Kinetic Modeling and Photocatalytic Reactor Designed for Removal of Resorcinol in Water by Nano $ZnFe_2O_4$/Copper Slag as Catalyst: Using Full Factorial Design of Experiment

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ABSTRACT: *In this research new catalyst prepared by supporting $ZnFe_2O_4$ on Copper Slag (CS) and characterization of this catalyst was done by using Scanning Electron Microscopy (SEM) image, Energy-Dispersive X-ray (EDX) spectroscopy, BET surface area, and X-Ray Diffraction (XRD) patterns. UV + H_2O_2 processes by $ZnFe_2O_4$/CS photocatalyst was used for degradation of Resorcinol as a pollutant in water. Circulate Packed Bed Reactor (CPBR) with a total volume of 1 liter and an effective volume of 0.2 liters was used in this process. Design of Experiments (DoEs) was utilized and kinetics of the photocatalytic degradation process was modeled using full factorial design. The experiments were designed considering three variables at three-levels (including pH, the initial concentration of Resorcinol, and initial concentration of H_2O_2). The results showed that pH=5, the initial concentration of Resorcinol=50 ppm and H_2O_2 initial concentration=40 ppm had the highest Resorcinol degradation constant rate ($k= 3.506 \times 10^{-3}$).*

KEYWORDS: *Photodegradation; $ZnFe_2O_4$; Copper slag; Full factorial.*

INTRODUCTION

Exposure to many phenolic compounds such as Resorcinol can affect the biological function of living organisms. Resorcinol is listed as Endocrine Disrupting Chemicals (EDCs) [1].

Resorcinol is used as a chemical to synthesize organic compounds, especially pharmaceutical compounds. This compound is also used in the production of diazo dye and additives in plastics [2]. Conventional wastewater treatment methods such as chemical, physical, and biological processes are not always suitable for treating moderate to high concentration wastewaters. Advanced Oxidation Processes (AOPs) are alternative techniques

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for the destruction of phenolic compounds and many other organics in wastewater. AOPs rely on the production of highly reactive hydroxyl radicals. These hydroxyl radicals are the strongest oxidants that can be used in water and can actually, oxidise any compound present in the water. This term usually refers to a subset of chemical processes that use ozone (O_3), hydrogen peroxide (H_2O_2) and UV light and catalyst.

The photocatalytic method is one of the most appealing (AOPs) techniques. $ZnFe_2O_4$ such as TiO_2 is one of the most widely used photocatalysts because of its relatively long lifetime of electron-hole pair and chemical stability [3,4]. UV irradiation of $ZnFe_2O_4$ can efficiently generate electron-hole pairs, which induce strong oxidizing agents such as hydroxide radicals and O_2^- by interacting with H_2O and dissolved O_2 in aqueous solution [5]. These radicals can decompose VOCs to non-toxic molecules such as CO_2 and H_2O. In this process, is the main problem is the separation of the catalyst from the solution [4].

One way to eliminate this problem is fixing the catalyst on a suitable base. Copper Slag is very stable and cheaper then it was chosen as the base of the $ZnFe_2O_4$ for the increasing catalyst surface. Mechanical and thermal property of CS is suitable for use as a support of catalyst [6,7].

In this research, a new catalyst prepared by supporting $ZnFe_2O_4$ on Copper Slag and characterized using Scanning Electron Microscopy (SEM) image, BET and X-Ray diffraction patterns. For degradation of Resorcinol was used UV + H_2O_2 process in the presence of $ZnFe_2O_4$ /CS as a photocatalyst.

The full factorial methodology is a set of statistical techniques and applied mathematics in modeling experimental results. This method can be used for studying the effect of several factors (with different levels) and their influence on each other. For photocatalytic degradation of the Resorcinol, the process was used three factors and three levels full factorial experimental design [8-10].

