Photocatalytic degradation of phenol by LaFeO_3 nanocrystalline synthesized by gel combustion method via citric acid route

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Abstract

Focusing on the photocatalytic degradation of phenol under visible light, the synthesized lanthanum orthoferrites (LaFeO_3) by gel combustion method using citric acid as sacrificial agent were investigated. With the highest reaction temperature of 200 °C, the physicochemical properties of synthesized samples were characterized by X-Ray diffraction (XRD) analysis, Brunauer–Emmet–Teller (BET), and Energy Dispersive X-Ray spectroscopy (EDS). On the other hand, UV–Vis spectroscopy analysis was carried out to determine the phenol photodegradation activities and mechanism. The results suggested the well-defined LaFeO_3 nanocrystals with specific area of $28 \text{ m}^2 \text{ g}^{-1}$ were successfully synthesized. Besides that, variations in operating parameters such as pH, catalyst dosage and initial concentration of phenol in synthetic wastewater were also examined. In conclusion, LaFeO_3 nanocrystalline exhibited an exceptional photocatalytic activity for phenol degradation, thus providing a perfect alternative for pharmaceutical wastewater treatment.

Keywords Lanthanum orthoferrite · Gel combustion · Citric acid · Photocatalytic activity · Phenol

1 Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, ocean and groundwater by human activities. All water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging either to individual species and populations but also to the natural biological communities. It occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful constituents.

One of the most studied pollutant is pharmaceutical wastes. Effective treatment of pharmaceutical wastes is a big challenge because of the enormous quantity, complexity and hazardous nature. The pharmaceutical wastes comprise of drug residues with high biological oxygen

demand (BOD), chemical oxygen demand (COD), pharmaceutically active compounds like hormones, antibiotics (PhACs), toxic substances, surfactants and volatile organic compounds (VOCs) which constitute potential threat to biosphere. Many of these pharmaceutical wastes pose serious threat to human health and ecosystem because of their continuous accumulation in the ecosystem leading to even development of antibiotic-resistant microbial strains [1]. The term “pharmaceutical wastewater” mainly refers to the effluents and wastes generated during manufacturing of pharmaceuticals.

Phenol is an excellent example of pollutant that commonly found in pharmaceutical wastewater. Phenol, or previously also known as carboic acid is an aromatic organic compound consisting of a phenyl group ($-\text{C}_6\text{H}_5$) bonded to a hydroxyl group ($-\text{OH}$). Phenol-containing

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substances are toxic, carcinogenic, mutagenic and lead to teratogenic defects [2]. In Malaysia, phenol is designated as scheduled wastes under SW 3 group in First Schedule Environmental Quality Regulations 2005, which is “wastes containing principally organic constituents which may contain metals and inorganics materials” by Malaysia’s Department of Environment (DOE). As such, the discharge of industrial effluent of phenol into any inland waters within catchment areas (Standard A) must be less than 0.001 mg/L, while the discharge into any inland waters or Malaysian waters (Standard B) is set to be at 1.0 mg/L and lower. Furthermore, as phenol and its compounds are gazetted under Malaysian law as scheduled wastes, they must be stringently managed, regarding the disposal, exportation and/or importation of these compounds.

To confront and prevent increasing water consumption and deficiency of water resources, treated effluent recycling is considered as a strategic approach to sustained management of water resources around the world. One of the ways is by means of Advanced Oxidation Processes technologies. Advanced Oxidation Processes (AOPs) can be generally defined as aqueous-phase oxidation methods based on highly reactive, unselective species such as (primarily, not exclusively) hydroxyl radicals ($\text{OH}\cdot$), leading to the destruction of the pollutants [3]. Furthermore, $\text{OH}\cdot$ radicals attack most part of organic molecules with rate constants usually in the order of $10^6\text{--}10^9\text{ M}^{-1}\text{ s}^{-1}$, making them an extraordinary potent reactive species [4]. The usage of heterogeneous semiconductor photocatalysts such as titanium dioxide (TiO_2), zinc oxide (ZnO), silver phosphate (AgPO_4), and cadmium sulfide (CdS) as part of AOPs have been studied by many researchers as they possessed several unique properties including non-toxic, high chemical stability and environmental friendliness (when it is not released towards the environment, and efficiently retrieved after the treatment for reuse or disposal) [5]. However, the reaction of photocatalysts will usually be paired with the usage of UV light as the main light source, as most of them have large band gaps than can only be activated by high energy UV light. Due to that, alternative photocatalysts such as perovskites are favored as they can be activated by visible light, which will reduce the total cost for wastewater treatment as lower energy input is needed, and subsequently reducing the risk of developing cancerous cells in human operators as UV light is known to induce it.

