

Enhanced photocatalytic degradation of 2,4-dichlorophenol in water solution using Sr-doped ZnAl₂O₄ nanoparticles

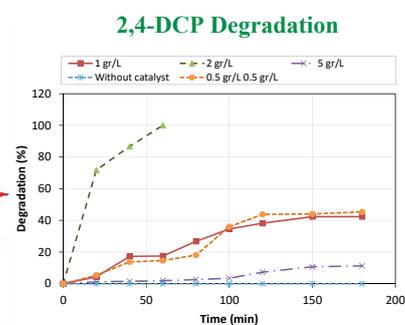
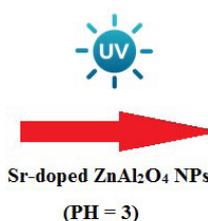
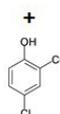
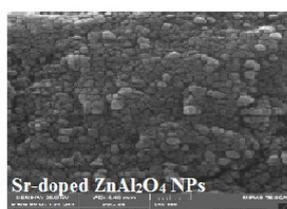
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HIGHLIGHTS

- ZnAl₂O₄ and Sr-doped ZnAl₂O₄ nanoparticles were synthesized by co-precipitation and were characterized using XRD, FE-SEM, BET, and EDX techniques.
- The photocatalytic degradation of 2,4-DCP by ZnAl₂O₄ and Sr-doped ZnAl₂O₄ samples was comparatively studied under UV irradiation.
- The reusability of the catalyst was evaluated.
- The results demonstrate that Sr-doped ZnAl₂O₄ nanoparticles exhibit considerably high catalytic stability with more than 90% degradation after the third catalytic cycle.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnAl₂O₄ and Sr-doped ZnAl₂O₄ nanoparticles were synthesized by co-precipitation using ammonia as precipitating agent, followed by thermal treatment at 700°C. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and the Brunauer-Emmett-Teller (BET) were employed to clarify the structure and morphology of the samples. In addition, the presence of Sr in Sr-doped ZnAl₂O₄ NPs was further evidenced from energy-dispersive X-ray analysis (EDX). The Photocatalytic activity of ZnAl₂O₄ and Sr-doped ZnAl₂O₄ nanoparticles were evaluated in the photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous media under the UV irradiation technique. The effect of various parameters, including catalyst dosage, 2,4-DCP concentration, pH, and temperature, on the degradation of 2,4-DCP was investigated. With 0.6 wt% Sr doped ZnAl₂O₄ samples after 60 min irradiation, 100% of 2,4-DCP photodegradation was observed in acidic conditions, while with undoped ZnAl₂O₄ samples only 67% 2,4-DCP was removed upon UV irradiation for 200 min. The reusability of the catalyst was examined under optimized conditions. The results demonstrate that Sr-doped ZnAl₂O₄ nanoparticles exhibit considerably high catalytic stability with more than 90% degradation after the third catalytic cycle.

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1. Introduction

The widespread occurrence of toxic organic compounds in the aquatic environment has increased concern for public health. Chlorophenols are well-known environmental pollutants owing to their high potential of zootoxicity and phytotoxicity. In particular, 2,4-dichlorophenol (DCP) has been listed by the US EPA as a priority pollutant the community has a right to know about [1,2]. These compounds infect the aquatic environment through various outputs of industrial and non-industrial activities. Accordingly, the elimination of the phenolic compounds from industrial effluents is an imperative requirement to ensure human health [3-6]. The removal of phenolic compounds from wastewater and drinking water supplies has recently received widespread attention [7]. Traditional methods of wastewater treatment, such as physical, biological and enzymatic processes [8-10], with their limitations and disadvantages are unable to decompose all of the phenolic compounds. Since the usage of these proceedings are costly and could possibly introduce more contaminants into the environment, developing efficient technologies to minimize these limitations while producing the desired complete mineralization of organic contaminants is of particular importance. Thus, studying destruction and decomposition methods which convert phenolic compounds into safe materials and non-hazardous species is a demanding area of research. Recently, photocatalytic decomposition of phenolic compounds with different semiconductor materials and with or without ultraviolet light has been reported to be a useful method for removing these compounds from the aquatic environment. Among the semiconductors in the photocatalytic degradation process, TiO_2 , ZnO , CuO , CeO_2 , V_2O_5 , BaO-ZnO nano-composite, etc. are employed due to their ability to produce hydroxyl radicals which destroys numerous types of organic contaminants. Moreover, they are able to destroy a wide range of phenolic compounds without generation of harmful byproducts while being environmentally friendly and cost effective [11-18]. ZnAl_2O_4 with high thermal and chemical stability, hydrophobic behavior and high mechanical resistance [19] is widely applied as a catalyst in various organic transformations such as dehydration [20], acetylation [21] hydrogenation and dehydrogenation [22]. ZnAl_2O_4 is also a semiconductor material suitable for ultraviolet (UV) photoelectronic