If all variables are assumed to be measured, the full factorial experimental design can be expressed as follows:

$$Y = f\left(x_1, x_2, x_3, \cdots x_i\right) \quad (1)$$

The goal is to optimize the response variable Y. The assumption is that the independent variables x, continuously and trial and error control are very little and negligible. Then be sure to find a good approximation for the functional relationship between independent variables and the equation of the first order. This factorial design results in 11 tests with all possible combinations of x_1, x_2, and x_3. Photocatalytic degradation efficiency (Y) was measured for each of these tests. The first-order model with all possible interactions was chosen to fit the experimental:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (2)$$

EXPERIMENTAL SECTION

Materials

In this study, Resorcinol, Zinc, and Iron nitrate salt and other materials were provided by Merck Company (Germany). Copper Slag purchased from the Iranian company of Messbareh. The pH values were adjusted to the desired level using dilute NaOH and H_2SO_4. The shape, size and surface morphology of the synthesized $ZnFe_2O_4$/CS were examined using the obtained images of a Philips XL-30 Scanning Electron Microscope (SEM). The X-Ray Diffraction (XRD) analysis of the samples was done using a DX27-mini diffractometer. BET surface area of materials was determined by N_2 adsorption–desorption method at 77 K, measured using a BELSORP-mini II instrument. The samples were degassed under vacuum at 473 K for 12 hours before the BET measurement. All Ultraviolet/Visible (UV/Vis) absorption spectra for the determination of COD were obtained using an Agilent 8453 spectrophotometer. A Metrohm pH meter model 827 was used for the measurement of pH amounts. Likewise, in order to separate the catalyst from samples, an ALC 4232 centrifuge was employed.

Experimental method

50 mL 0.25 M Zinc nitrate solution (prepared from $Zn(NO_3)_2.6H_2O$) was added to the 50 mL 0.5 M Ferric nitrate solutions (prepared from $Fe(NO_3)_3.9H_2O$), 100 mL 2M molar urea solutions were added to this solution and reflux for 12 hours in a hot water bath at 90 °C. The precipitates isolated by filtering were washed with distilled water and drying in 110 °C and heated in a furnace at 550 °C for 4 hours. To stabilize the catalyst on Copper Slag, Copper Slag was mixed with $ZnFe_2O_4$

