

FeVO₄ nanoparticles synthesis, characterization and photocatalytic activity evaluation for the degradation of 2-chlorophenol

Asma Shafique^a, I.A. Bhatti^a, A. Ashar^{a,b}, M. Mohsin^a, Sheikh Asrar Ahmad^c, Jan Nisar^d, Tariq Javed^{e,*}, M. Iqbal^{f,*}

^aDepartment of Chemistry, University of Agriculture, Faisalabad, 38040, Pakistan, emails: chemnceac@outlook.com (A. Shafique), ijazchem@yahoo.com (I.A. Bhatti), ambreenashar2013@gmail.com (A. Ashar), m.mohsin618@gmail.com (M. Mohsin)

^bDepartment of Chemistry, Government College Women University, Faisalabad, 38040, Pakistan

^cDepartment of Chemistry, Division of Science and Technology, University of Education Lahore, Vehari Campus, Pakistan, email: asrarchemist@ue.edu.pk (S.A. Ahmad)

^dNational Center of Excellence in Physical Chemistry, University of Peshawar, Peshawar, 25120, Pakistan, email: pashkalawati@gmail.com (J. Nisar)

^eDepartment of Chemistry, University of Sahiwal, Sahiwal 57000, Pakistan, email: jtariqchemist@gmail.com (T. Javed)

^fDepartment of Chemistry, The University of Lahore, Lahore, 53700, Pakistan, email: munawar.iqbal@chem.uol.edu.pk (M. Iqbal)

Received 30 August 2019; Accepted 22 January 2020

ABSTRACT

Heterostructured nanoparticles are active under visible light and have gained much attention for the remediation of persistent organic pollutants under visible light irradiation. Iron vanadate (FeVO₄) was prepared by the co-precipitation technique and characterized by X-ray diffraction, scanning electron microscope, energy dispersive X-rays, and zeta particle sizer techniques. The particle size of FeVO₄ was in the range of 190–210 nm with maximum abundance at 150 nm. The particle was in a spherical shape and agglomerated form. The band-gap of FeVO₄ particles was 2.95 eV. Photocatalytic activity was evaluated by degrading 2-chlorophenol (2-CP) under solar light irradiation. The process variables, that is, catalyst dose, pH, initial concentration of CP, H₂O₂ concentration, and irradiation time are optimized using response surface methodology. At optimized conditions, up to 91% degradation of 2-CP was achieved and degradation was mentored by ultraviolet-visible spectroscopy and high-performance liquid chromatography analysis. The observed and predicted 2-CP degradation responses were in agreement with low residual values. Results revealed that FeVO₄ is active under solar light irradiation that could possibly be used for the treatment of wastewater containing toxic dyes.

Keywords: Heterostructured nanoparticle; Iron vanadate; photocatalytic activity; advance oxidation process; 2-chlorophenol

1. Introduction

Phenol and its derivatives are toxic and hazardous pollutants, which enter into the environment by various anthropogenic activities and used as disinfectant and preservation agents for fiber, paint, wood, and leather [1–3]. It is also used for the synthesis of pesticides, herbicides, fungicides, pharmaceuticals, insecticides, and dyes. Due to its toxicity, solubility, and stability in water, 2-CP containing water

needs to be treated before being discharged into water bodies. Hence, wastewater needs to be treated and an advanced oxidation process based on photocatalyst is one of the promising techniques [4–10]. Different chemical, thermal, and biological methods are being used for the removal of 2-CP from water. The treatments like reverse osmosis, adsorption, coagulation, ultra-filtration, and precipitation produce secondary pollutants and also demand the post-treatment for proper functioning. Biological method needs longer

* Corresponding authors.

degradation time and microorganisms are sensitive to the environmental conditions and toxic by-products. All these conventional treatments are time-consuming, ineffective, and non-compatible with the environment [11–21].

In this regard, there is an urgent need to develop an innovative, facile, and environment-friendly method for water purification. The ultimate goal is to attain the complete mineralization of organic pollutants into carbon dioxide and water [22–24]. In this context, the advance oxidation process is a highly efficient technology [25,26]. These processes are accomplished by the *in situ* production of strong oxidizing species such as hydroxyl radical ($\cdot\text{OH}$) and superoxide anion radical ($\text{O}_2^{\cdot-}$) which are responsible to trigger the free radical reaction to degrade the organic compound in an aqueous medium to harmless substances [13,27]. Heterogeneous photocatalysis is an advance oxidation process which is an efficient and promising approach for the degradation of the organic contaminants in the atmospheric and aquatic environment. For the photocatalytic degradation of pollutants, semiconductor-based photocatalysis is an efficient technique and has proved a real interest for the researchers due to its innovative, less expensive, and robust nature [28]. Semiconductor based photocatalysis involves the generation of electron and hole pair in valence and conduction band, respectively, by the excitation of electrons from the valence band to conduction band when the light of suitable energy equivalent to band-gap falls on the semiconductor material. Electron and hole pairs generated are responsible for the secondary redox reactions to degrade persistent organic pollutants. However, it has some limitations such as a large band-gap which requires photon of ultraviolet (UV) origin and thus limits the efficacy of the photocatalyst [29].

Different techniques are used to overcome the intrinsic limitations by reducing the size of photocatalytic materials at the nanoscale, formulation of composites at the nanoscale level, doping of materials with metals and non-metals and formation of metal-organic frameworks are useful to control band-gap of the photocatalysts [29,30]. For the degradation of organic pollutants, materials constitute a smaller band-gap and are active under visible light have dominant importance in heterogeneous photocatalysis. Inorganic compounds such as multi-metallic oxides of vanadates, tungstates, and molybdates having shorter band-gap are efficient for catalytic applications [29,31–33]. Orthovanadates (AVO_4) based on transition metals are an important class of inorganic materials which have versatility in applications in several fields especially in catalysis. The large number of new compounds can be formed due to many stable oxidation states of the vanadium [25].