Lanthanum orthoferrite, LaFeO_3 , is a considerable perovskite-like material to be used as photocatalyst as it has an optimal band gap that responds to a wide range of wavelengths, in both ultraviolet and visible light ranges. However, it is worth noting that properties and catalytic activities of LaFeO_3 and other perovskites strongly depend on several factors, which are methods of preparation, crystallinity,

particle size, surface morphology and optical band gap [6]. According to Hao and Zhang [7], LaFeO_3 synthesized by high temperature solid reaction methods resulted in the formation of large size particles with small specific surface area, lowering the photocatalytic activity of the catalyst. The specific surface area and crystal structure will be tremendously affected in high-temperature thermal treatments that usually lead to the sintering of resulting particles (commonly known as ‘precursor’) to yield final products, which eventually decreases the specific surface area. Furthermore, the resulting reduction of surface area will greatly influence the performance of the perovskites [8]. On the other hand, methods such as hydrothermal preparation of nano- LaFeO_3 may result in the formation of well-crystalline, high specific surface area LaFeO_3 , but this process is time-consuming and difficult for large scale production [9]. Therefore, gel-combustion method is one of the best alternatives to high-temperature processes as it does not require any specialized apparatus, can be prepared within a short period of time and use a significant less amount of energy. It is based on the rapid exothermic reactions between metal nitrates and organic fuels, which in this case, citric acid, to yield powdered-like samples with high crystallinity [7, 10–12].

However, to the best of our knowledge, there are limited studies focusing on the photocatalytic activities of LaFeO_3 synthesized by gel combustion method for pharmaceutical wastewater, specifically phenol. Hence, in this research, the efficiency of synthesized LaFeO_3 nanocrystalline by gel combustion method via citric acid route to degrade phenol found in synthetic pharmaceutical wastewater by photocatalytic activity will be discussed.

2 Experimental

2.1 Methods for LaFeO_3 nanoparticles synthesis

Lanthanum(III) nitrate hexahydrate, $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$), 25% ammonia solution were purchased from Sigma-Aldrich Ltd. and are analytical grade. According to stoichiometric preparation of lanthanum orthoferrite, the calculated amount of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were dissolved in citric acid solution at 60°C of constant stirring. The amount of citric acid needed was equal to the molar amount of metal nitrates in the solution. As both metal nitrates visually dissolved, 25% ammonia solution was added to adjust the pH to 7 and subsequently stabilize the sol. The nitrate-citrate sol was then poured into a ceramic crucible and heated slowly to 120°C . The changes in viscosity and color of the sol to brown confirmed the formation of dry gel. The dry gel was

later subjected to react at 200 °C for 24 h to transform it into loose powder. The obtained powder was the LaFeO₃ nanocrystalline with fine crystal powder and no further calcination at high temperature needed.

2.2 Methods of characterization

The crystalline structure of the synthesized LaFeO₃ samples were characterized by X-ray powder diffraction (XRD, PANalytical XPERT-PRO) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 45 kV. Brunauer–Emmett–Teller (BET) surface area analysis was carried out using BELSORP-max Ver 1.3.0 instrument by mean of N₂ adsorption at –196.15 °C. Morphological (TEM images) and elemental composition (Energy Dispersive X-Ray spectroscopy (EDS)) of synthesized LaFeO₃ were studied using JEOL JEM-ARM200F ACCELARM Atomic Resolution Analytical Electron Microscope, while Shimadzu UV3600Plus spectrophotometer was utilized to determine optical properties of the powders.