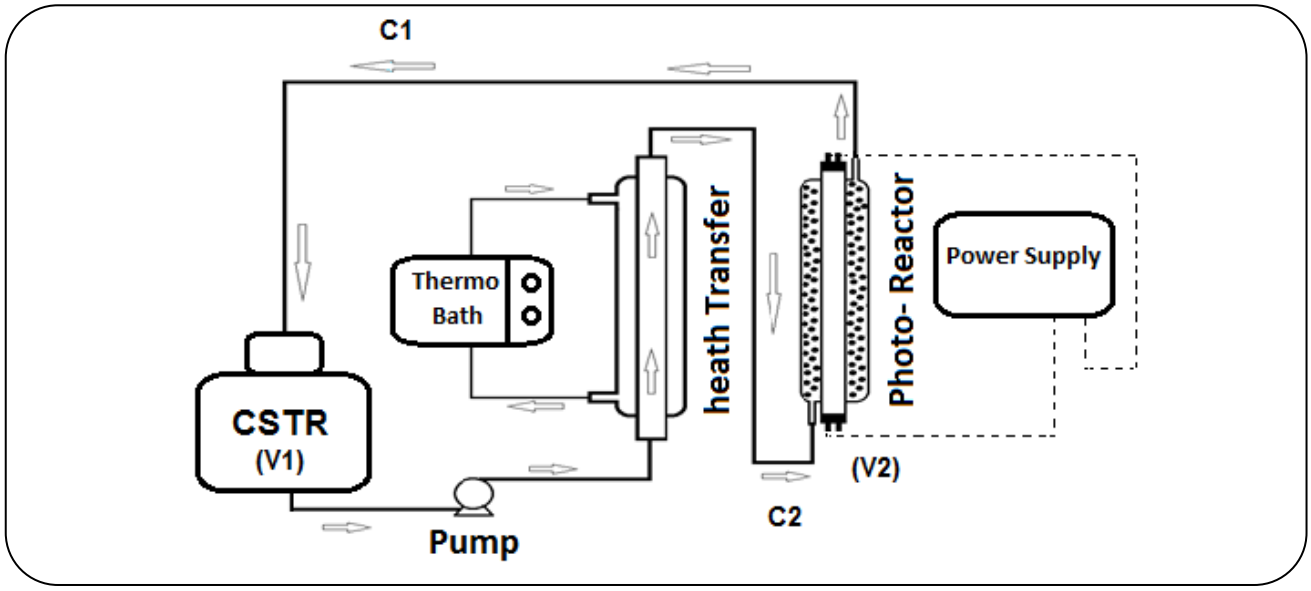


Fig. 1: Schematic view of the experimental apparatus.

powder and was put into the furnace for 6 hours at 550 °C [11].

The schematic view of the apparatus was shown in Fig. 1. Circulate Packed Bed Reactor (CPBR) with a total volume of 1 liter and effective volume of 0.2 liter was used in this process. One UV lamp with a power of (15 W, Philips) was placed directly in the reactor and around the UV lamp was filled with catalyst. The CPBR was filled with 70 grams of catalyst $ZnFe_2O_4$ / Copper slag.

Full factorial experimental design

Based on the Full Factorial experimental design method, several experiments were conducted and factors influencing the photocatalytic degradation were studied. The factors influencing the photocatalytic degradation (pH, the initial concentration of Resorcinol ($C_{Resorcinol}$) and initial concentration of Hydrogen peroxide (C_{H2O2})) were studied.

The photocatalytic efficiency of pure $ZnFe_2O_4$ NPs and $ZnFe_2O_4$/ Copper Slag on the Resorcinol degradation was investigated using design of experiments. The experiments were designed considering three variables, including pH, the initial concentration of Resorcinol and H_2O_2 concentration at three-levels. The experimental range and levels of variables are shown in Table 1. Although a wide range of release of resorcinol has been reported in various industrial effluents. These values can be reduced to between 50 and 150 by conventional methods in wastewater treatment.Then initial concentration of Resorcinol from 50 to 150 ppm at three levels (50, 100 and 150 ppm), pH varied from 5 to 9 at three levels (5, 7 and 9), and H_2O_2 concentration from 20 to 40 ppm at three levels (20, 30 and 40 ppm). In Table 2, 11 experiments related to this factorial design and their experimental conditions have been listed. The removal efficiency of Resorcinol was a dependent response. In order to do DOEs, Minitab 16 version 16.2.0 statistical software was utilized. Also, an analysis of variance (ANOVA) was run in order to analyze the results.

For photocatalytic degradation experiments, the different volume levels of H_2O_2 were added to the Resorcinol solution. Using a dilute solution of NaOH and sulfuric acid pH of solutions was adjusted. The resulting solution was transferred to the feed tank and send in to the reactor by using a water pump. At certain time intervals, samples were taken and COD was measured [12]. During the photocatalytic process, COD test (Standard Methods 5220) was used to determine the amount of Resorcinol that remove from aqueous solution [12].

Analysis of variance (ANOVA) is a set consist of a number of statistical methods used to analyses the differences among group means and their associated procedures. ANOVAs are useful for testing three or more means variables for statistical significance. ANOVA was used for graphical analyses of the data to obtain

Table 1: Experimental range and levels of the variables.

Variables	Range and levels		
	–1	0	+1
pH	5	7	9
Initial Con. of Resorcinol (ppm)	50	100	150
H_2O_2 Con. (ppm)	20	30	40

Table 2: Experimental conditions for the photocatalytic process.

