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Preparation and Application of a Nano α-Fe_2O_3/SAPO-34 Photocatalyst for Removal of the Anti-cancer Drug Doxorubicin using the Taguchi Approach

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Abstract: The synthesis of α-Fe_2O_3/SAPO-34 nano photocatalyst was the first step of this study. The α-Fe_2O_3 nanocatalyst was synthesized applying forced hydrolysis and reflux condensation followed by solid-state dispersion that was used for supporting α-Fe_2O_3 on SAPO-34. The next step was a characterization of the catalyst that was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR). Then, for optimizing the operational parameters in Doxorubicin's degradation process the effect of Doxorubicin concentration, the amount of α-Fe_2O_3/SAPO-34 nano photocatalyst, the pH, and H_2O_2 concentration was studied via the Taguchi method. The AL_9 orthogonal array was adjusted and nine crucial runs were conducted. For calculating Signal/Noise ratio, each run was repeated three times. As the results showed, the concentration of Doxorubicin is the most effective parameter. Optimized conditions for removing the anti-cancer drug (based on Signal/Noise ratio) were Doxorubicin concentration (20 ppm), H_2O_2 concentration (3 mol/L), catalyst amount (50 mg/L) and pH = 8.

Keywords: Doxorubicin, Photocatalytic degradation, α-Fe_2O_3/SAPO-34, Design of experiment, Taguchi method

1 Introduction

Much research has been conducted on the environmental fate of drugs since a wide range of them cannot be removed through traditional sewage treatment methods [1]. Pharmaceuticals in the environment are a drastic menace for the ecosystem and human health. When it comes to anti-cancer drugs, the threat is more dangerous since they are potentially genotoxic, mutagenic, carcinogenic, and teratogenic, even at low concentrations [2]. Cytotoxic drugs have been widely used as remedies for various types of cancers, and the number of cancerous patients under chemotherapy treatments based on these drugs is increasing gradually [3]. Doxorubicin (DOX) is one of the anthracycline antitumor antibiotics, with its trade name Adriamycin. DOX is used for the treatment of different cancers such as bladder, stomach, breast, ovarian, lung, thyroid, multiple myeloma, soft tissue sarcoma, leukemia, Hodgkin's lymphoma and other kinds of cancers [4]. In the pharmaceutical industry, this drug can be excreted to the environment through formulation sites and production excretion. It also enters the environment as unmetabolized substances or their metabolites via urine and faeces of the drug consumers [5]. Several methods have been reported for removing the anti-cancer drugs such as using a membrane, the adsorption onto activated carbon, electrolysis, sonolysis and ozonation [5-8]. According to the obtained results, the traditional biological, physical and chemical water and sewage treatments are ineffective for removing pharmaceuticals [9]. AOP (Advanced Oxidation Process) can be a convenient alternative with high removal efficiency, which could be applied as both pre-treatment and post-treatment [10]. It can be used for sewage modification in biological treatment and multiplying biodegradation through partial oxidation. Also, it is useful in the degradation of resistant compounds [10]. Among AOP's, photocatalytic oxidation by hematite (α-Fe_2O_3) is one of the most efficient technologies, due to its high stability, nontoxicity, environmentally friendly and corrosion-resistant nature [11]. In 2009, Baharati et-al. made a significant change in the formation of pores on the surface of α-Fe_2O_3 nanocatalysts and

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improved their photocatalytic activity by using a kagenite topotactic transformation via a reflux condensation method [12]. However, in photocatalytic processes that use heterogeneous nanocatalysts, recovery, and reusability of the catalyst from aqueous solution are the biggest problems [13], which can be solved by supporting the nanostructure on an appropriate catalyst support. Silicoaluminophosphates (SAPOs), the porous materials with Al-P-Si bridges in their structure, have been widely used in the isomerization of alkanes, preparing para-xylenes, oligomerization of olefins, alkylation of aromatics and also as catalyst in the conversion of methanol to olefins (MTO) [14]. Small pores of the eight-membered ring (with pore diameter about 3.8 Å), moderate acidity and excellent hydrothermal stability, are the main reasons which cause SAPO-34 molecular sieve to be considered as one of the most important silico- aluminophosphates. It can act as a membrane or adsorbent in adsorption reactions [15], catalyst support [16] and catalyst in petrochemical reactions, especially in the conversion of methanol to olefins (MTO) [17].