application due to its wide energy bandgap (about 3.8 eV) [23,24]. In recent years, zinc aluminate nanoparticles have gained considerable interest in the catalysis field [25-28]. Photocatalytic performance of bismuth doped zinc aluminate and $\text{ZnO/ZnAl}_2\text{O}_4$ catalyst have been studied by Kirankumar *et al.* and Huo *et al.*, respectively, under UV-light irradiation [29,30]. The photocatalytic degradation of toluene with the Ag-doped ZnAl_2O_4 and ZnAl_2O_4 samples was comparatively studied by Zhu *et al.* under UV-light irradiation. The results indicated that the Ag-doped ZnAl_2O_4 sample exhibited a higher capacity for the degradation of toluene [31]. To our knowledge, Sr-doped ZnAl_2O_4 spinel nano-particles have not reported for photocatalytic activity.

In the present work, ZnAl_2O_4 and Sr-doped ZnAl_2O_4 nanoparticles are synthesized by the co-precipitation method using ammonia as the precipitating agent and then characterized. The photocatalytic performances for degradation of 2,4-DCP over the 0.6 wt% Sr doped ZnAl_2O_4 and undoped ZnAl_2O_4 photocatalysts were comparatively studied. The treatment conditions, such as pH, photocatalytic dosage, 2,4-DCP concentration, and temperature, have been optimized. Moreover, the reusability of the catalyst was examined under optimized conditions.

2. Experimental

2.1. Material and instrumentation

All reagents were purchased from Merck and Aldrich and used without further purification. Phase identification and crystallite size determination were carried out by XRD measurements using a STOE-STADI MP diffractometer with $\text{Cu-K}\alpha$ radiation. FE-SEM was taken by a Tescan Mira3 photograph to examine the shape of the samples. The Brunauer-Emmett-Teller (BET) surface area was measured by a Quantachrome Nova 2200 instrument and Elemental analyses of the product was conducted using an energy-dispersive X-ray spectroscope (EDX).

2.2. Synthesis procedure

Zinc aluminate (ZnAl_2O_4) and strontium doped zinc aluminate (Sr-doped ZnAl_2O_4) nanoparticles were synthesized by the co-precipitation method. An aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

and $\text{Sr}(\text{NO}_3)_2$ were prepared in 200 ml of ultra-pure water and were stirred for 15 min (solution A). Solution B was prepared by dissolving 15 ml precipitating agent ammonia in 50 ml of ultra-pure water and 50 ml of ethanol. Solution B was slowly added drop-wise to solution A under vigorous magnetic stirring. The mixture was aged for 1h at room temperature. The resulting precipitate was filtered, washed with water several times then dried in an oven at 100°C for 5 h, and finally calcined at 700°C for 3 h.

2.3. Photocatalytic degradation procedure

The photocatalytic degradation of the 2,4-DCP solution was performed using a solution of the 2,4-DCP substrate in water and Sr-doped ZnAl_2O_4 NPs as catalyst. The solution was stirred under UV irradiation (273 nm), with three 8 W ultraviolet lamp as the source, in Pyrex flasks at room temperature. The absorption spectrum of the suspension mixture was measured periodically using a UV-Vis spectrophotometer (UNICO S2100) after centrifugation at a speed of 4000 rpm/min for 2 min to ensure the degradation of the 2,4-DCP solution. The degradation yield was calculated from the Eq. (1):

$$\text{Degradation yield (\%)} = (C_i - C_0) / C_0 \times 100 \quad (1)$$

where C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of 2,4-DCP at the initial stage and C_t ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of 2,4-DCP at time t (min).