Exp.No	pH	Initial Con. of Resorcinol (ppm)	H_2O_2 Con. (ppm)
1	5	50	20
2	9	50	20
3	5	150	20
4	9	150	20
5	5	50	40
6	9	50	40
7	5	150	40
8	9	150	40
9	7	100	30
10	7	100	30
11	7	100	30

the interaction between the process variables and the responses. In this research, three variables are investigated in three levels, so Anva's approach is appropriate for analyzing the results. The quality of the fit polynomial model was expressed with the coefficient of determination, R^2, and its statistical significance was checked by Fisher's F-test in the same program. Model terms were evaluated by the P-value

RESULTS AND DISCUSSION

Catalyst identification

The identification of the catalyst was performed by XRD and SEM techniques. The corresponding powder X-ray diffraction (XRD) pattern provides further crystallinity and phase information about the obtained $ZnFe_2O_4$. The observed peak positions (as shown in Fig. 2) Are consistent with the characteristic peaks reported for $ZnFe_2O_4$ in the literature [13]. The major crystalline phases present in copper slag were Fayalite ($2FeO.SiO_2$) specified peaks at the 2θ =52, Magnetite (Fe_3O_4), Hedenbergite Ca (Fe, Mg) $(SiO_3)_2$, Hematite and

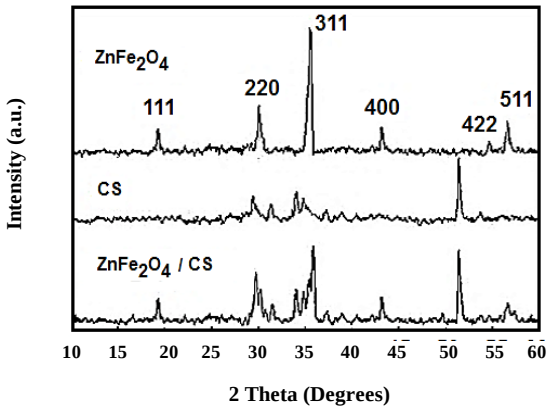
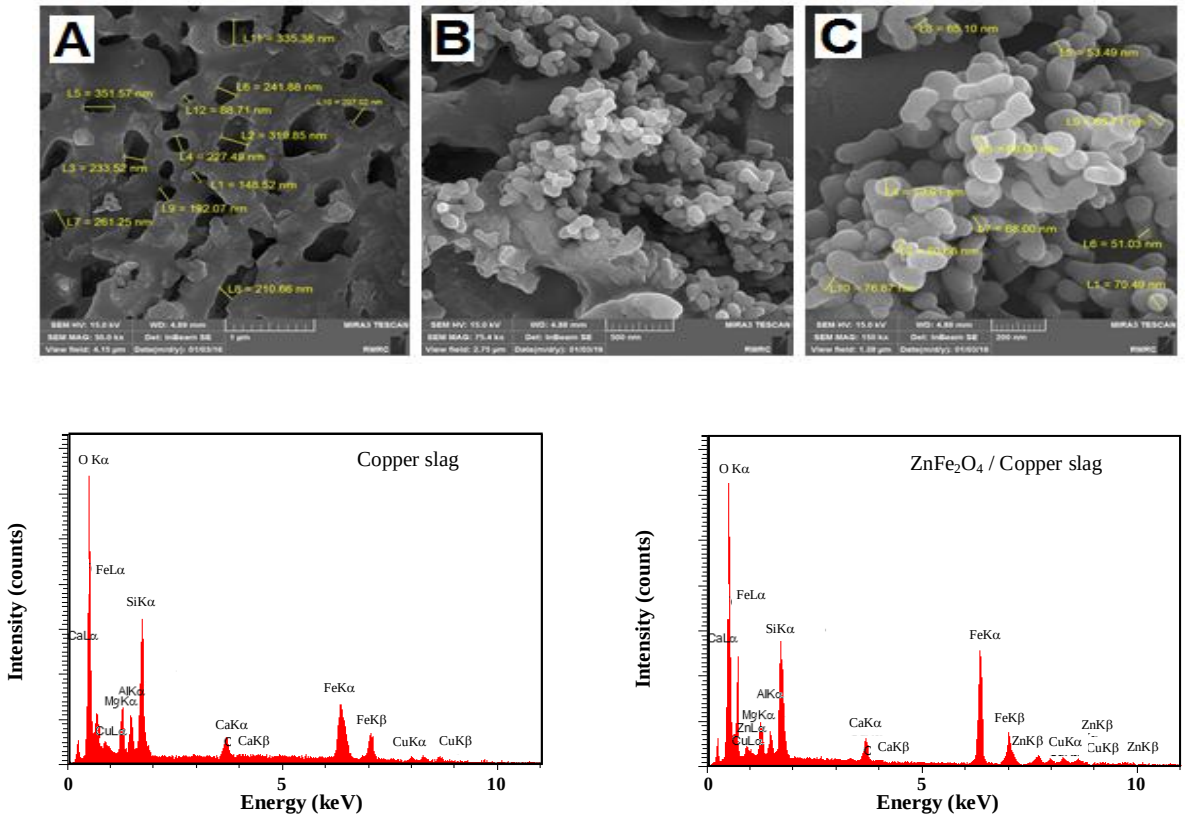