Vanadium has the ability to combine with metal ions due to variable oxidation state and vanadates emerged an important class of materials that have been used in diverse fields such as photocatalyst, lithium-ion batteries, water splitting, catalyst, supercapacitors, antibacterial, ion-exchange materials, luminescence, and photoluminescence device and gas sensors [34]. V_2O_5 has been successfully employed to fabricate a diverse type of heterostructured materials (LaVO_4 , EuVO_4 , and BiVO_4). V_2O_5 is a n-type semiconductor with narrow band-gap considered for using in photocatalytic degradation and water treatment. However, studies on $\text{FeVO}_4/\text{V}_2\text{O}_5$ to prepare heterostructured nanoparticles are rare and

on the basis of band-gap tuning, their photocatalytic activity (PCA) can be enhanced. Different methods have been reported to synthesize iron vanadate (FeVO_4), that is, sol-gel, wet chemical, microwave, hydrothermal, solid-state, and precipitation [34].

Based on the aforementioned facts, FeVO_4 heterostructured nanoparticles were prepared by solution chemistry and characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM), Energy dispersive X-rays (EDX), diffused reflectance spectroscopy (DRS), and Zeta particle sizer techniques. The PCA was evaluated by degrading 2-chlorophenol (2-CP, Fig. 1) under sunlight irradiation. The process variables, that is, catalyst dose, pH, the concentration of CP, H_2O_2 concentration, irradiation time were optimized using response surface methodology (RSM). Under optimized conditions rate constant of the photocatalytic reaction was determined and the efficiency of synthesized FeVO_4 was compared with commercial catalysts.

2. Material and methods

2.1. Chemicals and reagents

All the chemical reagents used were of analytical grade. Ferric nitrate [$\text{Fe}(\text{NO}_3)_3$], ammonium salts of vanadates, polyethylene glycol (PEG), ethylene, and ethanol were purchased from Sigma-Aldrich (St. Louis, United States). Commercial FeVO_4/C was purchased from Merck (Lincoln Ave, Rahway, United States) and is used without any purification and characterization. Ultrapure water of resistivity of 18.2 M Ω cm (at 25°C) was used for the preparation of solutions.

2.2. Synthesis procedure

For the fabrication of FeVO_4 , the co-precipitation method was adopted as reported by Nithya et al. [35]. Ammonium metavanadate (NH_4VO_3) and $\text{Fe}(\text{NO}_3)_3$ were used as precursors. Iron nitrate (0.1 M) solution was prepared by dissolving 4.84 g/200 mL water and ammonium metavanadate (0.1 M) was prepared by dissolving 2.43 g/200 mL of water. NH_4VO_3 solution was heated at 75°C till a clear solution was obtained. Then, 5 mL of PEG was added and the solution was stirred for 30 min. Then, iron nitrate solution was mixed dropwise along with slow stirring. Yellowish-brown precipitates were appeared and the reaction was continued for 8 h. Precipitates were filtered and washed several times with water and ethanol and dried at 70°C. The synthesized FeVO_4/S was characterized by SEM, EDX, XRD, Particle Sizer, and DRS techniques.

Table 1
Experimental design showing the process variable and their levels

| Name | Symbols | Range and levels | | |
|--------------------------|---------|------------------|------------|-----------|
| | | Low (-1) | Middle (0) | High (+1) |
| Catalyst load, g/L | A | 1 | 2 | 3 or 1.5 |
| pH | B | 3 | 6 | 9 |
| 2-CP conc., mg/L | C | 10 | 20 | 30 |
| H_2O_2 % | D | 3 | 5 | 7 |

2.3. Photo-catalytic activity

The PCA was evaluated by degrading 2-CP as a function of catalyst load, pH, 2-CP concentration, and H₂O₂ concentration, whose level is shown in Table 1 and responses are presented in Table 2. Central composite design (CCD) was employed for statistical modeling of the degradation process. After mixing the 2-CP and catalysts and adjusting the conditions (pH adjustment and H₂O₂ addition), the mixture was kept in the dark for 30 min in order to ensure the adsorption-desorption of the catalyst surface. The photocatalytic experiments were done under artificial solar radiation (150 W D65 tubes) in a closed reactor. After stipulated time intervals, 2 mL sample was drawn, filtered by Millipore filter and analyzed for dye residual concentration of 2-CP. Blank experiments were also performed under similar conditions to evaluate the pure effect of photolysis, H₂O₂ and a commercial sample of FeVO₄. Triplicate degradation experiments were run under ambient conditions (25°C) and data thus obtained is averaged. The 2-CP percentage of degradation

was estimated by employing the relation shown in Eq. (1). Where C_i is the initial concentration of 2-CP and C_f is the concentration of 2-CP after photocatalytic treatment.

$$2\text{-CP degradation (\%)} = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (1)$$

2.4. Spectrophotometric and HPLC analysis

The 2-CP degradation was monitored by HPLC and ultraviolet-visible spectroscopy (243 nm). For HPLC analysis, HPLC (Hewlett-Packard, Alexandria, United States, Series 1100) equipped with a UV detector at 243 nm and C18 column was used. Acetonitrile and water were used as eluent A and B with a volume ratio of 70:30, which were filtered and degasified and used as a mobile phase with a flow rate of 1 cm³/min with injection volume 1 µL.

3. Results and discussion

3.1. Characterization

The FeVO₄ was characterized by EDX, XRD, Particle size analysis, and SEM techniques. EDX analysis was carried out in order to determine the elemental composition and percentage purity of FeVO₄. EDX analysis indicated the presence of V, O, and Fe in the material synthesized (Fig. 2). The intensities of the peaks can also be correlated with the percentage of respective elements. Hosseinpour-Mashkani et al. [36] also reported similar results for FeVO₄

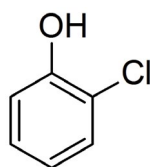


Fig. 1. Structure of 2-chlorophenol used for PCA evaluation.