2.3 Photocatalytic degradation of phenol

The photocatalytic degradation activity of phenol by LaFeO₃ was carried out in customized photo reactor (Fig. 1). 0.1 g of LaFeO₃ was suspended in 100 mL phenol solution (30 mg/L at pH6) with 10 mL/L of 3% hydrogen peroxide (H₂O₂) added that act as degradation catalyst. The addition of H₂O₂ is known to enhanced the photocatalytic activities of LaFeO₃ due to simultaneous effect of Fenton-like and photocatalysis mechanism, based on a study carried out by Soltanabadi et al. [13]. The mixture was continuously stirred to prohibit the settling of LaFeO₃ at the bottom of the beaker. For the first 2 h, the mixture was kept in the dark for the establishment

of absorption–desorption equilibrium. Following that, the mixture was then irradiated with 100 W LED light as the source of visible light for 4 h. The distance between the samples and the source are fixed at 5 cm. Aliquots were obtained for analysis every 60 min using 0.45 μm filtered syringe to hinder the presence of LaFeO₃ in samples. Phenol concentration was monitored by measuring value of absorbance of samples using Perkin Elmer Lambda 25 UV–Vis spectrometry. Normalized absorption of phenol followed in $\lambda = 270 \text{ nm}$. The experiment was later replicated with different loading of LaFeO₃ catalysts, which were 0.3 g and 0.5 g. This is important to understand the optimized loading of LaFeO₃ nanoparticles needed for photocatalytic degradation of phenol.

On separate study, the effect of initial pH and initial concentration of the phenol solution towards the photocatalytic activity of LaFeO₃ were also carried out. The pH of phenol solution was adjusted using 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) solution until desired pH was achieved. On the other hand, the initial concentration of 100 mL phenol solution was varied to 30 mg/L, 50 mg/L and 70 mg/L. The loading of LaFeO₃ was fixed at 0.1 g, while the experimental setup was in accordance to previous experiment.

Throughout the experiment, the temperature and pH of the phenol solution will be closely monitored.

The adsorption and photocatalytic performance of LaFeO₃ was evaluated by using Eq. (1):

$$\text{Removal of Phenol (in \%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t is the initial and final concentration of phenol (in mg/L), respectively.

Fig. 1 Illustration of customized photo reactor with visible light source

3 Result and Discussion

3.1 Characterizations

To determine the crystalline structure of the synthesized LaFeO_3 samples, the XRD patterns are shown in Fig. 2. The samples displayed a pure perovskite structure with narrow and strong orthorhombic phase peaks, that can be indexed based to powder diffraction file (JCPDS card no. 37-1493). No possible impurities nor contamination can be observed, suggesting that the single-phase LaFeO_3

Fig. 2 XRD pattern of synthesized LaFeO_3

were successfully synthesized [7]. On the other hand, the pseudo-particle size of both samples can be calculated based on the Scherrer formula [Eq. (2)]:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where τ is mean pseudo-size of particles, K is 0.9, λ ($K\alpha$ wavelength) is 0.1541 nm, β is full width at half maximum of (121) diffraction peak, in radian, and θ is the Bragg angle of the peak (in degree). It was estimated that particle size of LaFeO_3 to be 32.229 nm.

The BET surface analysis carried out shows that the synthesized LaFeO_3 nanoparticles showed the specific surface area (SSA) of $28.04 \text{ m}^2 \text{ g}^{-1}$. This relatively high SSA will theoretically provide more active site on the surface of LaFeO_3 for a better synergistic adsorption and photocatalytic degradation of phenol under visible light irradiation.

The TEM images (Fig. 3a, b) shows the morphological properties of successfully synthesized LaFeO_3 . Under $500,000\times$ magnification (Fig. 3a), the formation of nanocrystalline with geometrically different axes can be clearly observed, proving the orthorhombically perovskite structure of the LaFeO_3 . The nanocrystalline also exhibited porous-like structure on its surface that may be attributed by the large amount of gas released during combustion period. As the magnification increased to $800,000\times$ (Fig. 3b), uniform lattice fringes can be observed in the images, although in certain area the fringes may appeared inconsistent due to crystals staking on top of the other. The calculated interplanar d -spacing of 0.278 nm (Fig. 3b insert) can be assigned to (121) lattice plane, and this is in agreement to the XRD results and JCPDS card

Fig. 3 TEM images of synthesized LaFeO_3 under **a** $\times 50,000$ magnification, and **b** $\times 80,000$ magnification with calculated d -spacing insert

no. 37-1493, suggesting the formation of high-quality LaFeO_3 nanocrystalline with defined structure. Next, the elemental/chemical characterization of the LaFeO_3 samples carried out by EDS analysis exhibited the elemental composition of LaFeO_3 nanoparticles synthesized by gel combustion method consisted of La, Fe and O in stoichiometric molar ratio of 1:1:3. This finding is important to highlight the purity and composition of LaFeO_3 samples.