Several tests are needed for the optimization of operational parameters in the one-variate method, using a method with less required time for experimental investigations is in high demand. The design of experiments (DOE) is a method that has been used recently for decreasing the number of operations.

DOE minimized the overall testing time, experimental costs, determination of variables with the greatest impact on response as well as the elimination of additional factors, calculation of the importance of each variable, determination of error rate and optimized conditions [18]. Taguchi is one of the DOE methods used in different industries and wastewater treatment investigations. In 2013, Mohammadi and Kazemi used the Taguchi method with vacuum membrane distillation for optimization of results in phenolic wastewater treatment [19]. Daneshvar et-al. utilized this method for optimizing the effective experimental parameters in biodegradation of a dye solution containing Malachite Green [20]. Genichi Taguchi established the Taguchi method by the use of orthogonal arrays (OA). The method leads to decreasing the number of experiments and costs, determining the contribution of factors and errors, estimating the results in optimized conditions and arbitrary levels and investigating the factors with different levels [21]. In this study an, α-Fe_2O_3/SAPO-34 nano photocatalyst was applied for removing the anti-cancer drug DOX from aqueous solution. Supporting α-Fe_2O_3 on porous SAPO-34 leads to a promotion of the catalytic activity of the nanostructure. Moreover, optimized operational parameters of the process, their contribution and interaction were investigated through the design of the experiment with the Taguchi method.

2 Experimental

2.1 Materials and Apparatus

Iron (III) chloride hexahydrate was purchased from Daejung (98%, Korea). Fumed silica was prepared from Sigma-Aldrich (99.8%, USA). Aluminum isopropoxide and cyclohexylamine were obtained from Titrachem (98%, Iran). Hydrogen peroxide was used from Chem. Lab (30%, Belgium). Other reagents such as urea (99%), orthophosphoric acid (85%), ethanol (96%), sodium hydroxide (99%) and sulfuric acid (95-97%) were purchased from Merck (Germany). DOX was obtained from RPG Life Sciences Limited (Mumbai, India). For evaluating the decomposition of DOX, active pharmaceutical ingredient (API) of this pollutant and pure water (0.6-0.8 μS/cm) were used for preparing all solutions to prevent the effect of degradation on other species.

DOX is potentially categorized as a carcinogenic compound, and it must be handled with strict safety precautions [22]. A UV/Vis spectrophotometer (Perkin Elmer Lambda 25) with silica cells and a path length of 10 mm was applied to measure the absorbance. The particle size and surface morphology was analyzed by scanning electron microscopy (SEM, Philips XL 30). An X-ray diffractometer (Philips PW 1800) was administered to record X-ray powder diffraction (XRD) patterns. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum 400) was used for addressing surface functional groups of the catalyst. The solution pH values were measured by a Metrohm 780 pH meter. b All solutions were stirred with a magnetic stirrer (Heidelph, Germany).

2.2 α-Fe_2O_3/SAPO-34 Nanophotocatalyst Preparation

α-Fe_2O_3 nanoparticles were synthesized *via* forced hydrolysis and reflux condensation [12]. A Ferric chloride hexahydrate solution ($FeCl_3 \cdot 6\ H_2O$) (0.25 M) acted as the Fe^{3+} source and the urea solution ($(NH_2)_2CO$) (1 M) as the precipitating agent. These were prepared for releasing hydroxyl ions slowly during the reaction. Solutions were mixed and subsequently stirred for 30 min on a magnetic stirrer. The obtained solution was refluxed over a hot water bath (95 °C) for 12 h. The settled precipitate at

Table 1: Taguchi L_9 Orthogonal Array and Experimental Results for average of DOX Degradation

Run	Factors & Levels				The average percentage of degradation
	DOX concentration (ppm)	Catalyst amount (mg/L)	pH	H_2O_2 concentration (mol/L)	
1	20	50	5	1	85
2	20	150	7	2	91
3	20	400	8	3	100
4	40	50	7	3	84
5	40	150	8	1	70
6	40	400	5	2	72
7	60	50	8	2	58
8	60	150	5	3	60
9	60	400	7	1	43

the bottom of the container was washed with 100 CC of a water-ethanol solution to remove by-products. Finally, it was dried at 80 °C for 2 h and calcinated at 300 °C for 1 h to obtain the hematite yellowish brown powder.