3. Result and discussion

3.1. Characterization of the ZnAl_2O_4 and Sr-doped ZnAl_2O_4 samples

X-ray powder diffraction analysis using an advance diffractometer (for a 2θ range from 0° to 80° with a step size of 0.01° (2θ)) with monochromatic Cu-K α radiation was performed on the samples to identify the crystalline phase and compare the particle size. Fig. 1 shows that the final product was ZnAl_2O_4 with the expected spinel structure, and all the peaks can be indexed as the spinel ZnAl_2O_4 phase (space group Fd-3m, Reference code: 01-074-1136). The characteristic peaks at 2θ of 31.35, 36.74, 44.75, 55.74, 59.43 and 65.43 correspond to the (220), (311), (400), (422), (511) and (440) crystallographic

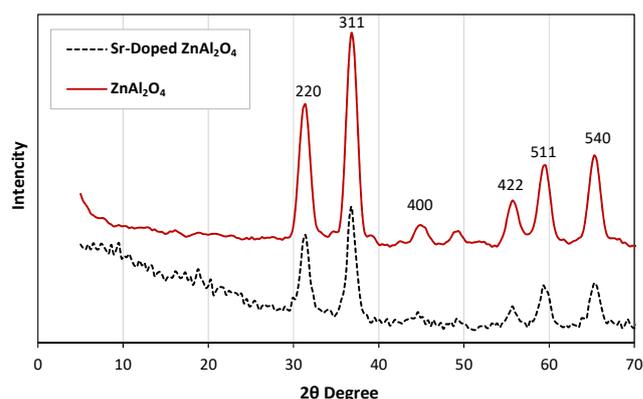


Fig. 1. XRD pattern of the ZnAl_2O_4 and Sr-doped ZnAl_2O_4 samples.

nucleation planes of the ZnAl_2O_4 spinel phase, respectively. Broadening of peaks and decrease in intensity of (311) is observed because of strontium substitution in zinc aluminate. The average sizes of the ZnAl_2O_4 and Sr-doped ZnAl_2O_4 samples determined by X-ray peak broadening analysis of the (311) reflection are about 35.5 nm and 35.3 nm, respectively. The average particle size of the Sr-doped ZnAl_2O_4 sample is slightly smaller than that of the ZnAl_2O_4 sample. No peaks corresponding to Sr species could be observed in the X-ray patterns. This is due to the low content of Sr in the sample; but as shown in Fig. 2, the presence of Sr in the ZnAl_2O_4 NPs was further evidenced by energy-dispersive X-ray analysis (EDX).

FE-SEM photograph of the ZnAl_2O_4 and Sr-doped ZnAl_2O_4 NPs in Fig. 3 demonstrates that the samples consisted of uniform shape and size particles with a diameter of less than 100 nm.

The surface area of the catalyst plays a vital role in the catalytic activity; increase in surface area and large pores have a positive influence on the photocatalytic activity [29]. The specific surface area and porosity of the two samples were determined (Fig. 4). The specific surface area was calculated from the desorption isotherms by the BET equation, using the data in a P/P_0 range between 0.05 and 1.0. The specific surface area of the ZnAl_2O_4 sample and Sr-doped ZnAl_2O_4 sample is 63.529 and 65.850 $\text{m}^2\cdot\text{g}^{-1}$, respectively. The specific surface area increases a little due to strontium loading. Analysis of the porosity was carried out by the BJH method. These two samples display a monomodal pore size distribution with the most frequent pore radii of about 8.8 nm and 4.6 nm, respectively (Fig. 4a). The prepared samples are mesoporous materials according to the distribution of pore sizes. The total pore volumes (at $P/P_0 = 0.99$)

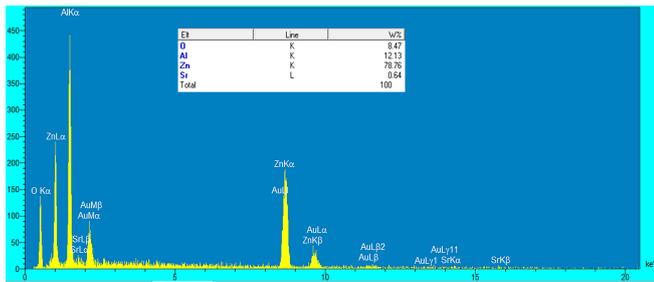


Fig. 2. EDX pattern of Sr-doped ZnAl₂O₄ nanoparticles.

