Full Factorial Experimental Design-Based Yates' Algorithm for Photodegradation of Anionic Dye Using $CoFe_2O_4$ Nanocatalyst

Moradi, Reza*[+]

Department of Chemistry, Tuyserkan Branch, Islamic Azad University, Tuyserkan, I.R. IRAN

ABSTRACT: *In this paper, cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized using the precipitation method. $CoFe_2O_4$ nanoparticles were used as a catalyst for photocatalytic degradation of azo dye in an aqueous solution. Acid Yellow 23 (AY23) was used as a model dye. The $CoFe_2O_4$ catalyst was characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). A batch photoreactor with a capacity of 1L, equipped with a lamp UV-C (15 W) was used. A statistical experimental design based on Yates' Algorithm was exerted to measure the effect of these four factors such as pH, catalyst amount, H_2O_2 concentration, and temperature at two levels. The (2^4) full factorial experimental design was utilized in this process. The significant effects of each factor and interaction on the process were determined using the Analysis of Variance (ANOVA) method. A pseudo-first-order reaction with a constant rate ($k= 0.048\ min^{-1}$) was obtained for the photocatalytic degradation reaction.*

KEYWORDS: *Cobalt ferrite; Full factorial; Degradation; Yates' algorithm.*

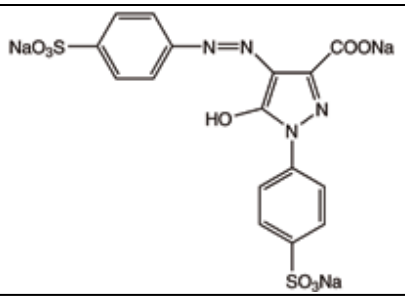
INTRODUCTION

One of the dye applications is in the textile industry. They are used as color or as a pigment in the textile industry. Dyes in terms of application are classified into anionic, cationic, direct, mordant, sulfur, reactive, vat, azoic, disperse, natural, and pigment [1]. Dyes are of the most toxic compounds in various industries which can cause severe problems in the environment [2-5]. So, decomposition of the dyes and wastewater treatment is very essential. The important techniques used for the removal of dyes pollutants include physical [6], chemical, biological, and Advanced Oxidation Processes (AOPs) [7,8] methods. In the AOPs method, the oxidizing agent is the hydroxyl radical ($HO^{\bullet}$) with an oxidation potential of ($E°= 2.72$ V/S.H.E), as previously reported. The four processes of AOPs that have been most widely studied are UV/O_3 [9,10], UV/H_2O_2 [11], UV/O_2 [12], Fenton, and photo-Fenton reagent [13,14], and electrocatalytic degradation [15,6]. AOPs have been widely investigated of which heterogeneous photocatalytic has become the most popular.

Several studies related to photocatalytic degradation of organic pollutants have been carried out using the powder $CoFe_2O_4$ in the solution to be treated [17-19]. $CoFe_2O_4$ nanoparticles are a blend of metal oxides, CoO and Fe_2O_3, which belong to intermediate elements of the periodic table. The $CoFe_2O_4$ compound is called cobalt ferrite

***** *To whom correspondence should be addressed.*
+ E-mail: reza.moradi_bi@yahoo.com
1021-9986/2021/4/1083-1094 12/$/6.02

Table 1: The structure and characteristics of AY23 dye.

Dye	Structure	λ_{max} (nm)	C.I.	MW (g/mol)
AY23		423	19140	534.37

and used as the catalyst. Cobalt ferrite is a large group of spinel compounds. They are paramagnetic and include single electrons that enhanced the photocatalytic activity to compare with others nanoparticles.

Some types of experimental design methods including one factor at a time, multi-factor at a time, full factorial experimental design [20-22], and fractional factorial experimental design. These techniques have found much use in the chemical industry for the design and analysis of industrial experiments. Factorial experimental design and analysis is a statistical method that is valuable in these applications. Data collected and analyzed by these methods result in equations expressing the relationships between significant dependent variables on the independent variables. It provides redundancy, which is of use in the testing significance of the dependent variable. The application of these techniques gives considerable power to the experimenter.

Full factorial experimental design is one of the applied methods of data analysis in chemistry and chemical engineering. In this study, an experimental design-based Yates' Algorithm which has not been presented in other papers, has been used. The classical calculations method was used for the design of experiments and analyzes the results in the process. The experiment is carried out using a (2^4) full factorial design with two levels (low and high) in order to examine the main effects and the interactions between operational parameters in the photocatalytic degradation of AY23. $CoFe_2O_4$ nanoparticles were characterized by SEM and XRD. The reaction kinetics was studied.

EXPERIMENTAL SECTION

Materials

The azo dye, Acid Yellow 23 (AY23) was obtained from Merck Company. The structure and characteristics of AY23 are shown in Table 1. The pH values were adjusted at the desired level using dilute NaOH and H_2SO_4. Other materials such as $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $FeCl_2$, and H_2O_2 were all Merck products (Germany). Double distilled water was used for the preparation of requisite solutions.

Apparatus

Fig. 1 shows the batch photoreactor, which used for the photocatalytic decomposition of AY23. In this setup, a reactor with a capacity of 1 L and a low mercury pressure Philips lamp 15W (UV-C, light intensity about 260 mW/cm^2) was used. UV/Vis Spectrophotometer, Jenway (6505) was employed to measure the absorbance using glass cells of path length 1 cm. XRD analysis of the samples was done performed in the XRD diffractometer Philips-XPert MPD, tube: Co kα , wavelength: λ=1.78897Å , Voltage: 40 kV, Current: 30 mA. The morphology of nanoparticles was investigated by SEM (Philips XL30 microscope). For the Chemical Oxygen Demand (COD) measurement, COD meter model AL250 AQUALYTIC was used.