In the second step, the porous SAPO-34 catalyst support was prepared via a hydrothermal method [23]. The molar ratio of the synthesis gel was 1 Al_2O_3: 1 P_2O_5: 0.24 SiO_2: 0.15 cyclohexylamine: 20 H_2O. Initially, 6.8 g aluminum isopropoxide as Al source was mixed with 3.3 g orthophosphoric acid as P source, and the mixture was dissolved in 14 g deionized water and stirred for 1h. Then 0.99 g cyclohexylamine as the template was dissolved in 10 g deionized water and stirred for 1 h. The solutions were mixed and stirred for a further period of 1h. Then, 0.96 g fumed silica was added as Si source, and the mixture was stirred for 2 h. Finally, the synthesized gel was transferred into a 60 ml stainless steel autoclave and kept at 200 °C for 24 h. The obtained product was dried at room temperature after filtration, and washing with 1000 mL deionized water. Then it was calcinated at 550 °C for 20 h to remove the framework.

In the third step, α-Fe_2O_3/SAPO-34 nano photocatalyst was prepared via a solid-state dispersion (SSD) method [24]. In this method, 3:1 weight ratio of the SAPO-34 catalyst support and α-Fe_2O_3 photocatalyst were mixed while ethanol was added dropwise to obtain a mud-like mixture. The mixture was dried at 80 °C for 2 h and calcinated at 300 °C for 1 h to reach a yellowish brown powder.

2.3 Design of Experiment with the Taguchi Method

The L_9 orthogonal array (four factors with three levels in nine runs, Table 1) was employed for the determination of the optimized experimental factors in the removal of the anti-cancer drug DOX. Each row of Table 1 indicates one run. Nine suggested experiments by the Taguchi method were repeated three times and finally, the average of experimental results were used by Qualitek-4 software to optimize the conditions and adjustment of control factors. In the Taguchi approach, the terms 'signal' and 'noise' represent desirable and undesirable values for the output characteristic, respectively. Signal/Noise (S/N) ratio is used for measuring the quality characteristic deviating from the desired value. The S/N ratio is different according to the type of characteristic (1. Nominal is better 2. Smaller is better 3. Bigger is better). Since the aim of this study is more degradation of the pollutant in aqueous media, the S/N ratio with 'bigger is better' characteristic is needed which is defined by the following equation [25]:

$$\frac{s}{n} = -10\log\left(\frac{1}{n}\sum\frac{1}{y_i^2}\right).$$

Where, n is the repetition number under the experimental condition and y_i is the ith experiment performance value.

2.4 Investigating the Method of Photocatalytic Activity on Pollutant Degradation

To study the photocatalytic activity, a homemade batch reactor was used. Three Philips lamps (UV-C) 15 W were used as the irradiation source. The multi-factor method was used to optimize the photocatalytic degradation condition. Before irradiation, the prepared solution was allowed to equilibrate for 15 min in the dark. The stirring speed was kept constant at 500 rpm through the radiation to obtain a homogenous solution. Sampling was performed after 30 min had elapsed.

3 Results and Discussion

3.1 The Characteristics of α-Fe_2O_3/SAPO-34 Nanophotocatalyst

The XRD pattern of α-Fe_2O_3/SAPO-34 (Figure 1) includes SAPO-34 catalyst support, too. The results indicated that the SAPO-34 frame structure has not been destroyed after loading the α-Fe_2O_3. The average size of α-Fe_2O_3/SAPO-34 nanoparticles (93 nm) was obtained by applying the Debye-Scherrer equation. As it can be clearly seen in the SEM image (Figure 2), the iron oxide nanoparticles supported on SAPO-34 are not the same size and they are not distributed uniformly on the catalyst surface which results in increasing the photocatalytic activity of nanoparticles (Figure 2). In the FT-IR spectra of α-Fe_2O_3/SAPO-34 nano photocatalyst (Figure 3A), the absorption peaks at about 3430 and 1640 cm^{-1} are related to the stretching and bending modes of OH. The peak at about 720 cm^{-1} belongs to the Fe-O bond [26]. Also, the formation of new bonds between α-Fe_2O_3 and SAPO-34 are implied by other spectral changes between 450 and 700 cm^{-1} (Figure 3).