Fig 2: The XRD patterns of photocatalyst $ZnFe_2O_4$, Copper slag (CS) and $ZnFe_2O_4$/CS.

Maghemite specified peaks in the range of 2θ =28-31, which is consistent with previous research [14].

Moreover, the mean sizes of the as-synthesized nanoparticles are calculated from the peak broadening in the XRD pattern by using the Debye–Scherrer formula. The average sizes of $ZnFe_2O_4$ are 65 nanometers.



Materials	Unit	O	Mg	Al	Si	Ca	Fe	Cu	Zn
Copper slag	Weight%	36.12	2.11	1.08	16.17	4.64	38.23	0.56	-------
	Atomic%	59.27	2.31	1.05	16.17	3.05	17.92	2.31	-------
$ZnFe_2O_4$/CS	Weight%	31.72	1.82	0.95	15.14	4.11	39.32	0.47	6.47
	Atomic%	56.56	2.16	1.01	15.42	2.93	20.03	0.21	1.68

Fig 3: SEM images and their EDX analysis of Copper Slag (A) and $ZnFe_2O_4$/CS (B, C).

The surface morphology and the approximate particle size of the $ZnFe_2O_4$ were characterized by SEM. The results (Fig. 3) show that the particles are smooth, homogeneous surface and very similar Nano-spherical particles. The sizes of particles are different, but all of these particles have a similar shape. As shown in Fig. 3, all surfaces of CS have covered with $ZnFe_2O_4$ Nanoparticle. The EDX analysis of the product (due to changes in the atomic% of Copper Slug and $ZnFe_2O_4$ / Copper Slug) also proved that the material formed on the surface could include particles of Nano $ZnFe_2O_4$

Low-temperature (77 K) nitrogen adsorption-desorption isotherms are used for pore structure analysis of porous materials. The Brunauer–Emmett–Teller (BET) method is used for the determination of the surface area of new materials. Fig. 4 shows the adsorption-desorption isotherms and BET surface area for the Copper slag, and $ZnFe_2O_4$/CS. The adsorption isotherms of the Copper Slag sample are of type IV and present hysteresis loops of type H_2 classification with previous research [15]. Indicating that the structure is mainly mesoporous with pores with narrow mouths (ink-bottle pores). The presented type IV isotherm and present hysteresis loops of type H1, characteristic of mesoporous materials with bottleneck (cylindrical pore geometry) pores and spherical particles arranged in a fairly uniform way for $ZnFe_2O_4$ and $ZnFe_2O_4$/CS.

The BET surfaces area of Copper slag and $ZnFe_2O_4$/CS were determined 13.21 and 16.25 (m^2/g) respectively. As the size of the particle becomes smaller, the surface becomes wider. Because the $ZnFe_2O_4$ particles of the nanoscale are located, its surface has increased.