Preparation of $CoFe_2O_4$ nanoparticles

$CoFe_2O_4$ was prepared by the precipitation method [17]. The synthesis of $CoFe_2O_4$ was done by using 2.5 M of $Fe(NO_3)_3$ and 1.25 M of $Co(NO_3)_2$ solutions. To a mixture of 60 mL of each solution, a certain volume of 6 M NaOH solution was added until a pH~10 was obtained. At this stage, dropwise $FeCl_2$ solution (1M) was added into the mixture until the mole ratio of Fe^{2+}/Fe^{3+} 0.02 was obtained. By the dropwise addition of NaOH solution (6M), the pH value of the resulting mixture was adjusted to ca. 10.0. This mixture was refluxed for 2 h. Finally, the $CoFe_2O_4$ nanoparticles were washed for several times with de-ionized water and dried in an oven at 110 °C for 2 h and calcined in a furnace at 700 °C for 4 h.

Table 2: Factors and levels used in the (2^4) factorial design.

		Range and levels	
Variables (Factors)	Coding	Low (–)	High (+)
A) pH	X_1	4	6
B) Catalyst amount (mg/ L)	X_2	25	50
C) H_2O_2 concentration (ppm)	X_3	15	20
D) Temperature (°C)	X_4	25	35

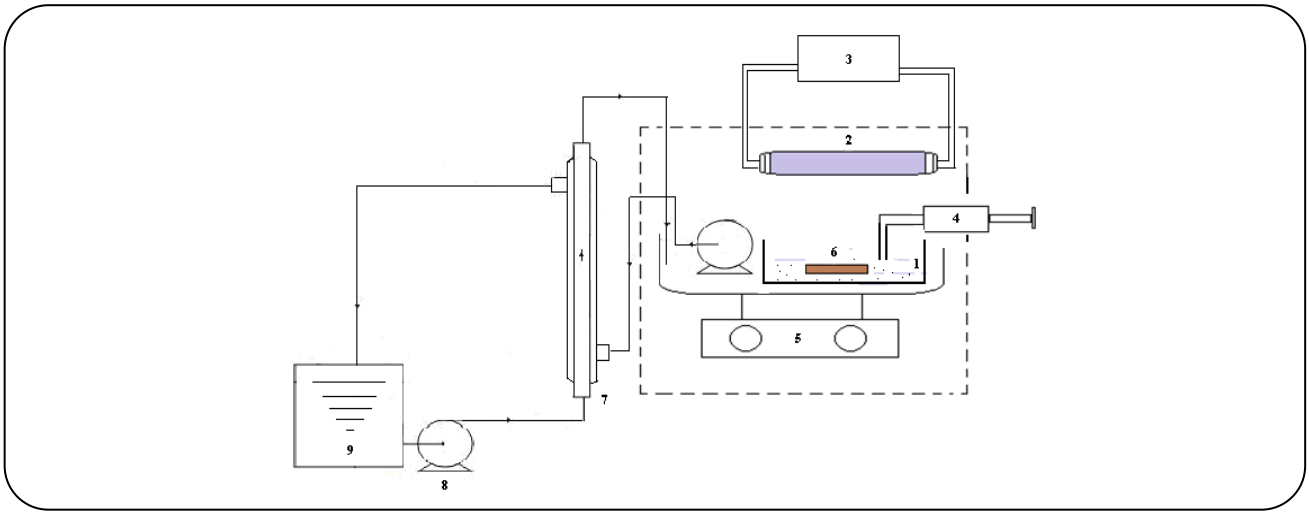


Fig. 1: Schematic diagram of batch photoreactor. (1) reaction flask (Pyrex), (2) UV lamp, (3) power supply, (4) sampling, (5) heater stirrer, (6) magnetic bar, (7) condenser, (8) pumps, (9) tank.

Full factorial experimental design

The photodegradation efficiency of AY23 by $CoFe_2O_4$ nanoparticles was investigated using a full experimental design. The experiments were designed considering four variables (Factors) including pH, catalyst amount, H_2O_2 concentration, and temperature at two levels (low (–) and high (+)). Factorial designs are usually discussed in terms of coded factor spaces. Variables and levels used in (2^4) full factorial experimental design are shown in Table 2. The experiments were carried out by varying the pH 4 or 6, catalyst amount 25 mg/L or 50 mg/L, H_2O_2 concentration 15 ppm or 20 ppm, and temperature 25°C or 35°C.

Procedure

For the photodegradation of AY23, a solution containing specific concentrations of dye (35 ppm) and a certain amount of catalyst (according to Table 2) were prepared. The suspension pH values were adjusted at the desired level using dilute H_2SO_4 0.1N (the pH values were measured with Horiba M12 pH meter) and then were allowed to equilibrate for 30 min in darkness. In order to carry out each experiment (according to Table 3), 1 L AY23 solution was made at a specified concentration and was transferred to the reaction flask (Pyrex). The degradation reaction took place under the radiation of a mercury lamp. The concentration of the samples was determined (at 2 min intervals and centrifuged with centrifuge 4232 ALC) using a spectrophotometer (UV-Vis spectrophotometer, Jenway (6505) at λ_{max}= 423 nm. The photodegradation efficiency (Y) as a function of time is given by Eq. (1):

$$Y = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where C_o and C are the concentration of dye at t = 0 and t, respectively.