3.2 Optical Properties

The diffuse reflectance spectra, Kubelka–Munk curve and band gap determination of synthesized LaFeO_3 nanocrystalline were shown in Fig. 4a, b. As can be observed in Fig. 4a, LaFeO_3 nanocrystalline possessed an excellent optical absorption capability in entire wavelength, from UV to visible to near-infrared region. It is postulated that this behaviour will contribute to good photocatalytic activity of LaFeO_3 across broad spectrum of light, and this result is in accordance to previous studies [13, 14]. In order to better classify the synthesized LaFeO_3 as a good photocatalyst, especially for photodegradation of organic contaminants such as phenol, the study of their band gap is important. Additionally, accurate determination of the band gap it is necessary to find the type of transition and to determine the optical band gap. This can be done following Eq. (3) [15]:

$$\alpha h\nu = k(h\nu - E_g)^{1/n} \quad (3)$$

where k is an energy-independent constant and E_g the optical band gap. The exponent n is determined by the type of transition, where $n = 1/2$ was used for indirect allowed transitions. As illustrated in Fig. 4b, the band gap of synthesized LaFeO_3 was determined as 2.42 eV, and this

is within the range of optimal band gap for visible light activation of LaFeO_3 photocatalyst, based on previous studies carried out by Scafetta et al. [14] and Köferstein et al. [15].

3.3 Effects of catalyst loading on the photocatalytic degradation of phenol

As illustrated in Fig. 5, the photolysis of phenol with 3% hydrogen peroxide act as the only catalyst led to a very low phenol reduction, precisely at 18.7% only. On the other hand, with the presence of LaFeO_3 nanocrystalline, higher activity of phenol removal by mean of photocatalytic degradation can be clearly observed. Two hours prior to irradiation of visible light, the concentration of phenol was slightly decreased, mainly due to the adsorption of phenolic compound onto the surface of LaFeO_3 nanocrystalline. Phenol degradation after irradiation of visible light is then increased substantially, regarding any amount of LaFeO_3 nanocrystalline used.

This is explained in terms of a high photo transformation quantum yield, where the reactive excited states activate through photochemical processes. These results also reflect the potential of photocatalyst to harvest light in the visible light region, so that the yield of hydroxyl radicals available for phenol removal is higher. Hydrogen abstraction yields a phenoxyl radical which will then reacts with dissolved oxygen to yield peroxy radical species that further react, leading to formation of carbon dioxide and water [16]. This result also showed that the synergistic act of adsorption and degradation is favorable in the use heterogenous photocatalyst as this will increase the effectiveness of the process, compared to the usage of radical-forming agents such as hydrogen peroxide only. Adsorption of the phenol molecules onto the available

Fig. 4 Diffuse reflectance (%R) spectra versus Kubelka–Munk curves, and **b** band gap determination of LaFeO_3 nanocrystalline

Fig. 5 The effect of different LaFeO_3 loading towards the photocatalytic degradation of phenol, where (black down triangle) is hydrogen peroxide as control, (black square) is 0.1 g, (black circle) is 0.3 g and (black triangle) is 0.5 g

active sites on the surface of LaFeO_3 catalysts will maximize the contact time for radicals generated to completely mineralized the phenol without formation of intermediate compounds (see Sect. 3.4).

However, the optimum loading of LaFeO_3 nanocrystalline which act as light-driven catalysts is important to avoid ineffective excess amount of catalyst and to ensure the total absorption of efficient photons. Illustrated in Fig. 6, increasing the amount of catalyst will significantly increase the percentage of phenol degraded mainly because the catalyst will attribute to a larger number of active sites for generation of more radicals, but this may also have resulted in the decrease in the penetration of the photon flux. The increasing turbidity of the suspension reduces light penetration due to the enhancement of light scattering; the result is the decrease of the number of activated sites on the photocatalyst surface and shrinking of the effective photoactivated volume of suspension.

From the results, 0.3 g of LaFeO_3 loading is more efficient (57.2% of phenol degradation), compared with 0.1 g catalyst loading (33.9%), while the performance of 0.5 g of catalyst was significantly reduced with only 39.5% of phenol was successfully degraded. Therefore, the optimum

Fig. 6 Illustration of photon flux penetration

catalyst dosage for photocatalytic degradation of phenol is concluded to be at 0.3 g.