Table 2
Experimental layout showing the predicted and actual 2-CP degradation values

| Run | Experimental conditions | | | | Degradation (%) age | |
|-----|-------------------------|-------|-----------------------|-----------------------------------|---------------------|-----------|
| | Catalyst load (g/L) | pH | 2-Chlorophenol (mg/L) | H ₂ O ₂ (%) | Actual | Predicted |
| 1 | 3 | 9 | 30 | 3 | 35 | 34.77 |
| 2 | 3 | 9 | 10 | 3 | 63 | 62.73 |
| 3 | 3 | 3 | 30 | 7 | 38 | 37.76 |
| 4 | 1 | 9 | 10 | 7 | 54 | 53.73 |
| 5 | 3 | 3 | 10 | 7 | 70 | 69.74 |
| 6 | 1 | 3 | 30 | 3 | 21 | 20.76 |
| 7 | 1 | 9 | 30 | 7 | 36 | 35.77 |
| 8 | 1 | 3 | 10 | 3 | 48 | 47.73 |
| 9 | 0.32 | 6 | 20 | 5 | 42 | 42.35 |
| 10 | 3.68 | 6 | 20 | 5 | 43 | 43.36 |
| 11 | 2 | 0.96 | 20 | 5 | 46 | 46.35 |
| 12 | 2 | 11.10 | 20 | 5 | 47 | 47.35 |
| 13 | 2 | 6 | 3.18 | 5 | 91 | 91.398 |
| 14 | 2 | 6 | 36.82 | 5 | 47 | 47.31 |
| 15 | 2 | 6 | 20 | 1.64 | 50 | 50.35 |
| 16 | 2 | 6 | 20 | 8.37 | 66 | 66.36 |
| 17 | 2 | 6 | 20 | 5 | 77 | 76.03 |
| 18 | 2 | 6 | 20 | 5 | 76 | 76.04 |
| 19 | 2 | 6 | 20 | 5 | 76 | 76.04 |
| 20 | 2 | 6 | 20 | 5 | 75 | 76.03 |
| 21 | 2 | 6 | 20 | 5 | 77 | 76.03 |

synthesized by the ultrasonic approach. XRD pattern of FeVO_4 is shown in Fig. 3. XRD pattern is attributed to the pure form of FeVO_4 , which is $\text{FeVO}_4 \cdot n\text{H}_2\text{O}$ and in line with JCPDS card no. 27-0257. Average crystallite size (L) of FeVO_4 was calculated using the relation shown in Eq. (2) [37].

$$L = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where $\lambda = 1.54 \text{ \AA}$ (λ_{max} for X-rays), $k = 0.9$ (shape constant), $\theta = 2\theta/2$ (Bragg's angle of diffraction), $\beta = \text{FWHM}$ (in radian; full width at half maximum peak intensity) and the average crystallite size of FeVO_4 was found to be 35 nm. These findings are in line with reported studies, that is, Deng et al. [38] investigated the influence of calcination temperature on the crystallinity of iron vanadate and it was observed that at 100°C broad peaks were observed, which showed the formation of amorphous compound. It was revealed that clear and intense XRD diffraction peaks were obtained by increasing the calcination temperature up to 500°C to 600°C , respectively, and concluded that gradual transformation occurs from amorphous to crystalline nature. Similarly, Nithya et al. [35] studied the effects of surfactants, reaction time and calcination temperature on the crystallinity of FeVO_4 prepared by the co-precipitation method. XRD confirmed the single phase of FeVO_4 with triclinic structure and high crystallinity. In this study, optimum temperature and reaction time furnished the crystalline sample and by increasing the temperature, the phase was changed. It was also depicted that the addition of surfactants increased the calculated X-ray density of nanocrystallites and was comparable with the standard reported value of 3.647 g/cm^3 (PDF No. 38–1372).

SEM analysis was employed to investigate the morphology and surface properties of FeVO_4 and results are shown in Fig. 4. The FeVO_4 has a fluffy texture and highly porous structure ranging in the size of 100–200 nm. These small

granules and fluffy textured FeVO_4 has great potential for catalytic activity. According to previous reports, the drying process at low temperature furnished less crystalline structure and more amorphous contents lead toward the fluffy shaped structure. It has been observed that at temperature lower than 60°C more dispersed shape and greater agglomeration effects were seen, while compact and small grains having an average size of 150 nm were obtained at high temperature. Zeta particle sizer was used to assess the particle size of FeVO_4 and results revealed that particle size was in 100–200 nm range with maximum distribution at 150 nm (Fig. 5). The morphology has greater efficacy in catalytic activity, which enables the charge carriers to move to the surface by providing the channel to the electrons transfer. The morphology and size of as prepared FeVO_4 can be effected by the synthesis conditions, that is, Chan et al. [39] prepared flake-like structure through precipitation method and particle size was up to $8 \mu\text{m}$ and base exerted strong influence on the morphology of NPs. Ozturk and Soyulu [40] also studied the effect of pH and surfactant on the morphology of FeVO_4 , which was found dependent on the addition of surfactant. Ma et al. [41] also reported the controllable synthesis of porous FeVO_4 nanorods, which was found dependent on synthesis conditions.

Optical property of the FeVO_4 was exhibited by its sunlight harvesting capacity which was found in the visible region. Diffused reflectance spectra revealed the band-gap edge at 400 nm and an increase in absorption of solar radiation bellow 520 nm (Fig. 6a). The DRS values for reflectance (%R) were used to estimate the band energy as shown in Eq. (4b) using the Kubelka Munk equation [42]. The maximum absorbing capacity of the FeVO_4 revealed band-gap to be 2.95 eV.