RESULTS AND DISCUSSION

The characterization of $CoFe_2O_4$ nanoparticles

The morphology and size of the $CoFe_2O_4$ nanoparticles are shown in SEM image (Fig. 2). In 500 nanoscale

Table 3: Experimental design matrix, experimental results photodegradation efficiency for AY23 (%).

Run Number	Factors				Treatment Combination (TC)	Response (Y)
	A	B	C	D		
1	–	–	–	–	(1)	51.27
2	+	–	–	–	a	77.56
3	–	+	–	–	b	56.63
4	+	+	–	–	ab	69.39
5	–	–	+	–	c	74.20
6	+	–	+	–	ac	61.69
7	–	+	+	–	bc	83.45
8	+	+	+	–	abc	70.12
9	–	–	–	+	d	40.02
10	+	–	–	+	ad	92.33
11	–	+	–	+	bd	49.78
12	+	+	–	+	abd	95.25
13	–	–	+	+	cd	80.18
14	+	–	+	+	acd	85.14
15	–	+	+	+	bcd	75.42
16	+	+	+	+	abcd	89.99

magnitudes, the average size of nanoparticles is between 35- 45 nanometers. The XRD pattern of the $CoFe_2O_4$ nanoparticles is illustrated in Fig. 3. The XRD pattern of the $CoFe_2O_4$ nanoparticles sample (2θ ranges from 10° to 80°) peaks appeared at 30.1°, 35.1°, 37.1°, 43.2°, 53.7°, 56.9°, 60.2 and 74.1° attributed to (220), (311), (222), (400), (422), (511), (440) and (533) which indicated that the cubic spinel phase of $CoFe_2O_4$ crystals was obtained according to the standard JCPDS (No. 22–1086) [23]. So, no characteristic peak of impurity was found in the pattern showed that the synthesized of the $CoFe_2O_4$ nanoparticles at 700 °C were pure crystalline phase.

The crystallite size of the $CoFe_2O_4$ nanoparticles was calculated using the Debye-Scherer formula [24]:

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

where D is the average crystallite size, λ is the wavelength of Co kα , β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle. The strong and sharp peak is located at angles 2θ of 35.1. The average crystallite size of the $CoFe_2O_4$ nanoparticles was estimated about 42 nm according to the following calculations:

λ= 1.79Å, 2θ = 35.1 degree, θ = 35.1/2 = 17.55 degree, Cos θ = 0.953 degree

β = 0.231 degree, $\beta = 0.231 \times 3.14/180 = 4.029\times10^{-3}$ radian

$D = (0.9) \times (1.79Å) / (4.029\times10^{-3}) \times (0.953) = 419.53$ Å

D = 419.53 Å → 41.953 nm ~ 42 nm.

UV-Vis spectra

The absorbance of AY23 solutions during the process at initial and after 38 min irradiation time versus wavelength (λ) are shown in Fig. 4. The spectrum of AY23 in the visible region exhibits the main band with a maximum at 423 nm. The decrease of absorption peaks of AY23 at λ_{max}= 423 nm in this figure indicates a rapid degradation of the azo dye. Complete discoloration of dye was observed after 38 min under optimal conditions.

Classical mathematical treatment of a full factorial design

In this study, the experimental design used is a two-level and four factors (A, B, C, and D). The design is called

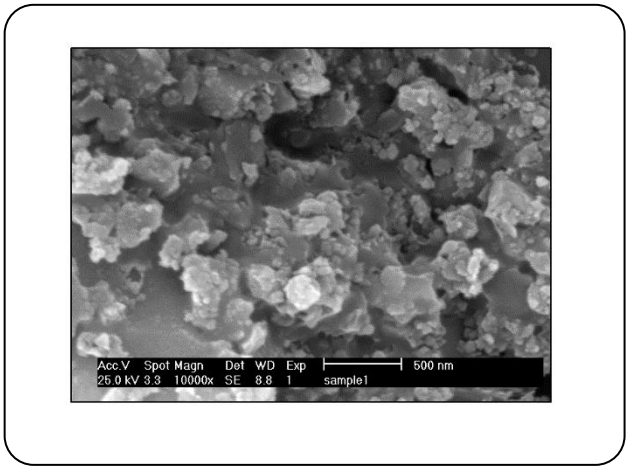


Fig. 2: SEM image of $CoFe_2O_4$ nanoparticles.

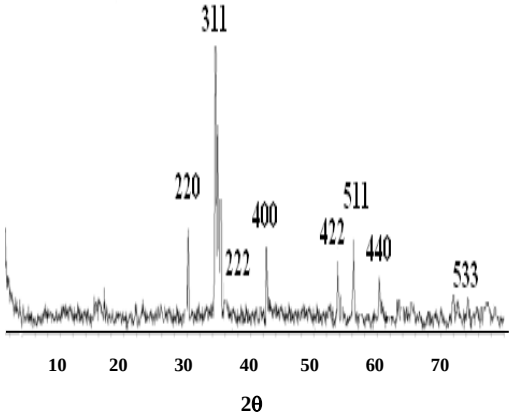


Fig. 3: XRD pattern of $CoFe_2O_4$ nanoparticles.

