Oxidation of phenol using LaMnO$_3$ perovskite, TiO$_2$, H$_2$O$_2$ and UV radiation

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LaMnO$_3$ perovskite has been used for the treatment of aqueous solution of phenol using stoichiometric amount of H$_2$O$_2$ and combination of TiO$_2$ and UV radiation. The oxidation of phenol was studied with [UV radiation]; [H$_2$O$_2$ and UV]; [TiO$_2$ and UV]; [LaMnO$_3$ and UV]; [TiO$_2$, H$_2$O$_2$ and UV]; [LaMnO$_3$, H$_2$O$_2$ and UV]; to establish the effectiveness of different systems when compared with perovskite catalyst. Results show that the phenol degradation efficiencies decreased in the following order [LaMnO$_3$, H$_2$O$_2$ and UV] > [TiO$_2$, H$_2$O$_2$ and UV] > [LaMnO$_3$ and UV] > [TiO$_2$ and UV] > [H$_2$O$_2$ and UV] > [UV]. UV-VIS spectra result of phenol degradation shows that as the concentration of catalyst increases, its activity increases. The optimum concentration of catalyst was 0.60 g/L for 100 ppm phenol solution. Perovskite catalyst after reaction is completely regenerated by calcinations at 800°C for 2 h and retains a similar catalytic performance.

Keywords: Perovskite, Phenol, Hydrogen peroxide, Photochemical reactor, AOPs

Phenol is one of the most prevalent chemical pollutants from many industries. Phenol has been widely used in industrial processes as synthetic intermediates or as raw material in the manufacturing of pesticides, insecticides, wood preservatives etc. It can be found not only in industrial wastewater but also in soils, surface and ground water courses, both as a consequences of its release in industrial effluents or improper waste disposal practices. It is characterised by high toxicity and poor degradability.

Many researchers have been working towards development of AOPs (Advanced oxidation processes) for the treatment of wastewater using titanium dioxide as a catalyst with H$_2$O$_2$. H$_2$O$_2$ is a desirable oxidant since it does not form any harmful by-products and it is a non-toxic. Perovskite-type oxides have attracted a great interest for the development of environment friendly catalytic materials. They have been used in processes such as catalytic combustion for the automotive control emission and catalytic destruction of chlorinated compound. Phenol is one of the most recalcitrant chemical in wastewater to degrade. However, application of perovskite catalyst in the field of water treatment has been limited. The present study attempts to investigate the performance of LaMnO$_3$ perovskite for the treatment of phenolic solution using H$_2$O$_2$ and also compare with other oxidative option, such as TiO$_2$ and UV radiation.

Experimental Procedure

Catalytic experiments

Experiments were carried out in photochemical reactor made of pyrex glass equipped with a water condenser, water circulating jacket, magnetic stirrer and an opening for supply of air. A schematic diagram of the photochemical reactor is shown Fig. 1.

For experiments an aqueous solution of phenol was placed into the photoreactor. The required quantities of photocatalyst and H$_2$O$_2$ were added. Stoichiometric amount of H$_2$O$_2$ required for total oxidation of phenol was calculated as per the following reaction.

![Fig. 1—Schematic diagram of photochemical reactor](image-url)
C₆H₆O + 14H₂O₂ → 6CO₂ + 17H₂O

The suspension was stirred and continuously purged with air throughout the experiment. Experiments were also conducted in the absence of catalyst and H₂O₂ to see their individual effect.

UV irradiation was carried out using 6W low pressure mercury lamp. It was positioned and immersed in the solution in the centre of the reactor emitting radiation at 254 nm. The lighted length of the lamp was 190 mm with a quartz sleeve diameter of 16 mm. The reactor was surrounded with cooling water jacket to maintain a constant temperature.

Phenol concentration was estimated using a UV/VIS single beam Spectro-photometer-Ver 3.30 (Chemito 2100).

Catalyst preparation and characterization

LaMnO₃ perovskite catalyst was prepared by co-precipitation method. Stoichiometric amount of La(NO₃)₃.6H₂O (Merck-India Ltd.) and Mn(NO₃)₂.6H₂O (Merck-India Ltd) were dissolved separately in double distilled water, two aqueous solution were mixed and stirred for 5 min. Ammonium hydroxide was added dropwise to the aqueous mixture to precipitate the metal oxyhydroxide. The precipitate formed was vacuum filtered and washed thoroughly with distilled water till the pH of filtrate was neutral. Thereafter, the resultant precipitate was kept in oven at 70°C for 24 h before calcination in muffle furnace at 800°C for 8 h.