3.2. PCA optimization for the degradation of 2-CP

The PCA of FeVO_4 was evaluated by degrading 2-CP as a modal compound. The process variables like the concentration of 2-CP, pH, H_2O_2 concentration, and catalyst

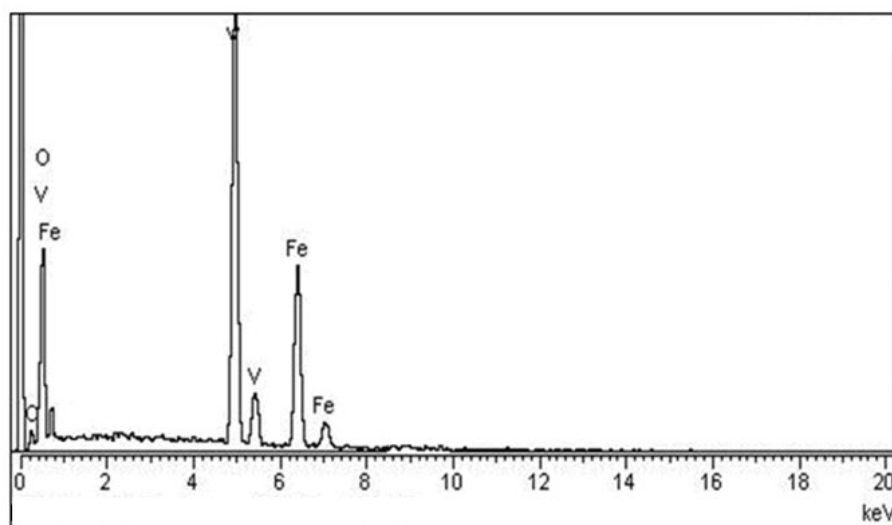


Fig. 2. EDX analysis of FeVO_4 .

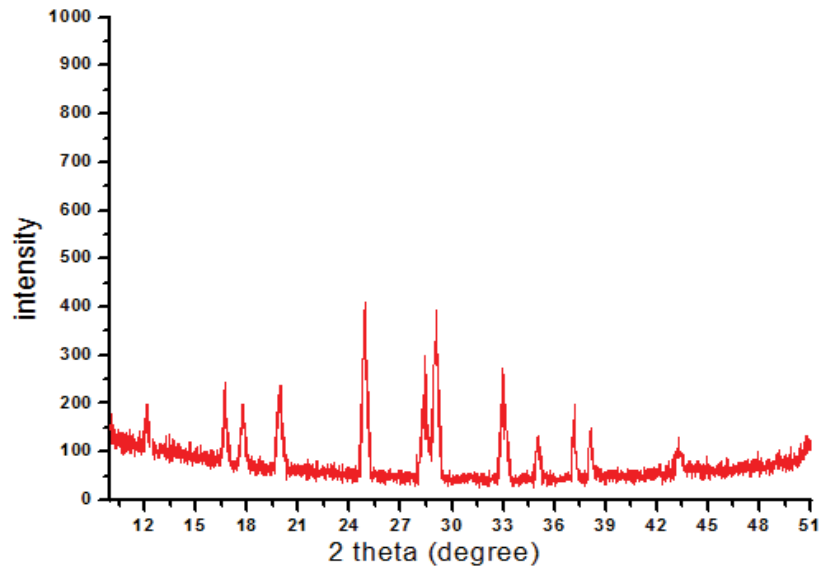


Fig. 3. XRD pattern of FeVO_4 .