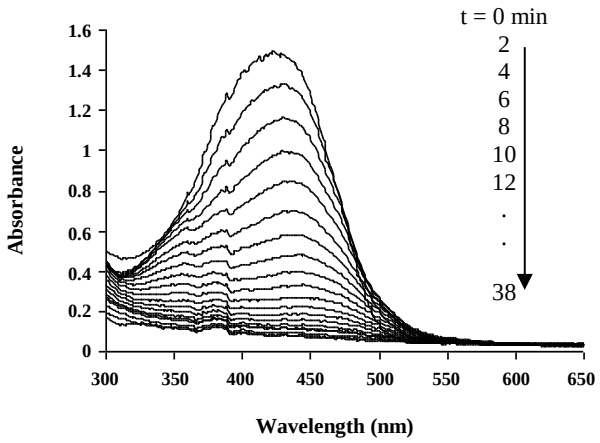


Fig. 4: UV-Vis spectra of AY23 in photodegradation (pH= 6, catalyst amount= 50 mg/L, H_2O_2 concentration= 15 ppm, temperature= 35 °C and irradiation time= 38 min).

a (2^4) factorial design, which has 16 experiments. Using the (– and +) notation to represent the low and high levels of the factors; listed the sixteen experiments in the (2^4) design as in Table 3. This is called the design matrix. The first column of Table 3 lists the experiment numbers (1-16). The next four columns list the abbreviated coded factor levels (– and +) for factors A, B, C, and D. Table 4 gives contrast constants for the (2^4) design. The first column of Table 4 gives a notation often used to describe the Treatment Combinations (TC), where the presence of the appropriate lower-case letter indicates that the factor is at the high level and its absence that the factor is at the low level. The number 1 is used to indicate that all factors are at a low level. The next fifteen columns list the four factors and eleven interactions of the model: the six two-factor interactions (AB, AC, BC, AD, CD, and BD), the four three-factor interactions (ABC, ABD, ACD, and BCD), and single four-factor interaction (ABCD). Finally, the last column of Table 4 lists the average responses (photodegradation efficiency (Y)) of each experiment.

In the classical factorial design literature, a factor effect is defined as the difference in average responses between the experiments carried out at the high level of the factor and the experiments carried out at the low level of the factor. Thus, in a (2^4**)** full factorial design, the main effect of A would be calculated as:

A= (Average responses at high level of A) – (3)
(Average responses at low level of A)

Average responses at high level of A=
1/8 × (77.56 + 69.39 + 61.69 + 70.12 + 92.33 + 95.25 + 85.14 + 89.99) = 80.18375.

Average responses at low level of A=
1/8 × (51.27 + 56.63 + 74.20 + 83.45 + 40.02 + 49.78 + 80.18 + 75.42) = 63.86875.

The main effect of A= 80.18375– 63.86875 = 16.315.

The interactions effect can be calculated similarly. Therefore, the effect of each factor/interaction is listed in Table 5. The effect of each factor on response was found to be in the following order: pH (16.315), H_2O_2 concentration (10.995), temperature (7.975), and catalyst amount (3.455). It can be seen that pH has the main effect on response. The least effective factor in the response is catalyst amount. The interaction between pH × catalyst amount, catalyst amount × H_2O_2 concentration, catalyst amount × temperature, H_2O_2 concentration × temperature,

Table 4: Contrast constants for the (2^4) design.

TC	Factors and their interactions															Response (Y)
	A	B	AB	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD	
(1)	–	–	+	–	+	+	–	–	+	+	–	+	–	–	+	51.27
a	+	–	–	–	–	+	+	–	–	+	+	+	+	–	–	77.56
b	–	+	–	–	+	–	+	–	+	–	+	+	–	+	–	56.63
ab	+	+	+	–	–	–	–	–	–	–	–	+	+	+	+	69.39
c	–	–	+	+	–	–	+	–	+	+	–	–	+	+	–	74.20
ac	+	–	–	+	+	–	–	–	–	+	+	–	–	+	+	61.69
bc	–	+	–	+	–	+	–	–	+	–	+	–	+	–	+	83.45
abc	+	+	+	+	+	+	+	–	–	–	–	–	–	–	–	70.12
d	–	–	+	–	+	+	–	+	–	–	+	–	+	+	–	40.02
ad	+	–	–	–	–	+	+	+	+	–	–	–	–	+	+	92.33
bd	–	+	–	–	+	–	+	+	–	+	–	–	+	–	+	49.78
abd	+	+	+	–	–	–	–	+	+	+	+	–	–	–	–	95.25
cd	–	–	+	+	–	–	+	+	–	–	+	+	–	–	+	80.18
acd	+	–	–	+	+	–	–	+	+	–	–	+	+	–	–	85.14
bcd	–	+	–	+	–	+	–	+	–	+	–	+	–	+	–	75.42
abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	89.99

Table 5: Effect of each factor/interaction on response.

Factors/interactions	Effect
A	16.315
B	3.455
AB	–1.4475
C	10.995
AC	–17.8925
BC	0.9875
ABC	3.645
D	7.975
AD	13.0125
BD	–0.2625
ABD	2.14
CD	2.3425
ACD	–1.67
BCD	–4.135
ABCD	0.4675

pH × catalyst amount ×H_2O_2 concentration, pH × catalyst amount × temperature, pH × H_2O_2 concentration × temperature, catalyst amount × H_2O_2 concentration × temperature, and pH × catalyst amount × H_2O_2 concentration × temperature have a little effect on response. The interaction between pH × H_2O_2 concentration and pH × temperature has a great effect on response. Thus the most effective interaction is that between pH × H_2O_2 concentration (AC).

