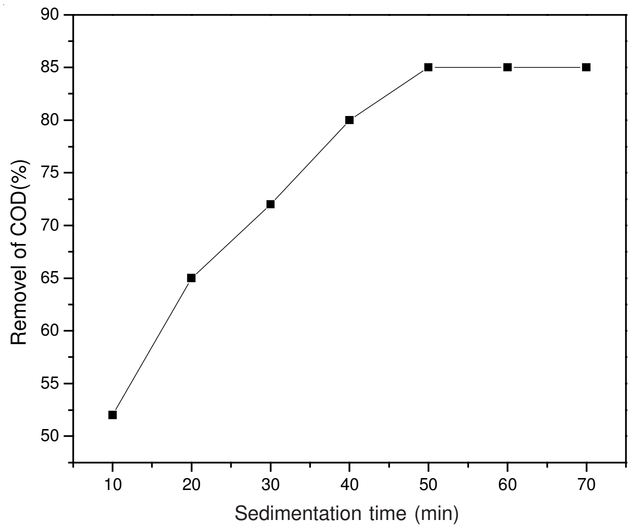

Fig. 6. Removal of chemical oxygen demand (COD) (%) *versus* sedimentation time

Effect of pH: The effect of pH (2-12) on chemical oxygen demand removal was carried out using optimum dosage (60 mg) of the adsorbent with optimum stirring (1 h) and sedimentation times (1 h) and the results are shown in Fig. 7. It is seen from the Fig. 7 that the maximum removal of chemical oxygen demand occurs at alkaline pH 10-12.

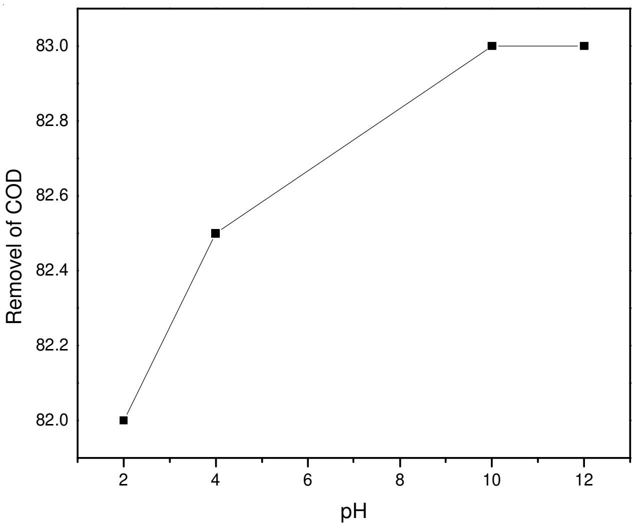

Fig. 7. Removal of chemical oxygen demand (COD) (%) *versus* pH

Conclusion

$LaMnO_{3+\delta}$ powder was synthesized by a novel low temperature solution combustion method. It produces readily a homogenous, crystalline powder having good surface area. It has a cubic phase. The surface area of the compound is *ca.* 24 m^2/g. The SEM micrographs show that the powder product is voluminous, fluffy and porous. $LaMnO_{3+\delta}$ is very effective in removing chemical oxygen demand from the effluent. It removes 85 % of chemical oxygen demand present in the effluent.

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