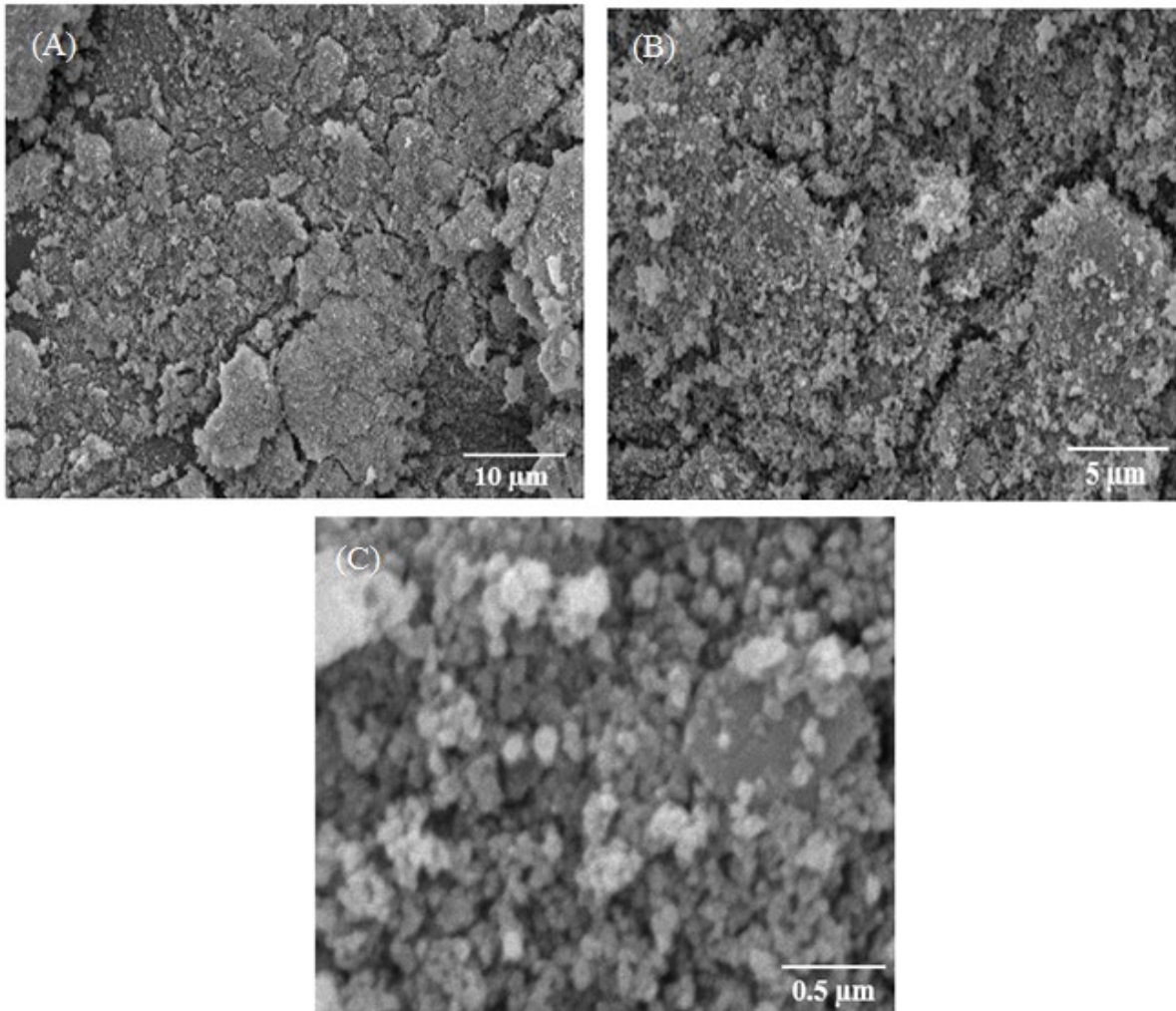


Fig. 4. SEM images of FeVO_4 . Scale bar: (a) 10 μm, (b) 5 μm, and (c) 0.5 μm.

load were optimized using RSM and effect was evaluated on the basis of 2-CP degradation. It is quite evident from the results that the degradation process was affected significantly by the process variables and the observed vs. predicted degradation is shown in Table 2. The statistical analysis of the degradation data is shown in Tables 3 and 4. A sequential process was employed for model fitting and model summary statistics were utilized for the selection of model, while insignificant lack of fit test showed good predictability for the elaboration of the optimum response. Moreover, the adequacy of the model was further analyzed through analysis of variance (ANOVA) and based on F and p -values, the efficacy of the model was evaluated. Larger F -value and smaller the value of p indicated that the model was suitable to ensure the optimal response [4,43]. Model fitting could be assessed through the determination of interaction between operational parameters in order to determine their effect on responses. F -value having 0.01 chances of noise ensures that the model is highly significant, all process variables are interdependent and have an effect on the PCA. Lower value of F calculated from ANOVA also ensures the role of different variables on the response [25,43]. The regression model also revealed that A , B , C , D , AB , AD , A^2 , B^2 , C^2 , and D^2 values are significant, while other remaining interactions such as BC , CD , BD , and AC have an insignificant effect on the response with $P > 0.05$ (A = photocatalyst load, B = pH, C = 2-chlorophenol concentration, and D = H_2O_2 %). Furthermore, R^2 -values 0.9993 for the quadratic model and 0.9996 for a cubic model with negligible deviation also indicated that the model was highly significant and insignificant lack of fit test indicated good predictability. Agreement of experimental values with predicted values showed the reliability of the CCD for optimization of process variables for the degradation of 2-CP. Optimized conditions for different operational variables were; 2 g/L catalyst load, pH 6, and 2-CP concentration 10 mg/L. For the verification of predicted values, an experiment was run under optimized conditions and the observed degradation value was found to be in concordant with the predicted results and 91% degradation of the 2-CP was achieved under optimum conditions. Contour

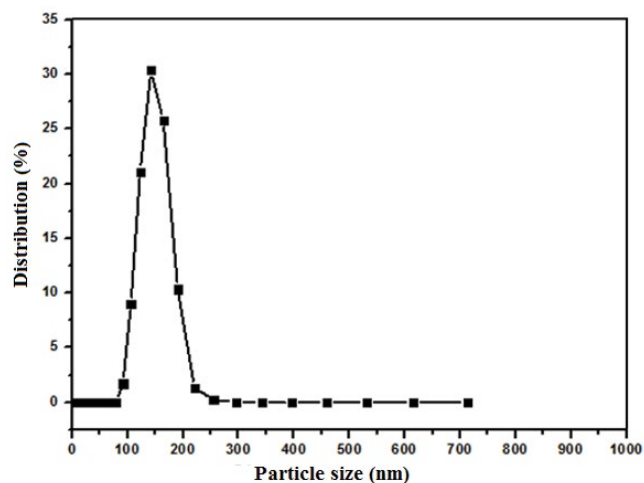


Fig. 5. Particle size distribution of $FeVO_4$.

diagrams showing the degradation of 2-CP can be seen in Figs. 7a–f. Percentage degradation of 2-CP was studied as a function of various process variables and it was observed that there exists a linear relationship between independent variables.

3.2.1. Effect of photocatalyst dose on PCA

Catalyst dose is one of the important parameters in the photocatalytic process and optimum value is at the best to enhance the PCA at the lowest catalyst dose. so that an increase in catalyst concentration up to a certain limit enhanced the degradation, which is correlated with the generation of hydroxyl radicals [29], and beyond a certain dose of catalyst agglomeration may occur and PCA may reduce due to low penetration of the light [44]. Reduction in degradation rate by increasing the catalyst dose might be due to the possibility of higher recombination rate of electron to hole pair and also higher dosage than the optimum value might cause agglomeration which ultimately causes the poor penetration of light (Figs. 6a–c). The mechanism for the photocatalytic degradation of 2-CP is shown in Eqs. (3)–(6) [8,29,45,46].