Yates' algorithm

There is a quick way to calculate the effects of factorial design presented by Yates'. The Yates' algorithm describes here and illustrates its use for the (2^4) full factorial design discussed. To apply the Yates' algorithm, the results should be placed in a standard order. The results are the numerical values of the estimated factor effects. As shown in Table 6, the Yates calculations start by evaluating as many auxiliary columns as factors being considered, in our example four columns E1, E2, E3, and E4 for a (2^4) design. The first eight elements in column E1 are obtained by adding the pairs together (51.27 + 77.56 = 128.83, 56.63 +

69.39 = 126.02, and so on). The last eight elements in column E1 are obtained by subtracting the top response from the bottom response of each pair, thus 77.56 – 51.27 = 26.29, 69.39 – 56.63 = 12.76, and so on. In just the same way that column E1 is obtained from the "Response" column, column E2 is obtained from column E1, column E3 is obtained from column E2, and column E4 is obtained from column E3. Finally, obtain the "Effect" column have only to divide these values by the appropriate divisor, as before, which is 16 (the number of runs) for the first element and 8 (half of the runs) for the others. Calculations can be made sure that the first value in column E4 (1152.42) is the sum of all the responses.

Statistical analysis

The statistically significant variables were tested using analysis of variance (ANOVA). It can be shown that in a two-level experiment, like this one, the sum of squares (SS) for the (2^4) full factorial design is given by equation (4):

$$SS_{(factor/interaction)} = N/8\ (\text{the estimate effect of factor/interaction})^2 \quad (4)$$

where N is the total number of measurements, including replicates. In this case, N is 32 since two replicate measurements were made for each combination of factor levels. For example, SS_A is:

$SS_A = 32/8\ (16.315)^2 = 1064.7169$.

It can be shown that each sum of squares has one degree of freedom (DOF). Since the Mean Square (MS) is given by equation (5):

$$MS = SS/DOF \quad (5)$$

Each MS is simply the corresponding SS. For example, MS_A is:

$MS_A = 1064.7169/1 = 1064.7169$.

To test for the significance of an effect, the MS is compared with the Error Mean Square (EMS) or residual mean square (RMS). RMS values are listed in Table 7. In Table 7, columns (1) and (2) are the values of each experiment that are repeated. Column (3) is the sum of the values of columns (1) and (2). RMS value is given by Eq. (6):

$$RMS = \left((50.27)^2 + (76.56)^2 + \ldots + (88.99)^2 + (52.27)^2 + (78.56)^2 + \ldots + (90.99)^2 - 1/2\,(102.54)^2 + (155.12)^2 + \ldots + (179.98)^2\right) = 32 \quad (6)$$

In order to test whether the difference between MS and RMS is significant, the calculated statistic F is given by Eq. (7):

$$F_{calculated} = MS/RMS \quad (7)$$

The critical value is $F_{1,\,16} = 4.494$ ($P = 0.05$). If be $F_{calculated} > F_{critical}$, then the effect is significant.

For example $F_{(A)\,calculated}$ is:

$F_{(A)\,calculated} = MS_A/RMS = 1064.7169/32 = 33.272$.

The results of ANOVA are listed in Table 8. Table 8 shows that the main factors such as pH, H_2O_2 concentration, and temperature are significant. Also, the interaction between pH × H_2O_2 concentration and pH × temperature is significant. Thus the factor of pH and interaction between pH × H_2O_2 concentration is highly significant.

The regression model

In a (2^4) factorial design, it is easy to express the results of the experiment in terms of a regression model. Because the (2^4) is just a factorial design, can be also used as either an effect or a means model. A first-order regression model is given by equation (8):

$$\hat{Y} = b_0 + b_1X_1 + b_3X_3 + b_4X_4 + b_{13}X_1X_3 + b_{14}X_1X_4 \quad (8)$$

Where $\hat{Y}$ is the predicted photodegradation efficiency, b_0 the average response, b_1, b_3, and b_4 the regression, b_{13}, and b_{14} are the interaction coefficients. The coded variables X_1, X_3, and X_4 represent pH, H_2O_2 concentration, and temperature respectively. The X_1X_3 and X_1X_4 terms are the interaction between pH × H_2O_2 concentration and pH × temperature respectively. The coded variables X_1, X_3 and X_4 take on values between – 1 and + 1. The $\hat{Y}$ at run (1) is:

$$\hat{Y} = 72.02625 + (16.315/2)(-1) + (10.995/2)(-1) + (7.975/2)(-1) - (17.8925/2)(-1)(-1) + (13.0125/2)(-1)(-1) = 51.9437$$

Table 6: Yates's algorithm for the (2^4) factorial design.