3.4 Effects of pH and initial phenol solution concentration on the photocatalytic degradation of phenol by LaFeO₃ nanocrystalline

The photocatalytic reaction gives a different effect when the pH values of the solution are varies. This may due to the semiconductor's surface state of protonation, its iso-electric point, and the fact that dissociation of phenol are strongly pH dependent [17]. When $\text{pH} < \text{pK}_a$ value, phenol forms as a neutral species ($\text{C}_6\text{H}_5\text{OH}$), whereas when $\text{pH} > \text{pK}_a$, the phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$) is form [18]. During adsorption, the surface charge promotes interaction between the catalyst and pollutant [19].

In this study, the pH of 100 mL phenol solution is varied in three different ranges, which were pH4 (acidic), pH6 (weak acid) and pH8 (basic), with the initial phenol concentration and catalyst loading were fixed at 30 mg/L and 0.1 g, respectively. The efficiency of the photocatalytic degradation of phenol depends on the acidity of the medium. Based on Fig. 7, the highest phenol removal is recorded at pH4 with the removal percentage of 72%. This is because at low pH, the surface of photocatalyst is occupied with H^+ ions, therefore maximising the the generation of $\text{HO}\cdot$ radicals and adsorption of phenolic compound onto the catalysts' surfaces to be degraded.

In the meantime, as pH increases, the extent of removal decreases at pH 6 (36% removal) and pH8 (25.5% removal). Same behavior is found by Shet and Shetty [20] when Ag

core-TiO₂ shell nanoparticles was used in photocatalytic degradation of phenol mediated by visible light. Increasing the pH of phenol solution will reduces the protonation of the LaFeO₃ nanocrystalline's surfaces, repelling the adsorption of phenol onto the surfaces as both are negatively charged, and eventually reducing phenol degradation [3].

The effect of initial phenol concentration was later investigated by varying the solution's concentration to 30 mg/L, 50 mg/L and 70 mg/L, while the catalyst loading and pH were fixed at 0.1 g and pH6, respectively. From Fig. 8, the highest removal of phenol can be observed when the initial phenol concentration was at 50 mg/L, where 72.2% of phenol was successfully degraded and mineralized. On the other hand, at initial concentration of 30 mg/L and 70 mg/L, lower percentage of phenol were removed, precisely at 33.9% and 25.2%, respectively. In theory, degradation rate will decrease as the initial concentration of contaminants increased above the critical value. This phenomenon can be explained based on the photocatalyst-contaminant mechanism, which requires adsorption of contaminants' molecules, which in this case, phenol molecules onto the surfaces' active sites of photocatalyst, so that the $\text{OH}\cdot$ and $\text{O}_2\cdot^-$ radicals generated via activation of light can react with the phenol molecules, leading to mineralization or degradation to carbon dioxide and water. Fixing the catalyst loading will eventually fixing the number of surfaces' active sites available, thus limiting the number of radicals formed. On the other hand, as the initial concentration of phenol increases, so does the number of molecules, leading to reduction in probability

Fig. 7 The effect of different pH towards the photocatalytic degradation of phenol, where (black square) is pH4, (black circle) is pH6 and (black triangle) is pH8

Fig. 8 The effect of different initial phenol concentration towards the photocatalytic degradation of phenol by LaFeO₃ nanocrystalline, where (black square) is 30 mg/L, (black circle) is 50 mg/L and (black triangle) is 70 mg/L

of catalyst-phenol molecule interaction, thus reducing the efficiency of the photocatalytic process [21].

As in this experiment, 50 mg/L was observed to be the critical value as the highest removal recorded at this initial concentration. At 30 mg/L, less phenolic compounds may be adsorbed onto the surface of LaFeO_3 nanocrystalline, reducing the effectiveness of the process as the photocatalyst-contaminant mechanism mentioned before cannot be completed. While at 70 mg/L, generation of radicals may be halted as large number of phenolic molecules were adsorbed onto the catalysts' surfaces, minimizing the availability of vacant active sites for radicals' generation [17]. Furthermore, complete mineralization of phenol may not be achieved, instead, formation of phenolic intermediates took place thus increasing the total carbon formation, leading to greater light absorption when spectrophotometry analysis was carried out.