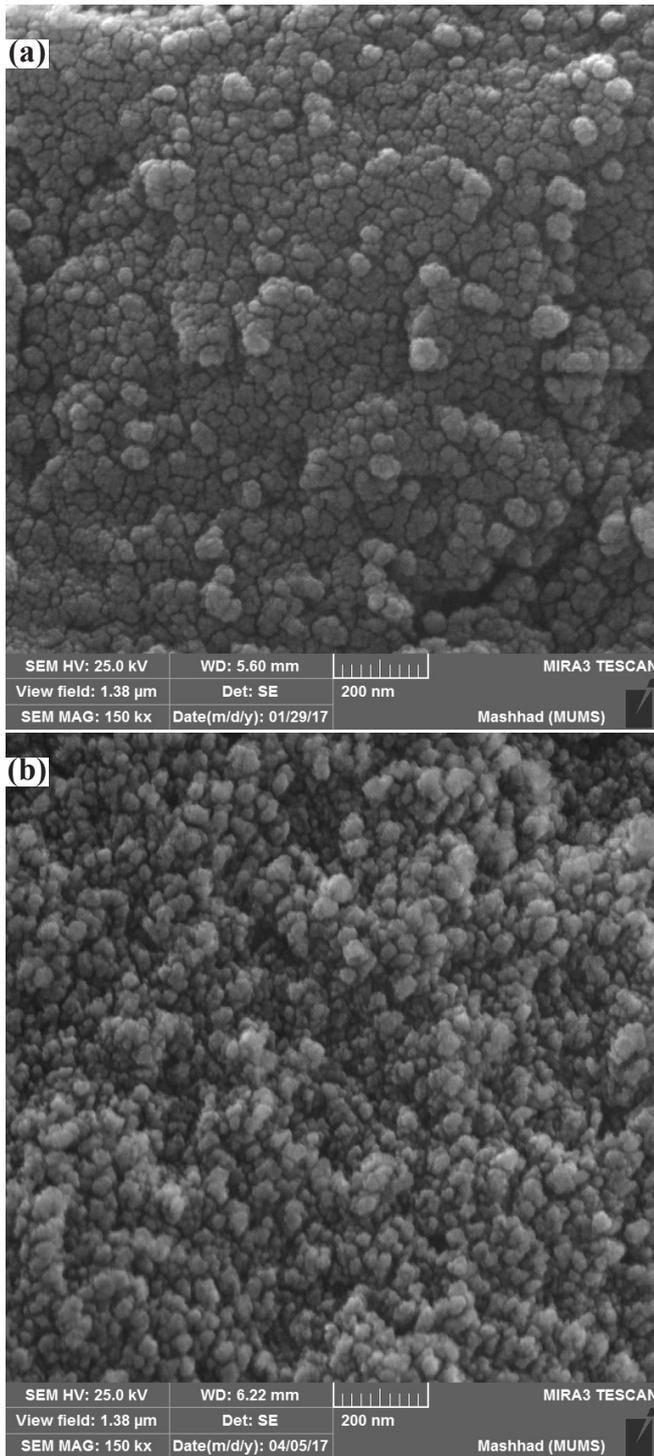


Fig. 3. FE-SEM photograph of (a) Sr-doped ZnAl₂O₄ and (b) ZnAl₂O₄ samples.