Run Number	TC	Response	E1	E2	E3	E4	Divisor	Effect
1	None	51.27	128.83	254.85	544.31	1152.42	16	72.026
2	a	77.56	126.02	289.46	608.11	130.52	8	16.315
3	b	56.63	135.89	277.38	13.21	27.64	8	3.455
4	ab	69.39	153.57	330.73	117.31	–11.58	8	–1.4475
5	c	74.20	132.35	39.05	14.87	87.96	8	10.995
6	ac	61.69	145.03	–25.84	12.77	–143.14	8	–17.8925
7	bc	83.45	165.32	97.78	–14.35	7.9	8	0.9875
8	abc	70.12	165.41	19.53	2.77	29.16	8	3.645
9	d	40.02	26.29	–2.81	34.61	63.8	8	7.975
10	ad	92.33	12.76	17.68	53.35	104.1	8	13.0125
11	bd	49.78	–12.51	12.68	–64.89	–2.1	8	–0.2625
12	abd	95.25	–13.33	0.09	–78.25	17.12	8	2.14
13	cd	80.18	52.31	–13.53	20.49	18.74	8	2.3425
14	acd	85.14	45.47	–0.82	–12.59	–13.36	8	–1.67
15	bcd	75.42	4.96	–6.84	12.71	–33.08	8	–4.135
16	abcd	89.99	14.57	9.61	16.45	3.74	8	0.4675

Table 7: RMS values for the (2^4) factorial design.

Run Number	TC	(1)	(2)	(3)
1	None	50.27	52.27	102.54
2	a	76.56	78.56	155.12
3	b	55.63	57.63	113.26
4	ab	68.39	70.39	138.78
5	c	73.20	75.20	148.4
6	ac	60.69	62.69	123.38
7	bc	82.45	84.45	166.9
8	abc	69.12	71.12	140.24
9	d	39.02	41.02	80.04
10	ad	91.33	93.33	184.66
11	bd	48.78	50.78	99.56
12	abd	94.25	96.25	190.5
13	cd	79.18	81.18	160.36
14	acd	84.14	86.14	170.28
15	bcd	74.42	76.42	150.84
16	abcd	88.99	90.99	179.98

Table 8: ANOVA table for the (2^4) factorial design.

Factor/interaction	SS	DOF	MS	F	Result
A	1064.7169	1	1064.7169	33.272	significant
B	47.7481	1	47.7481	1.492	no significant
AB	8.3810	1	8.3810	0.261	no significant
C	483.5601	1	483.5601	15.111	significant
AC	1280.5662	1	1280.5662	40.017	significant
BC	3.9006	1	3.9006	0.121	no significant
ABC	53.1441	1	53.1441	1.660	no significant
D	254.4025	1	254.4025	7.950	significant
AD	677.3006	1	677.3006	21.165	significant
BD	0.2756	1	0.2756	0.008	no significant
ABD	18.3184	1	18.3184	0.572	no significant
CD	21.9492	1	21.9492	0.685	no significant
ACD	11.1556	1	11.1556	0.348	no significant
BCD	68.3929	1	68.3929	2.137	no significant
ABCD	0.8742	1	0.8742	0.027	no significant
Error		16			
Total		31			

Residuals can be obtained as the difference between experimental and predicted etches rate deviations. The residual is given by Eq. (9):

$$e = Y - \hat{Y} \tag{9}$$

The values of Y, $\hat{Y}$ and e are listed in Table 9. Table 9 shows that pH, H_2O_2 concentration, temperature, pH × H_2O_2 concentration, and pH × temperature are the only significant effects and that the underlying assumptions of the analysis are satisfied.

Study the operational variables

The maximum photodegradation efficiency of AY23 obtained in this study was found to be 95.25%, corresponding to the operating conditions (pH=6, catalyst amount=50 mg/L, H_2O_2 concentration=15 ppm, and temperature= 35°C). The positive signs (run number: 12, Table 3) are related to factors such as pH, catalyst amount, and temperature. The photodegradation efficiency of AY23 at pH with levels 4 and 6, which the best results were obtained in acidic solution, (pH=6, X=95.25%). The charge of $CoFe_2O_4$ and its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For the above reasons, dye that has sulfite (SO_3^-) groups in its structure, which is negatively charged, the acidic solution favors adsorption of dye onto the photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AY23 in acidic solutions, which is due to the formation hydroxyl radical ($HO^•$) as it can be inferred from H_2O_2 oxidation [25]. The increase in catalyst amount increases the surface area available by more photocatalyst particles. So, the number of active sites on the photocatalyst surface increases that leads to the increase of the photocatalytic degradation efficiency [26]. The degradation of the dye has increased with increasing temperature. Although increasing the temperature decreases the rate of adsorption process on the catalyst surface, but due to accelerated decomposition of hydrogen peroxide increases and rapidly formed hydroxide radicals. So, with increasing temperature the reaction rate increases.

Table 9: Values of Y, $\hat{Y}$ and e for the (2^4) factorial design.

Run Number	TC	Y	$\hat{Y}$	$e = Y - \hat{Y}$
1	(1)	51.27	51.9437	–0.6737
2	a	77.56	73.1387	4.4213
3	b	56.63	51.9437	4.6863
4	ab	69.39	73.1387	–3.7487
5	c	74.20	80.8312	–6.6312
6	ac	61.69	66.2412	–4.5512
7	bc	83.45	80.8312	2.6188
8	abc	70.12	66.2412	3.8788
9	d	40.02	46.9062	–6.8862
10	ad	92.33	94.1262	–1.7962
11	bd	49.78	46.9062	2.8738
12	abd	95.25	94.1262	1.1238
13	cd	80.18	75.7812	4.3988
14	acd	85.14	87.2287	–2.0887
15	bcd	75.42	75.7937	–0.3737
16	abcd	89.99	87.2287	2.7613

The negative sign (run number: 12, Table 3) is related to factor H_2O_2 concentration. At a low concentration of H_2O_2 increase in photocatalytic degradation is observed. So, in the high concentrations leads to reduced photocatalytic degradation efficiency. This indicates that the excess amount of H_2O_2 is decomposed without promoting further degradation or maybe due to recombination of hydroxyl radicals and also the reaction of hydroxyl radicals with H_2O_2, the concentration of $HO^{\bullet}$ and so degradation efficiency is decreased [27].