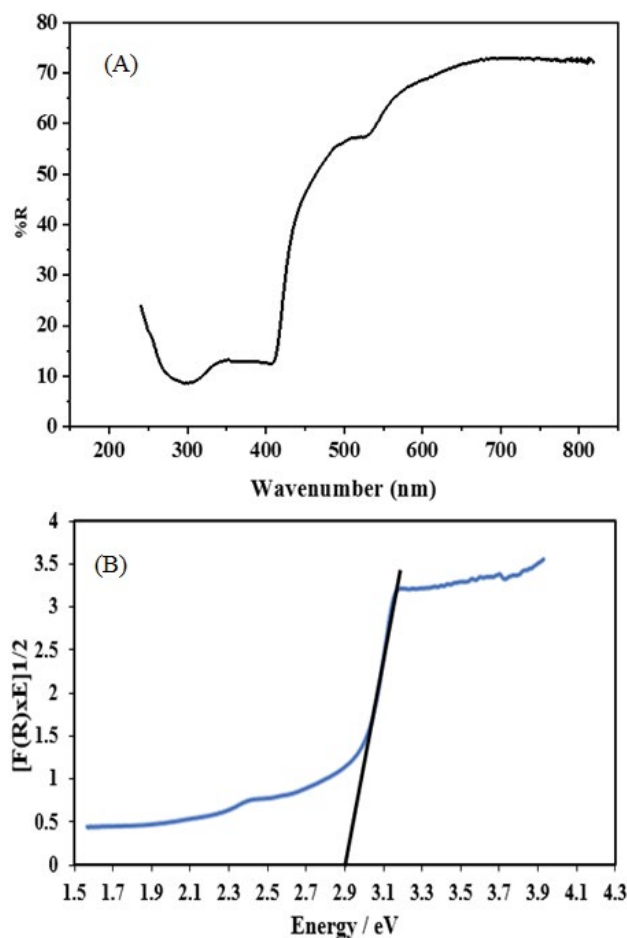


Fig. 6. (a) Diffused reflectance spectrum and (b) band gap energy of $FeVO_4$.

Table 3
Statistical analysis

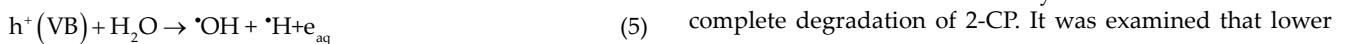
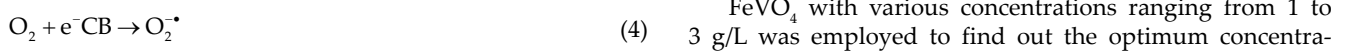
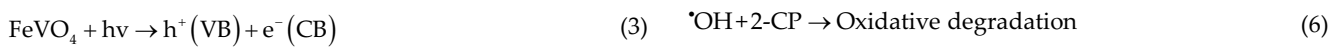
| (a) sequential model sum of squares [Type I] of model compound degraded by FeVO ₄ | | | | | | |
|--|---------------|----|-------------|----------|---------|-----------|
| Source | Sum of square | df | Mean square | F-value | p-value | |
| Mean vs. total | 66,080.19048 | 1 | 66,080.2 | | | |
| Linear vs. mean | 2,776.976354 | 4 | 694.244 | 2.80727 | 0.0611 | |
| 2FI vs. linear | 161.8923115 | 6 | 26.9821 | 0.0711 | 0.998 | |
| Quadratic vs. 2FI | 3,790.489609 | 4 | 947.622 | 1,277.33 | <0.0001 | Suggested |
| Cubic vs. quadratic | 1.651249422 | 2 | 0.82562 | 1.17946 | 0.3957 | Aliased |
| Residual | 2.8 | 4 | 0.7 | | | |
| Total | 72,814 | 21 | 3,467.33 | | | |

| (b) Lack of fit (modal summary statistics) | | | | | | | |
|--|----------------|----|-------------|-----------|---------|----------|---------|
| Source | Sum of squares | df | Mean square | Std. Dev. | F-value | PRESS | p-value |
| Linear | 3,954.03 | 12 | 329.503 | 15.7258 | 470.718 | 6,197.72 | <0.0001 |
| 2FI | 3,792.14 | 6 | 632.023 | 19.4806 | 902.891 | 58,145.6 | <0.0001 |
| Quadratic | 1.65125 | 2 | 0.82562 | 0.86132 | 1.17946 | 197.955 | 0.3957 |
| Cubic | 0 | 0 | | 0.83666 | | | |
| Pure error | 2.8 | 4 | 0.7 | | | | |

Quadratic R² = 0.99934, adj. R² = 0.9978, pred. R² = 0.9706; Cubic R² = 0.99958, adj. R² = 0.99792

Table 4
ANOVA of 2-CP degradation using FeVO₄

| Source model | Sum of square | df | Mean square | F-value | p-value | |
|-------------------------------------|---------------|----|-------------|--------------|---------|---------------|
| Model | 6,729.36 | 14 | 480.668 | 647.9103766 | <0.0001 | significant |
| A-Photocatalyst load | 0.5 | 1 | 0.5 | 0.673968074 | 0.4431 | |
| B-pH | 0.5 | 1 | 0.5 | 0.673968074 | 0.4431 | |
| C-2-Chlorophenol | 2,346.12 | 1 | 2,346.12 | 3,162.418157 | <0.0001 | |
| D-H ₂ O ₂ (%) | 128 | 1 | 128 | 172.535827 | <0.0001 | |
| AB | 2.57681 | 1 | 2.57681 | 3.473376358 | 0.1116 | |
| AC | 28.125 | 1 | 28.125 | 37.91070417 | 0.0008 | |
| AD | 3.84865 | 1 | 3.84865 | 5.187737037 | 0.0630 | |
| BC | 21.125 | 1 | 21.125 | 28.47515113 | 0.0018 | |
| BD | 103.092 | 1 | 103.092 | 138.9612296 | <0.0001 | |
| CD | 3.125 | 1 | 3.125 | 4.212300463 | 0.0860 | |
| A ² | 2,056.46 | 1 | 2,056.46 | 2,771.976129 | <0.0001 | |
| B ² | 1,590.51 | 1 | 1,590.51 | 2,143.905692 | <0.0001 | |
| C ² | 83.3438 | 1 | 83.3438 | 112.3421564 | <0.0001 | |
| D ² | 583.877 | 1 | 583.877 | 787.0292647 | <0.0001 | |
| Residual | 4.45125 | 6 | 0.74187 | | | |
| Lack of fit | 1.65125 | 2 | 0.82562 | 1.179463873 | 0.3957 | insignificant |
| Pure error | 2.8 | 4 | 0.7 | | | |
| Cor. total | 6,733.81 | 20 | | | | |