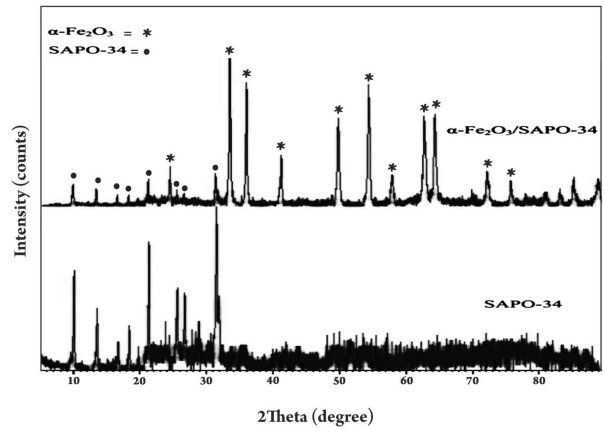

Figure 1: XRD powder patterns of α-Fe_2O_3/SAPO-34 and SAPO-34 as catalyst support.

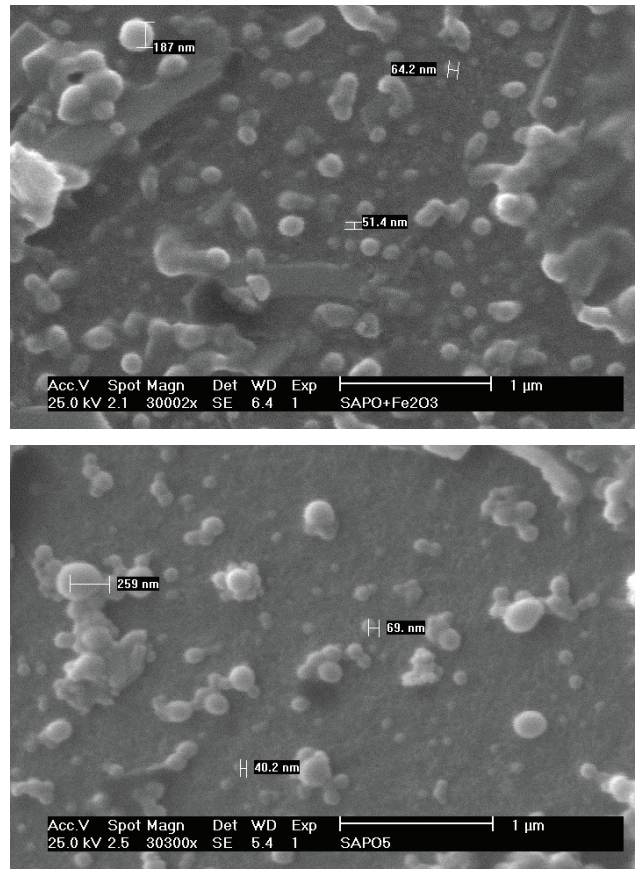

Figure 2: SEM images of α-Fe_2O_3/SAPO-34 nanoparticles (above) and SAPO-34 (below).

3.2 The Mechanism of the Photocatalytic Degradation Process

A UV–Vis spectrophotometer measured the pollutant concentration in each sample in λ_{max} =485 nm. The degradation efficiency of DOX was calculated using the following equation [27]: Degradation%= $(A_0\text{-}A_t)/A_0 \times 100$, where A_0 is the initial absorption of the sample and A_t is the absorption through the t sampling time.

Hematite is an n-type semiconductor, with a band gap of 2.2 eV, conduction band edge of +0.28 V and a valance band edge of +2.4 V [28]. Adsorption and desorption of molecules on the catalyst surface is the integral part of the photocatalytic process. Irradiation of UV light to α-Fe_2O_3/SAPO-34 porous nanoparticles leads to the ejection of valance band (VB) electrons into the conduction band (CB) and creates holes in the valance band. The photogenerated holes react with adsorbed water on the surface of the catalyst and produce highly reactive hydroxyl radicals (•OH). O_2 can act as an electron acceptor for the formation of the superoxide anion radical ($O_2^{\bullet -}$). Also, it can serve as both oxidizing agent and an additional source of •OH. The reactive radicals have high oxidative ability to degrade DOX into non-toxic organic compounds (1-4). So increased photocatalytic activity of α-Fe_2O_3/SAPO-34 is because of the suitable position of SAPO-34 for adsorption of DOX in the vicinity of α-Fe_2O_3 which is the source of reactive hydroxyl radical (•OH).