TiO₂ (anatase) AR grade catalyst (VWR International Ltd.) was used as a standard catalyst without any further treatment. X-ray diffraction (XRD) measurements were carried out by using XPERT PRO diffractometer system with CuKα radiation (λ=1.54060 nm). The accelerating voltage of 40 KV and emission current of 30 mA was used. Figure 2 illustrates the XRD patterns of the synthesized perovskite catalyst sample after calcination. It exhibits the typical pattern corresponding to perovskite structure with some impurities of La₂O₃ (JCPDS 83-1355) and La(OH)₃ (JCPDS 83-2034). Figure 3 illustrates the XRD pattern of pure anatase TiO₂ catalyst.

The specific surface area was estimated using BET method with Micromeritics ASAP20. Analysis show that LaMnO₃ and TiO₂ have specific surface area of 11.67 and 10.01 m² g⁻¹ respectively.

Results and Discussion

Photochemical oxidation of phenol over different system

The evaluation of perovskite catalyst system was carried out along with other combinations of photochemical oxidation processes with a purpose to assess the efficiency of phenol removal. Table 1, presents the data for set of experiments carried out along with the conversion of phenol for different system.

Comparison of UV/VIS absorption spectra for different systems

UV/VIS spectra of the reaction mixture for [UV], [H₂O₂ and UV], [TiO₂ and UV], degradation are presented in Fig. 4, and [LaMnO₃ and UV], [TiO₂, H₂O₂ and UV], [LaMnO₃, H₂O₂ and UV] in Fig. 5. Fig. 5 depicts that the systems [TiO₂ and H₂O₂ and UV] and [LaMnO₃, H₂O₂ and UV] give the higher efficiencies. Table 1 presents the removal efficiencies of 98 and 99.92% for [TiO₂, H₂O₂ and UV] and [LaMnO₃, H₂O₂ and UV] respectively. Other systems such as [UV] and [H₂O₂ and UV] do not provide higher efficiencies. When TiO₂ and LaMnO₃ are used with UV irradiation, phenol removal efficiencies improve to 46.92 and 58.34% respectively. Results also clearly indicate that H₂O₂ plays an important role. The mechanism of reactions have been established which explains the role of OH⁻ radicals.

Fig. 2—X-ray diffraction (XRD) pattern of sample: (P)-LaMnO₃, (O)-La₂O₃ and (*)-La(OH)₃

Fig. 3—X-ray diffraction (XRD) pattern of pure anatase TiO₂
At the solid liquid interface, electron transfer can occur both from the conduction band to an electron acceptor (O$_2$, H$^+$, etc.) in the solution and from the donor (OH$^-$, H$_2$O, organic matter, etc.) in the solution to the valance band hole. Moreover, the hydroxyl radicals formed are strong oxidant and attack organic pollutants present at or near the surface of semiconductor catalyst. It causes photodegradation of pollutants.

As such the process is a typical hydroxyl radicals reaction, its spectral change in phenol degradation was investigated for comparison with other systems. The characteristic peaks of phenol are found to be at 209 nm.

Photochemical oxidation of phenol over LaMnO$_3$ perovskites

As expected according to the above result, LaMnO$_3$+H$_2$O$_2$+UV system was found to be the most effective for phenol oxidation. It strongly suggests that the catalytic activity of the perovskite materials is greatly enhanced in the presence of H$_2$O$_2$. TiO$_2$ with H$_2$O$_2$ also provides higher phenol degradation efficiency which improves in the presence of perovskite as given in Table 1.

Influence of LaMnO$_3$ perovskite concentration

Photochemical oxidations of phenolic aqueous solutions were performed with 0.15, 0.30, 0.45 and 0.60 g/L of catalyst with a stoichiometric concentration of peroxide and exposed with UV radiation for 240 min. Table 2, presents the influence of catalyst concentration at different catalyst loading. By increasing the amount of catalyst, an enhancement in the phenol removal is readily observed, achieving complete phenol degradation. Highest phenol degradation efficiency of about 100% has been achieved with the highest catalyst content (0.6 g/L) with the stoichiometric amount of H$_2$O$_2$. UV/VIS spectra changes of aqueous solution of phenol (100 ppm), treated with different concentration of catalyst is shown in Fig. 6.

Stability test for LaMnO$_3$ perovskite catalyst

Stability test of LaMnO$_3$ catalyst was carried out with a view to establish the possibility of regeneration.
When LaMnO$_3$ perovskite catalyst is reused, its activity decreases slowly during successive tests. However, perovskite catalyst can be regenerated by calcination and yields similar catalytic performance. Thus, phenol degradation using perovskite catalyst can be a good option when used with stoichiometric amounts of H$_2$O$_2$ and in the presence of UV radiation.

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**References**


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Fig. 6—UV/VIS spectra changes of aqueous solution of phenol (100 ppm), treated with different LaMnO$_3$ catalyst concentration at irradiation time of 4 h

Table 3—Stability of LaMnO$_3$ perovskite catalyst

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