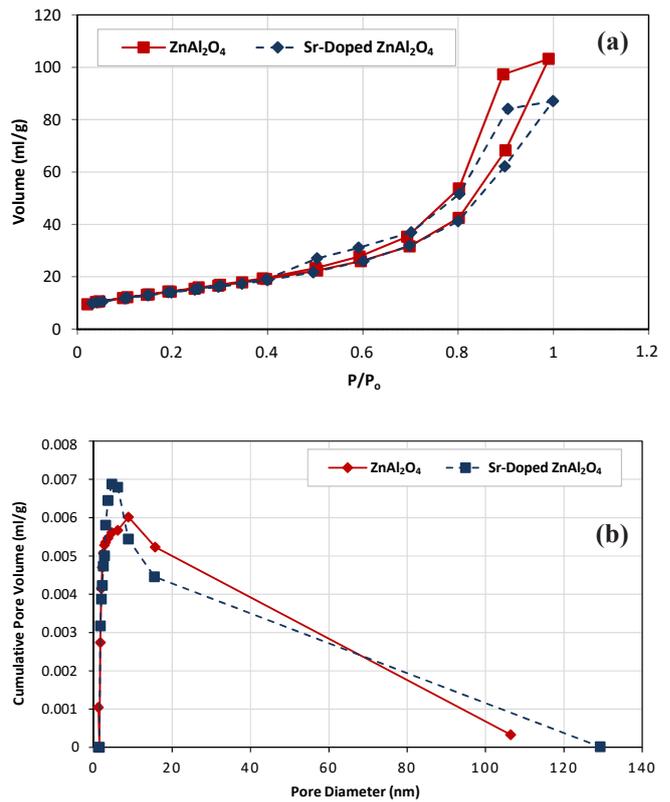


Fig. 4. (a) BJH pore size distributions and (b) N₂ adsorption-desorption isotherms of the ZnAl₂O₄ and Sr-doped ZnAl₂O₄ samples.

for the ZnAl₂O₄ and Sr-doped ZnAl₂O₄ samples are 0.163 and 0.139 cm³.g⁻¹ (Fig. 4b), respectively. The Sr-doped ZnAl₂O₄ sample has the highest surface area and monomodal pore size distribution. These features are important for the accessibility of reactant molecules to the catalysts [31].

3.2. Photocatalytic degradation of 2,4-DCP

The potential of Sr-doped ZnAl₂O₄ NPs as a catalyst was examined on the degradation removal of 2,4-DCP from aqueous solution. It is obvious that with the absorption of UV photons in the aqueous solutions, a cascade of reactive species including hydroxyl radicals (HO[•]) and superoxide anion (O₂^{•-}) is generated. The abundance of these species in the system is dependent on various factors including pH, the structure of photocatalyst, and electrochemical potential of the media [32].

3.3. Effect of pH

pH of the solution is an indispensable variable in photocatalytic reaction since it governs the surface

charge properties of the semiconductor photocatalyst [33]. The degradation behavior of 2,4-DCP with the concentration of 40 mg.L^{-1} were conducted during 0-180 min at pH 3, 5, 7, 9 and 11 using Sr-doped ZnAl_2O_4 NPs (2 g.L^{-1}). The obtained results summarized in Fig. 5 shows 2,4-DCP was only 100% degraded at pH 3, while degradation yield at other pH was negligible. The point of zero charge (pH_{pzc}) of ZnAl_2O_4 is about 7.8 [34], thus above this value the ZnAl_2O_4 surface is negatively charged and below it is positively charged. In the acidic solution phenol is primarily in its nonionic form, water solubility is minimized, and the adsorption onto the catalyst is maximized [35]. At higher pH, phenol tends to exist as a negatively charged phenolate species, which have extremely strong solubility in the solution and will not be significantly adsorbed on the catalyst surface [36]. Also, the coulombic repulsion between the OH^- and the negatively charged surface of the particles could prevent the formation of $\cdot\text{OH}$ radicals; hence, reducing the photodegradation rate of chlorophenol. Moreover, high pH favors the formation of carbonate ions which are effective scavengers of OH^- ions and can cause less degradation of chlorophenol [36]. With respect to the above results, we conclude that the degradation efficiency is favorable in the acidic condition.

3.4. Effect of initial 2,4-DCP concentration

The effect of initial DCP concentration on the degradation yield was investigated. In the same conditions as 2 g.L^{-1} of catalyst and $\text{pH} = 3$, various concentration of 2,4-DCP (20, 30, 40, 50, 60 and 70 mg.L^{-1}) were subject to the study. The obtained results are depicted in Fig. 6. As revealed in Fig. 6,

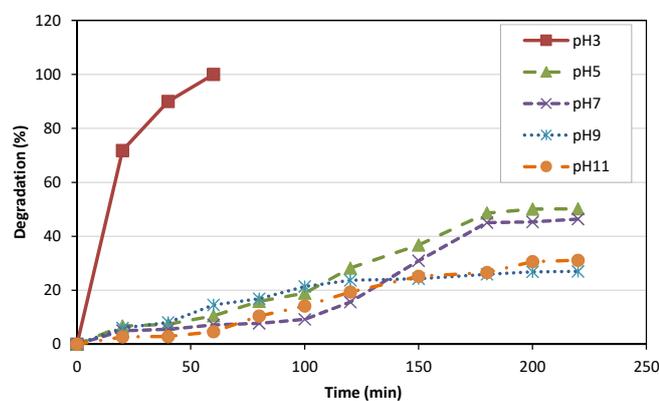


Fig. 5. Photocatalytic degradation of 2,4-DCP: effect of pH solution (catalyst: 2 g.L^{-1} , DCP concentration: 40 mg.L^{-1}).