3.5 Photocatalytic activity mechanisms

To further quantify the synergistic mechanism of photocatalysis and adsorption of LaFeO_3 for removal of phenol in synthetic wastewater, all parameters that shows highest removal of phenol in synthetic wastewater prepared was combined (pH4, 0.3 g of LaFeO_3 loading, and 50 mg/L of initial phenol concentration). The result shows that up to 92% of phenol successfully removed under this optimal condition. This results is higher compared to the study conducted in the past [22, 23]. However, the photocatalytic mechanism of LaFeO_3 nanocrystalline is the most important thing to consider and this can be determined by species trapping or scavenging experiments [24]. 1 mmol of 1-propanol (IPA), 1 mmol of ammonium oxalate (AO) and 1 mmol of p-benzoquinone (BQ) was added in the

reaction system as the hydroxyl radical ($\cdot\text{OH}$), hole (h^+) and superoxide radical ($\cdot\text{O}_2^-$) scavenger, respectively. As shown in Fig. 9, the photocatalytic degradation of phenol was slightly reduced by the addition of 1-propanol, indicating that the mechanism is not dominating by hydroxyl radicals ($\cdot\text{OH}$) species. On the other hand, drastic reduction in the percentage degradation of phenol was observed by the addition of BQ and AO indicating that both hole (h^+) and superoxide radical ($\cdot\text{O}_2^-$) are responsible for being dominant reactive species during the photocatalytic degradation of phenol by synthesized LaFeO_3 nanocrystalline.

Based on the experiments carried out, the photocatalytic mechanism of phenol removal by mean of photocatalyst was proposed, as shown in Fig. 10. First of all, LaFeO_3 nanocrystalline absorbed the photon energy caused the electron excitation from VB to CB and leaving the positive holes at the VB [Eq. (4)]. Due to less positivity of LaFeO_3 valence band, it is unable to generate enough hydroxyl radicals ($\cdot\text{OH}$) species for individual application in phenol degradation [24]. However, the photogenerated holes at the VB which possessed the high oxidative potential would allow direct oxidation of phenol and degraded them simultaneously [Eq. (5)]. Mohamed et al. [24] suggested that the direct hole oxidation can be easily initiated when the adsorption of the photocatalysts is enough, and the concentrations of pollutants on photocatalyst surface is relatively high, and this may apply to multiple photocatalysts with same mechanism. Moreover, they also proposed that increased adsorption of organic contaminants such as phenol is due to strong π - π interactions and the high surface area of the photocatalysts, leading to the higher photodegradation activity.

On the other hand, as the conduction band (CB) of LaFeO_3 is theoretically more negative, the photogenerated

Fig. 9 Effect of various scavengers on the visible-light photocatalytic activity of LaFeO_3 towards the degradation of phenol

Fig. 10 Proposed mechanism of visible light induced photocatalytic removal of phenol by LaFeO₃ nanocrystalline

electrons can reduce the molecular oxygen (O₂) into superoxide radicals (•O₂⁻) [Eq. (6)]. Furthermore, the superoxide radicals (•O₂⁻) also may react with H₂O and H⁺ to form •HO₂⁻ and H₂O₂, respectively [Eqs. (7) and (8)] and degrade phenol [Eq. (9)]. The graphical representation of overall separation and transfer of photogenerated electron–hole pairs within LaFeO₃ nanocrystalline, and photodegradation of phenol under visible light irradiation is illustrated in Fig. 10.

4 Conclusion

In conclusion, the lanthanum orthoferrite, LaFeO₃ nanocrystalline was successfully synthesized via combustion method and its performance for synergistic adsorption/photodegradation of phenol in synthetic pharmaceutical wastewater was studied. Morphological, optical and chemical properties of the LaFeO₃ nanocrystalline exhibited a well-crystalline form with excellent band gap

energy and it is aligned with previous studies carried out. It showed the outstanding efficiency for phenol removal at numerous parameters including different pH, catalyst loading and initial concentration of phenol. The scavenging experiments conducted proved that the photocatalytic mechanism of LaFeO₃ nanocrystalline is mostly contributed by the formation of VB holes and superoxide radicals. With further research, LaFeO₃ can be a suitable candidate for photocatalytic treatment of pharmaceutical wastewater.

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Compliance with ethical standards

Conflicts of interest The authors report no conflicts of interest in this work.

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