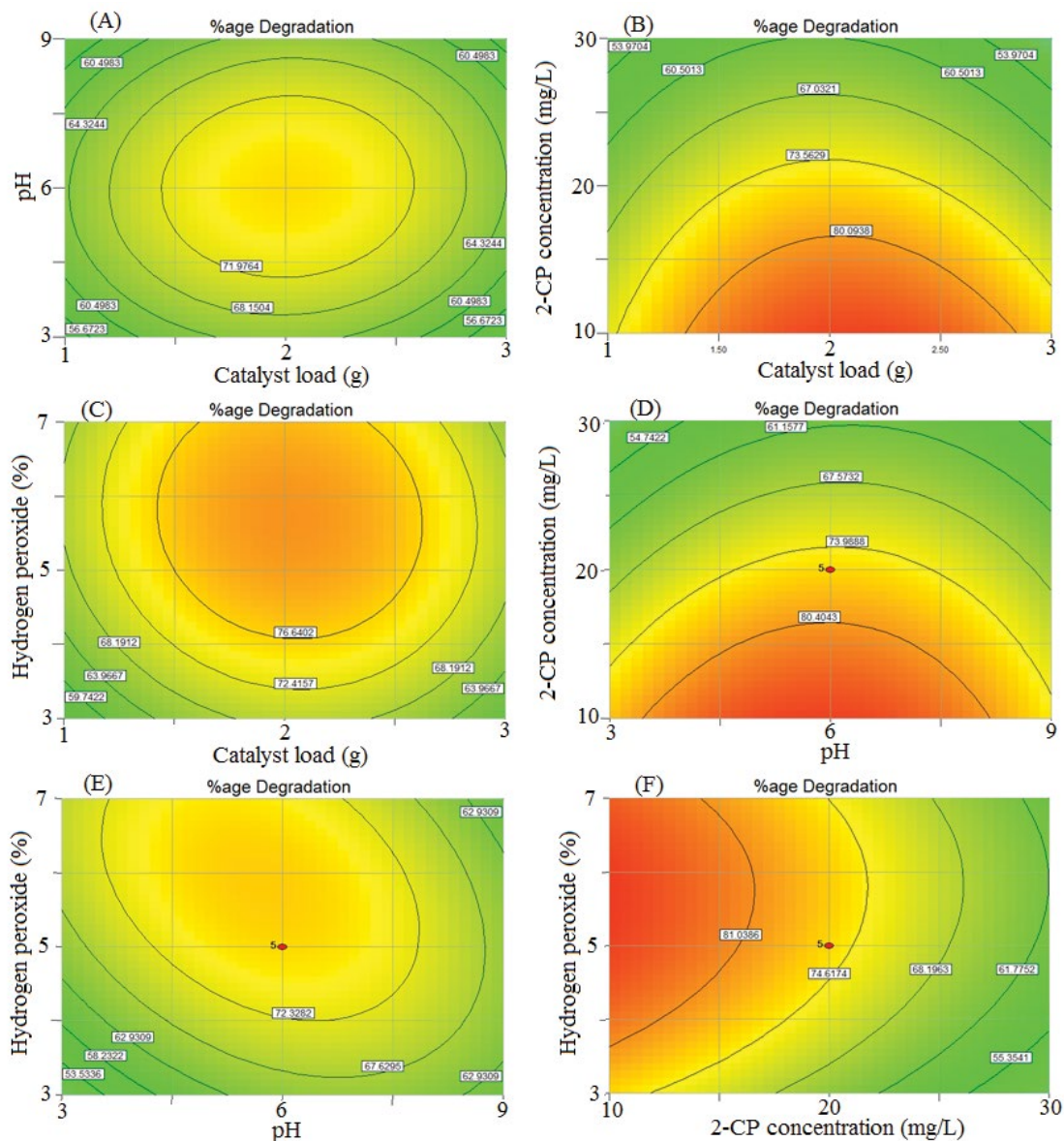


Fig. 7. Contour diagrams showing the degradation of 2-CP. (a) Catalyst load vs. pH, (b) Catalyst load vs. conc. of 2-chlorophenol, (c) Catalyst load vs. H₂O₂, (d) pH vs. conc. of 2-chlorophenol, (e) pH vs. H₂O₂, and (f) conc. of 2-chlorophenol vs. H₂O₂.

concentration of photocatalyst has no significant role in photodegradation, while degradation rate was increased by increasing the catalyst concentration and up to 91% degradation was attained at an optimum value of the catalyst

3.2.2. Effect of pH

Role of pH in photocatalytic degradation for complete mineralization of organic contaminants in wastewater is one of the important parameters. pH plays an effective role in degradation and detoxification of organic species, which creates electrostatic charge distribution upon the surface of photocatalyst which closely relates to catalytic activities on the surface. Protonation and deprotonation on the photocatalyst surface take place in the acidic or alkaline medium because

of the charge bearing capacity of pH in different reaction media [25]. It was observed that FeVO₄ showed maximum degradation when the pH was 6 (Figs. 7a, d, and e) because mostly organic species either contain a basic nature or acidic behavior and their protonation or deprotonation takes place which is the reason for the generation of unstable species [47–49]. Electron hole pair formation mechanism is more predominant at suitable pH value which contributes toward the generation of more oxidizing species. It is concluded that protonation is more prominent at lower pH, which creates a positive charge on the catalyst surface causes enhanced catalytic process. Depletion of degradation process takes place in basic pH due to columbic repulsion forces because of the same charge distribution between positive charge species and photocatalyst.