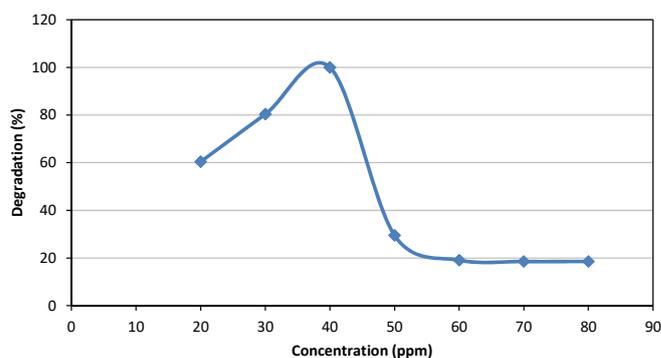


Fig. 6. Photocatalytic degradation of 2,4-DCP: effect of initial DCP concentration ($\text{pH} = 3$, catalyst: 2 g.L^{-1}).

as the DCP concentration increases, the degradation efficiency increases. However, at more than 40 mg.L^{-1} the degradation rate seems to strongly decrease, which may be due to the saturation of active sites on the adsorbent. Additionally, at a higher concentration the light penetration into the suspension is reduced; consequently, a decrease in the DCP degradation occurred. Hence, 40 mg.L^{-1} was considered to be the optimum substrate concentration for this study.

3.5. Effect of catalyst dosage

To optimize the Sr-doped ZnAl_2O_4 suspension concentration, the effect of various catalyst dosages, including 0.0, 0.5, 1, 2 and 5 g.L^{-1} , on the 2,4-DCP degradation was investigated. The results are illustrated in Fig. 7. In the absence of a catalyst, a negligible amount of 2,4-DCP is degraded under the same reaction conditions, but by increasing the catalyst amounts up to 2 g.L^{-1} the degradation efficiency increased. After that value, the efficiency decreased. The increase in

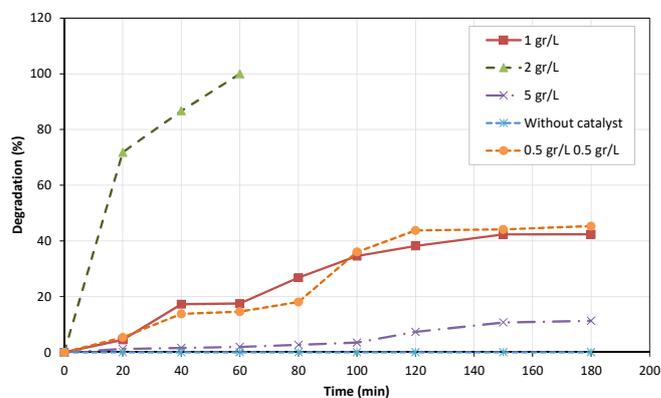


Fig. 7. Photocatalytic degradation of 2,4-DCP: effect of catalyst dosage ($\text{pH} = 3$, DCP concentration: 40 mg.L^{-1}).

the efficiency appears to be due to the increase in the total surface area, namely the number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. However, when the Sr-doped ZnAl_2O_4 photocatalyst was overdosed, the number of active sites on the Sr-doped ZnAl_2O_4 surface may become nearly constant due to decreased light penetration, increased light scattering, and the loss in surface area occasioned by agglomeration (particle-particles interactions) at high solid concentration [37]. Therefore, 2 g.L^{-1} of Sr-doped ZnAl_2O_4 suspension concentration was adopted as the optimal amount of photocatalyst for the sequential experiment.

3.6. Effect of temperature

Further experiments were made to study the effect of temperature on the photocatalytic degradation of 2,4-DCP. It was observed that the degradation efficiency of DCP increased as the temperature increased up to 50°C and was completed in a shorter time (60 min) as compared with 25°C (180 min). Further increasing the temperature up to 80°C caused the degradation efficiency to decrease (Fig. 8).