Kinetic of photocatalytic degradation of dye

Photocatalytic degradation reaction kinetic of dye completely corresponds to the kinetic of pseudo-first-order reaction model reaction [28]. In the kinetic equation of the pseudo-first-order relationship between COD ($[COD]_o$= 50 ppm) and time t is given by equation (10):

$$\frac{-d[COD]}{dt} = k[COD] \quad (10)$$

the integral equation is given by equation (11):

$$\ln\left(\frac{[COD]_0}{[COD]}\right) = kt \quad (11)$$

in which k is the apparent pseudo-first-order rate constant (that is affected by COD) and t the reaction time.

A plot of $\ln\left(\frac{[COD]_0}{[COD]}\right)$ versus t for the optimal condition of photocatalytic degradation of dye is shown in Fig. 5. The linear plot suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetic with rate coefficient k= 0.048 min^{-1}.

CONCLUSIONS

$CoFe_2O_4$ nanoparticles were successfully synthesized by the precipitation method for the photocatalytic degradation of the azo dye. Nanoparticles were characterized by SEM and XRD techniques. The full factorial experimental design based on design matrix and Yates' algorithm was used in this process. The interaction between pH × H_2O_2 concentration and pH × temperature was the most

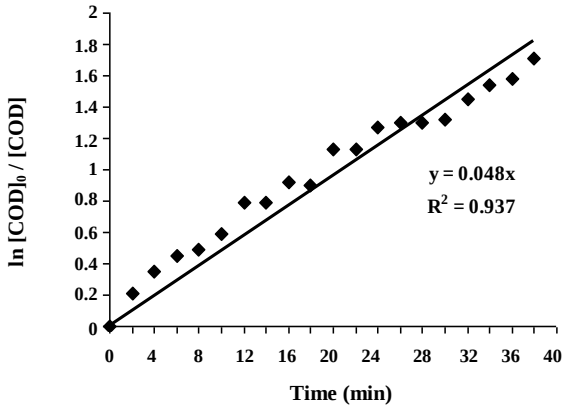


Fig. 5: Kinetic plot of pseudo-first order photocatalytic degradation of AY23 (pH= 6, catalyst amount= 50 mg/ L, H_2O_2 concentration= 15 ppm, temperature= 35 °C and irradiation time= 38 min).

influencing interaction. As observed, the most effective parameters in the photocatalytic degradation efficiency were pH and H_2O_2 concentration. Catalyst amount was the least effective factor in the response. The results of ANOVA show that the main factors such as pH, H_2O_2 concentration, and temperature are significant. Also, the interaction between pH × H_2O_2 concentration and pH × temperature is significant. Thus the factor of pH and interaction between pH × H_2O_2 concentration is highly significant. The regression model was studied. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye. Therefore a reaction rate constant of 0.048 min^{-1} was observed.

Received : Aug. 9, 2019 ; Accepted : Apr. 6, 2020

REFERENCES

[1] Zollinger H., "Color Chemistry Synthesis, Properties, and Applications of Organic Dyes and Pigments", Third Revised Edition, Wiley-VCH, (2003).

[2] Jiang H., Zhang G., Huang T., Chen J., Wang Q., Meng Q., Photocatalytic Membrane Reactor for Degradation of Acid Red B Wastewater, *Chem. Eng. J.*, **156**: 571-577 (2010).

[3] Jiang Y., Sun Y., Liu H., Zho F, Yin H., Solar Photocatalytic Decolorization of C.I. Basic Blue 41 in an Aqueous Suspension of TiO_2-ZnO, *Dyes Pigments*, **78**: 77-83 (2008).

[4] Yu C.H., Wu C.H., Ho T.H., Andy Hong P.K., Decolorization of C.I. Reactive Black 5 in UV/TiO_2, UV/Oxidant and UV/TiO_2/Oxidant Systems: A Comparative Study, *Chem. Eng. J.*, **158**: 578-583 (2010).

[5] Lee C., Yoon J., Application of Photoactivated Periodate to the Decolorization of Reactive Dye: Reaction Parameters and Mechanism, *J. Photochem. Photobiol. A: Chem.*, **165**: 35-41 (2004).

[6] Moradi R., Adsorption of Azo Dye Direct Blue 71 from Aqueous Solution Using $NiFe_2O_4$/CP Nanoparticles: Kinetic and Isotherm Model, *Russian J. Phys. Chem. A*, **92**: 2781-2789 (2018).

[7] Silva C.G., Faria J.L., Photochemical and Photocatalytic Degradation of an Azo Dye in Aqueous Solution by UV Irradiation, *J. Photochem. Photobiol. A: Chem.*, **155**: 133-143 (2003).

[8] Hojat Ansari S., Giahi M., Photochemical Degradation of Fluocinolone Acetonidin Drug in Aqueous Solutions Using Nanophotocatalyst ZnO Doped by C, N, and S, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**: 183-189 (2017).