3.2.3. Effect of 2-CP concentration

The degradation efficiency of the 2-CP was also studied by changing the initial concentration of 2-CP in the range of 10–30 mg/L. It was observed that the increase in the initial concentration of the 2-CP does not affect the degradation rate significantly. However, deactivation of the photocatalyst may occur due to the saturation of the active sites present on the catalyst surface which leads toward the low PCA and as the 2-CP concentration was increased, the reaction time was increased to ensure complete mineralization (Figs. 7b, d, and f).

3.3. Comparison of PCA of FeVO_4

PCA of FeVO_4 prepared and FeVO_4 commercial was compared by degrading of 2-CP. First samples were placed in the dark for adsorption of 2-CP on the material surface. Then, samples were irradiated for photocatalytic degradation of 2-CP and response are shown in Fig. 8 along with controls. It was observed that FeVO_4 prepared proved to be more effective catalyst as compared to commercial FeVO_4 /commercial. The effect of light and H_2O_2 was negligible. Kinetic study of photocatalytic degradation of 2-CP was also examined by applying the Langmuir Hinshelwood (LH) model [50]. Relation of LH kinetic model for the rate constant of pseudo first order reaction is given in Eq. (7).

$$\ln \frac{C_0}{C} = k_1 t \quad (7)$$

where C_0 is the initial concentration of 2-CP, C is the concentration after treatment, t : time, and k_1 : pseudo-first-order rate constant.

3.4. Degradation of product monitoring

High performance liquid chromatography (HPLC) was performed to monitor the degradation and by-product identification before and after treatment [51]. From the initial untreated sample, a clear distinct peak of 2-CP with a retention time of 6.313 min was obtained with an average peak area (764,456; Fig. 9). Reduction in peak area and peak intensity occurred in the treated 2-CP sample. A distinct peak with a retention time of 3.193 min was achieved after treating the sample. It is evident that after the attack of $\cdot\text{OH}$, an alkyl chain is formed which on further oxidation changed into straight-chained alcohols which on further oxidation transformed to low molecular weight carboxylic acids and then finally to CO_2 and H_2O [13,27]. Results revealed that FeVO_4 based advanced oxidation process is viable to degrade 2-CP under solar light irradiation and under the current scenario of environmental pollution [52–62], there is a need to prepare and utilize materials able to harvest solar light for photocatalytic applications.

4. Conclusions

In view of efficient PCA of heterostructured nanoparticles, FeVO_4 was prepared and characterized by advanced techniques. The average particle size was 150 nm. The FeVO_4

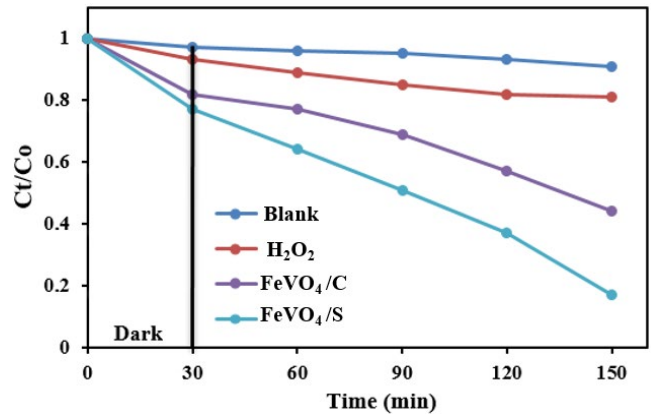


Fig. 8. Determination of photocatalytic degradation of 2-chlorophenol using synthesized and commercial FeVO_4 along with blanks.

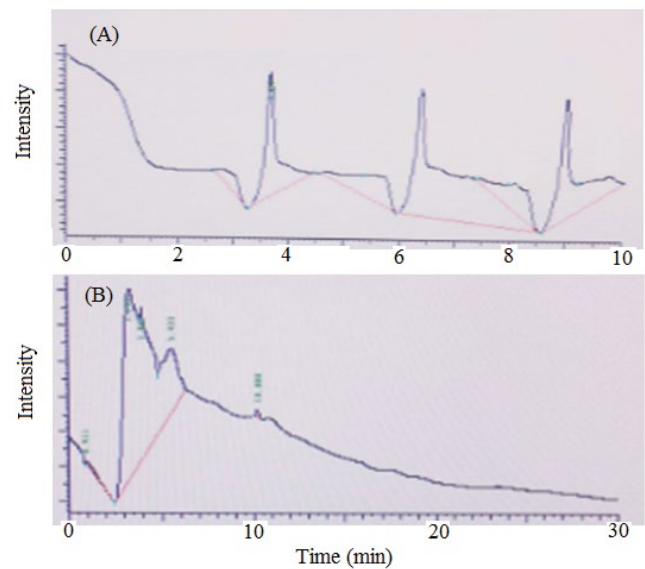


Fig. 9. HPLC chromatograms (a) untreated 2-chlorophenol and (b) treated sample of 2-chlorophenol.

particle was spherical, fluffy and in aggregate form with a band-gap value of 2.95 eV. 2-CP was treated under solar light irradiation using FeVO_4 as a function of catalyst dose, pH, the concentration of 2-CP, H_2O_2 concentration. At optimum conditions of process variables, up to 91% degradation of 2-CP was achieved. The observed and predicted degradation of 2-CP degradation was in agreement with very low residual values. Results revealed that FeVO_4 is promising for the harvesting of solar light for photocatalytic applications to treat effluent containing 2-CP and related pollutants in wastewater.

Acknowledgment

Research work was funded by Endowment Fund Secretariat, University of Agriculture Faisalabad, Pakistan (Project identification No. 1553).

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