3.7. Effect of anion additives

In the next step, the effect of the presence of inorganic anion additives on the 2,4-DCP degradation rate was studied at a 0.4 mg.L^{-1} anion level, 40 mg.L^{-1} initial DCP concentration and $\text{pH}=3$. Inorganic anions investigated include CO_3^{2-} , HPO_4^{2-} , SO_3^{2-} and Cl^- , all were used as Na salts. Fig. 9 shows a

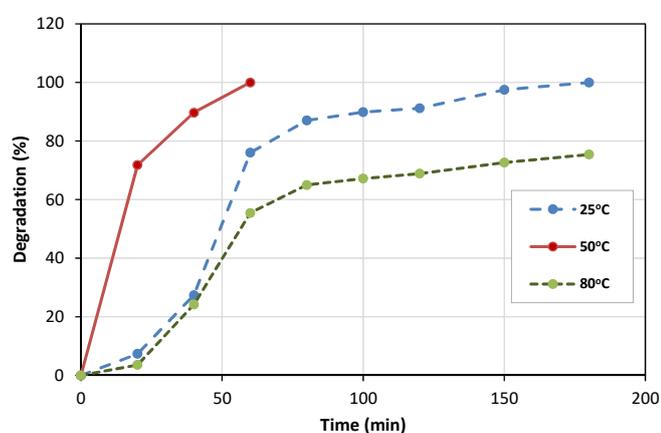


Fig. 8. Photocatalytic degradation of 2,4-DCP: effect of temperature ($\text{pH}=3$, DCP concentration: 40 mg.L^{-1}).

comparison of DCP removal in the presence of the added anions. The figure shows inhibition of the DCP removal rate in the order $\text{CO}_3^{2-} < \text{S}_2\text{O}_3^{2-} < \text{Cl}^- < \text{HPO}_4^{2-}$. The observed inhibition effect is often explained by competitive adsorption [38]. The mechanism of rate inhibition by HPO_4^{2-} has not been identified, but blockage of the active sites of the semiconductor particles has recently been suggested [39]. Sr-doped ZnAl_2O_4 NPs surface is positively charged at $\text{pH}=3$, and Cl^- can be easily adsorbed onto the positively charged surface of the catalyst by electrostatic attraction, leading to competitive adsorption.

3.8. Comparison of the photocatalytic activity of ZnAl_2O_4 and Sr-doped ZnAl_2O_4 NPs

Photocatalytic activity of the undoped and doped samples were studied in optimum reaction conditions where 100 % of phenol photodegradation was observed in 0.6 wt.% Sr doped ZnAl_2O_4 samples after 60 min irradiation, while with undoped ZnAl_2O_4 samples only 67% 2,4-DCP was removed upon UV irradiation for 200 min as shown in Fig. 10. It is clear that the photocatalytic activity is affected by various parameters such as crystalline size, surface area, and optical properties of the synthesized compounds. Doping of metal oxides with metals or transition metals creates quasi-stable energy states within the band gap and thus affects optical and electronic properties [40]. There are reports on the enhancement of photocatalytic activity in ZnO by doping with Co [41], Mn [42], Pb, and Ag [40]. Kirankumar *et al.* reported that doping of bismuth in zinc aluminate decreases the band gap and increases

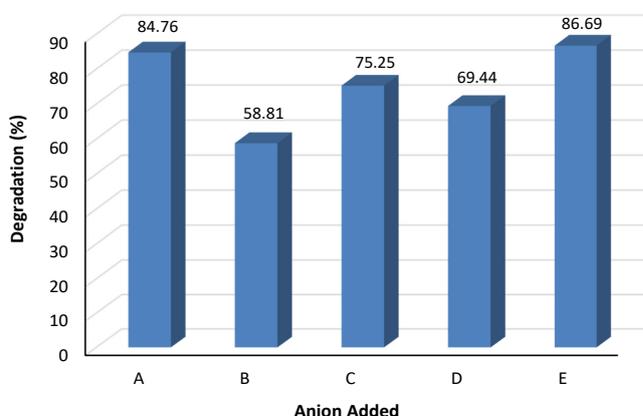


Fig. 9. The influence of inorganic anions on photocatalytic removal. Initial conditions: DCP concentration = 40 mg.L^{-1} , catalyst concentration = 2 g.L^{-1} , $\text{pH}=3$. A = CO_3^{2-} , B = HPO_4^{2-} , C = $\text{S}_2\text{O}_3^{2-}$, D = Cl^- , E = No anion added.