[9] Mahmoodi N.M., Photocatalytic Ozonation of Dyes Using Multiwalled Carbon Nanotube, *J. Mol. Catal. A: Chem.*, **366**: 254-260 (2013).

[10] Moussavi Gh., Mahmoudi M., Degradation and Biodegradability Improvement of the Reactive Red 198 Azo Dye Using Catalytic Ozonation with MgO Nanocrystals, *Chem. Eng. J.*, **152**: 1-7 (2009).

[11] Torkaman M., Moradi R., Keyvani B., Photocatalytic Degradation Azo Dye Direct Red 23 Using Carbon Nanotubes Particles by UV/H_2O_2 Process in Batch Photoreactor, *Rev. Roum. Chim.*, **61**: 763-772 (2016).

[12] Moradi R., Bodaghi A., Hosseini J., Gangali A., Study Degradation of 4-(2-Pyridylazo)Resorcinol Dye in Circulating Fluidized Bed Photo Reactor Using ZnO Nanoparticles, *Arch. Hyg. Sci.*, **8(1)**: 1-8 (2019).

[13] Moradi R., Gangali A., Synthesis of Fe_3O_4 Nanoparticles and Their Application in Photo-Fenton Degradation of Direct Red 23 Dye in Aqueous Solutions, *Russian J. Phys. Chem. A*, **93**: 2789-2797 (2019).

[14] Moradi R., Hosseini J., Efficiency of Photo-Fenton Process in Degradation of 2-Chlorophenol, *Arch. Hyg. Sci.*, **6(4)**: 326-332 (2017).

[15] Asadpour-Zeynali K., Aleshi M., Electrochemical Modification of Glassy Carbon Electrode by Bismuth-Chitosan Nanosheets for Electrocatalytic Reduction and Determination of Tartrazine, *Portugaliae Electrochim. Acta*, **32**: 369-379 (2014).

[16] Sobreira S., Pacheco M.J., Ciríaco L., Lopes A., Effect of the Hydrodynamic Conditions on the Electrochemical Degradation of Phenol on a BDD Anode, *Portugaliae Electrochim. Acta*, **29**: 343-348 (2011).

[17] Guo X., Li H., Zhao S., Fast Degradation of Acid OrangeII by Bicarbonate-Activated Hydrogen Peroxide with a Magnetic S-Modified $CoFe_2O_4$ Catalyst, *J. Taiwan Inst. Chem Eng.*, **55**: 90-100 (2015).

[18] Gong H., Chu W., Determination and Toxicity Evaluation of the Generated Products in Sulfamethoxazole Degradation by UV/$CoFe_2O_4$/TiO_2, *J. Hazard. Mater*., **314**: 197-203 (2016).

[19] Abou Taleb M.F., Adsorption and Photocatalytic Degradation of 2-CP in Wastewater on to CS/$CoFe_2O_4$ Nanocomposite Synthesized Using Gamma Radiation, *Carbohydrate Polym*., **114**: 65-72 (2014).

[20] Behazin E., Misra M., Mohanty A.K., Compatibilization of Toughened Polypropylene/ Biocarbon Biocomposites: A Full Factorial Design Optimization of Mechanical Properties, *Polym. Testing*, **61**: 364-372 (2017).

[21] Alizadeh Kordkandi S., Forouzesh M., Application of Full Factorial Design for Methylene Blue Dye Removal Using Heat-Activated Persulfate Oxidation, *J.Taiwan Inst. Chem Eng*., **45**: 2597-2604 (2014).

[22] Barka N., Abdennouri M., Boussaoud A., Galadi A., Baalala M., Bensitel M., Sahibed-Dine A., Nohair K., Sadiq M., Full Factorial Experimental Design Applied to Oxalic Acid Photocatalytic Degradation in TiO_2 Aqueous Suspension, *Arabian J. Chem*., **7**: 752-757 (2014).

[23] Fu W., Yang H., Li M., Li M., Yang N., Zou G., Anatase TiO_2 Nanolayer Coating on Cobalt Ferrite Nanoparticles for Magnetic Photocatalyst, *Materials Lett*., **59**: 3530-3534 (2005).

[24] Li, C., Hsieh, J.H., Cheng, J.C., Huang C.C., Optical and Photoelectrochemical Studies on Ag_2O/TiO_2 Double-Layer Thin Films, *Thin Solid Films*, **570**: 436-444 (2014).

[25] Saien J., Asgari M., Soleymani A.R., Taghavinia N., Photocatalytic Decomposition of Direct Red 16 and Kinetics Analysis in a Conic Body Packed Bed Reactor with Nanostructure Titania Coated Raschig Rings, *Chem. Eng. J*., **151**: 295-301(2009).

[26] Seyyedi K., Farbodnia Jahromi M.A., Decolorization of Azo Dye C.I. Direct Black 38 by Photocatalytic Method Using TiO_2 and Optimizing of Process, *APCBEE Procedia*, **10**:115-119 (2014).

[27] Daneshvar N., Salari D., Khataee A.R., Photocatalytic Degradation of Azo Dye Acid Red 14 in Water: Investigation of the Effect of Operational Parameters, *J. Photochem. Photobio. A*, **157**: 111-116 (2003).

[28] Moradi R., Mahanpoor K., Photocatalytic Degradation of Azo Dye Acid Red14 from Aqueous Solutions Using MWCNTs Nanocatalyst, *Arch. Hyg. Sci.*, **7(2)**: 71-80 (2018).