$$\alpha\text{-}Fe_2O_3/\text{SAPO-34} + h\nu \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

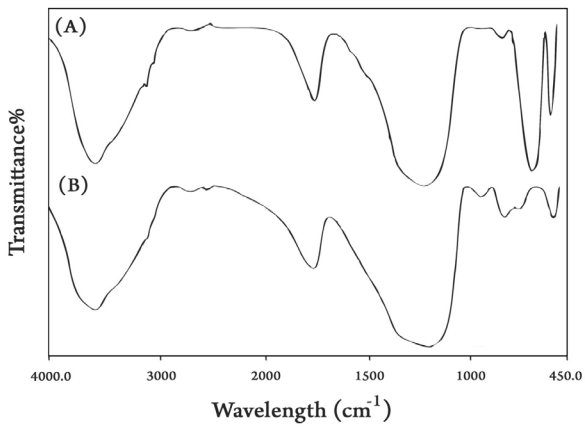

Figure 3: FTIR spectra of α-Fe_2O_3/SAPO-34 (A) and the catalyst support of SAPO-34(B).

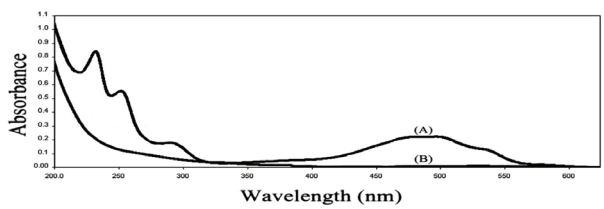

Figure 4: UV–Vis spectra of DOX in aqueous solution. Conditions in the third run: DOX concentration = 20 ppm, α-Fe_2O_3/SAPO-34 nano photocatalyst amount =400 mg/L, pH=8, H_2O_2 concentration = 3 mol/L, at: (A) t = 0, (B) t = 30 min.

$$h_{VB}^{+} + OH^{-} \rightarrow {}^{\bullet}OH \quad (2)$$

$$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$${}^{\bullet}OH / O_2^{\bullet -} + DOX \rightarrow CO_2 + H_2O \quad (4)$$

3.3 Determination of Optimized Condition with Taguchi Method

3.3.1 ANOVA Analysis

ANOVA (Table 2) is applied for estimating the error variance and determining the relative importance of various factors. It also demonstrates the reason of observed variation in the response which can be because of the alteration of level adjustments or standard experimental errors. The computable Parameters in ANOVA analysis are the values of the sum of squares (SS), the degree of freedom (DOF), mean square or variance (V) and F-test(F) for significance of the factors effect. For calculation of SS of factor A, the equation $SS_A = [\sum_{i=1}^{K_A}(\frac{A_i^2}{n_{A_i}})] - \frac{T^2}{N}$ is applied.

Table 2: ANOVA Analysis of Results.

Data Type: S/N Ratio	QC Type: Bigger is Better			
Factor	**DOF**	**SS**	**V**	**F**	**P%**
DOX concentration	2	34.786	17.393		82.173
Catalyst amount	2	1.136	0.568		2.684
pH	2	0.563	0.281		1.332
H_2O_2 concentration	2	5.844	2.922		13.806
Error	0				
Total	8	42.333			100%

Where k_A is the number of levels for factor A (k= 3 for all factors in the present study), n_{A_i} is the number of all observations at level i of factor A, A_i is the sum of all observations of level i of factor A, N is the number of all experiments, and T is the sum of all observations. P (the last column of Table 2) is the contribution percent of each factor on the response or elimination of the DOX drug ($P_A = (SS_A/SS_T) \times 100$), where SS_T is the sum of squares for all factors [29]. The higher percent of contribution means the greater effect of that factor on the response. So according to the Table 2, DOX concentration, H_2O_2 concentration, the catalyst amount and pH have the highest effect on the pollutant removal respectively.