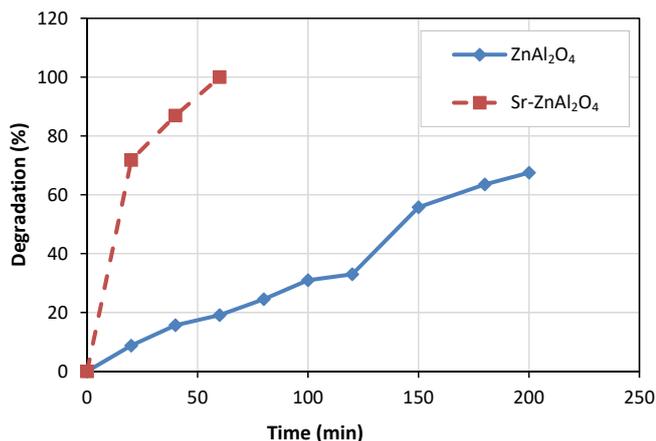


Fig. 10. Comparison of the photocatalytic activity of ZnAl₂O₄ and Sr-doped ZnAl₂O₄ nanoparticles in optimum reaction conditions.

the photocatalytic degradation of methylene blue [29]. Therefore the enhanced photocatalytic activity of doped zinc aluminate could be due to increased surface area, large pore volume, and lesser crystalline size of strontium doped zinc aluminate nanoparticles than zinc aluminate.

3.9. Recyclability of the catalyst

The reusability of the catalyst was examined under optimized conditions. After the first catalytic run, the catalyst was removed by centrifugation, and then washed with hot water and dried at 100°C. The results demonstrate that Sr-doped ZnAl₂O₄ nanoparticles exhibit considerably high catalytic stability; and as shown in Fig. 11, more than 90% degradation was achieved after the third catalytic cycle.

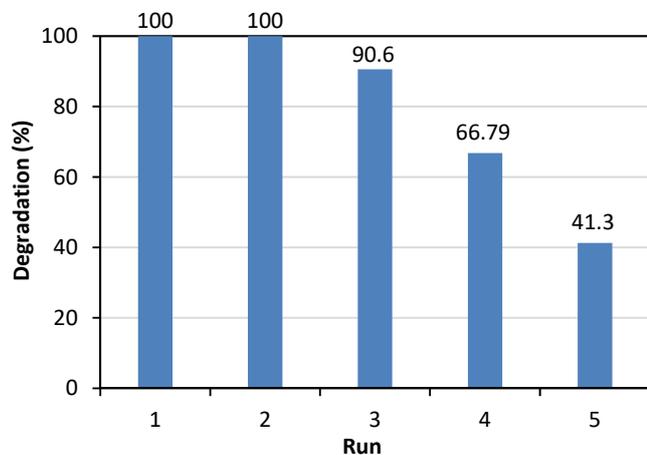


Fig. 11. Recycling tests of the Sr-doped ZnAl₂O₄ nanoparticles in optimum reaction conditions.

4. Conclusion

In summary, ZnAl₂O₄ and Sr-doped ZnAl₂O₄ nanoparticles were synthesized by co-precipitation using ammonia as precipitating agent and were characterized by using XRD, BET, FE-SEM and EDX techniques. The photocatalytic degradation of 2,4-DCP by ZnAl₂O₄ and Sr-doped ZnAl₂O₄ samples was comparatively studied under UV lamp irradiation. The effect of various parameters including catalyst dosage, 2,4-DCP concentration, pH, and temperature on the degradation of 2,4-DCP was investigated. Sr-doped ZnAl₂O₄ with 0.6 wt.% Sr was very effective compared with the undoped sample. One hundred percent of photodegradation of 2,4-DCP was achieved in 60 min, while in the undoped ZnAl₂O₄ sample only 67% 2,4-DCP was removed upon UV irradiation for 200 min. The reusability of the catalyst was also evaluated under optimized conditions. The results demonstrate that Sr-doped ZnAl₂O₄ nanoparticles exhibits considerably high catalytic stability with more than 90% degradation after the third catalytic cycle. Moreover, the presence of various anions inhibited the photodegradation efficiency with the order of CO₃²⁻ < S₂O₃²⁻ < Cl⁻ < HPO₄²⁻. These investigations demonstrated that the as-prepared Sr-doped ZnAl₂O₄ could act as an efficient potential catalyst for the treatment of chlorophenols in industrial wastewater.

Acknowledgments

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