3.3.2 Interaction between Factors

Table 3 illustrates the interactions between factors. The severity of interactions is related to angle size between two lines that are measured by the SI (severity index). If the angle between 2 lines is 90°, SI=100% and if the angle is zero, SI=0. The conclusion is that when the SI is bigger, the importance of interaction between two factors is greater. This method predicts that the interaction between pH at 8 and H_2O_2 concentration at 3 mol/L or the catalyst amount at 400 mg/L and H_2O_2 concentration at 3 mol/L are the most efficient. Whilst the interactions between DOX concentration at 20 ppm and H_2O_2concentration at 3 mol/L are the least effective. As it can be seen in Table 4, the optimized condition for setting the control factors is as follow:

- DOX concentration= 20 ppm
- H_2O_2 concentration=3 mol/L
- catalyst amount= 50 mg/L
- pH= 8

Table 3: Factors Interaction.

Number	Interacting factor pairs	Optimum level	SI%
1	pH × H_2O_2 concentration	8 , 3 mol/L	54.23
2	catalyst amount × H_2O_2 concentration	400 mg/L , 3 mol/L	38.17
3	catalyst amount × pH	400 mg/L , 8	25.36
4	DOX concentration × catalyst amount	20 ppm , 400 mg/L	14.83
5	DOX concentration × pH	20 ppm , 8	5.08
6	DOX concentration × H_2O_2 concentration	20 ppm , 3 mol/L	2.37

Table 4: Optimum Conditions and Performance.

Data Type: S/N Ratio		QC Type: Bigger is Better
Factor	**Level**	**Contribution**
DOX concentration	20 ppm	2.168
Catalyst amount	50 mg/L	0.358
pH	8	0.301
H_2O_2 concentration	3 mol/L	0.927

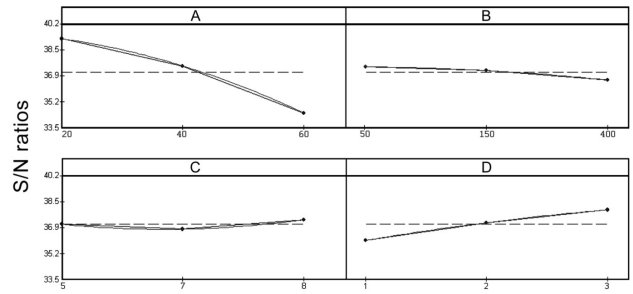

Figure 5: Effect of each parameter on S/N ratios in drug removal. (A) DOX concentration, (B) catalyst amount, (C) pH, (D) H_2O_2 concentration.

3.3.3 Analysis of the Optimized Condition Based on S/N Graphs

The effect of DOX concentration on S/N ratio in the removal of the pollutant is shown in Figure (5A). When the concentration of the pollutant increases, photodegradation percent decreases. This is because of the light absorbance by DOX molecules which does not allow the photons to reach the photocatalyst surface. Figure (5B) represents the S/N ratio for the catalyst amount. The amount of catalyst loading was optimized at about 50 mg/L. By using an excess amount of the catalyst, opacity and light diffraction is created in solution which results in decreasing the degradation efficiency. Figure (5C) shows that more •OH radicals can be generated in an alkaline media because of the reaction between hydroxyl ions (OH^-) and produced holes in the valance band. A larger number of •OH radicals, leads to more radical attacks to DOX molecules, so the process efficiency increases. Based on Figure (5D), degradation efficiency enhancement by increasing the amount of H_2O_2 could be attributed to increasing the concentration of reaction's hydroxyl radicals (1). So, since it was assumed that, the bigger response is better, the optimized conditions for removing the drug are: DOX concentration (20 ppm), H_2O_2 concentration (3 mol/L), catalyst amount (50 mg/L) and pH = 8.

$$e_{CB}^- + H_2O_2 \rightarrow OH^- \,^\bullet OH \quad (1)$$

4 Conclusion

Nanoparticles of α-Fe_2O_3 were successfully supported on the surface of SAPO-34 using a solid-state dispersion method. The as-prepared catalyst was characterized via XRD, SEM and FT-IR. The catalyst was found to be useful for the photocatalytic degradation of DOX drug in aqueous solution. The optimization of DOX degradation conditions was done by the Taguchi method. The results showed that the concentration of DOX is the most effective factor, and pH is the least efficient parameter in the degradation of the pollutant. The optimized conditions for removing the contaminant are: DOX concentration at 20 ppm > H_2O_2 concentration at 3 mol/L>catalyst amount at 50 mg/L>pH at 8.

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