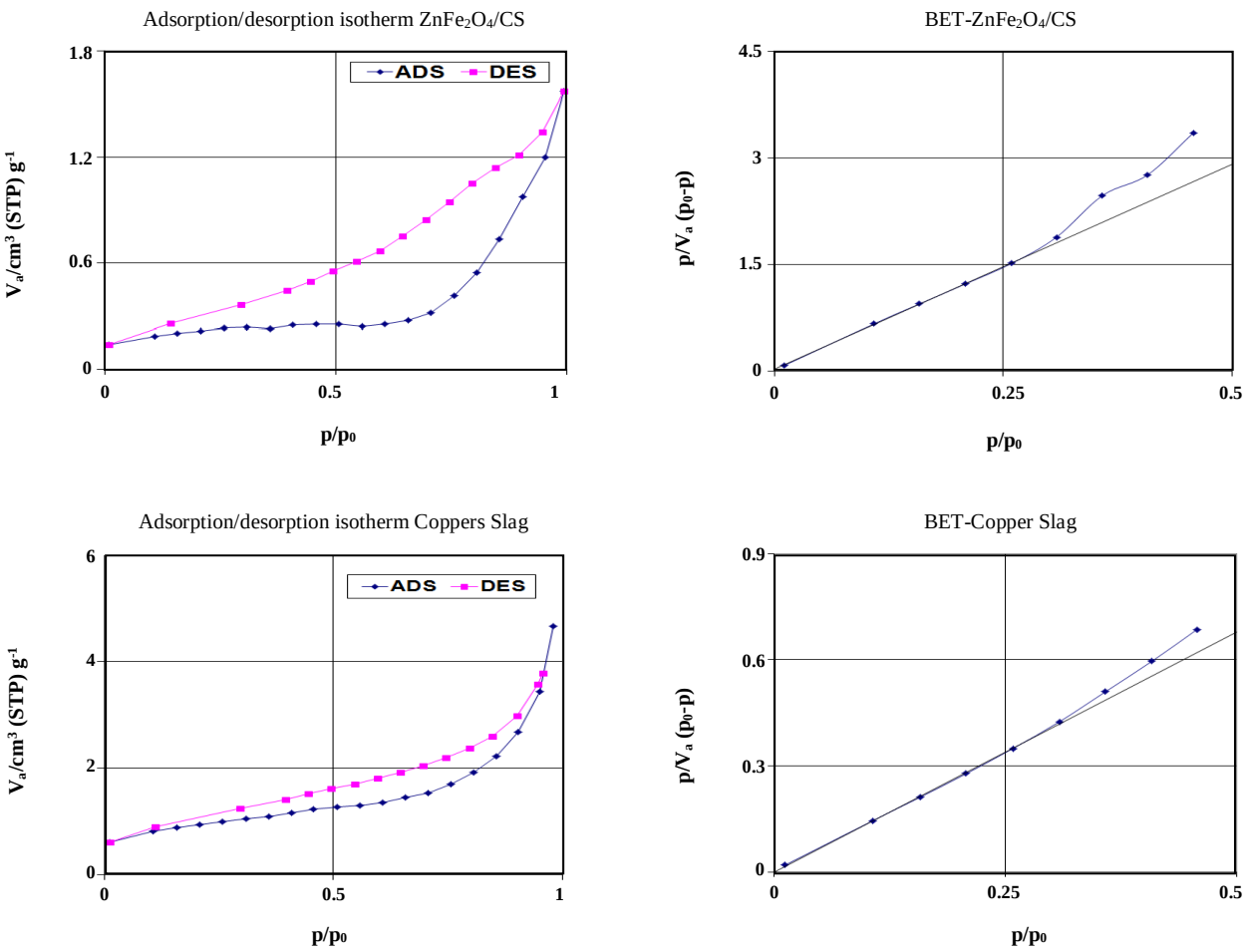


Fig 4: Adsorption-desorption isotherms and BET surface area for the Copper slag and $ZnFe_2O_4$/CS.

Design Equation for Packed-bed Batch Recirculated Photoreactor

One possible mode of operation of the combined reactor is the Packed-bed Batch Recirculated Photoreactor (PBRC) current of the effluent, which causes a gradual decrease of pollutant amount [16]. The prediction of pollutant concentrations in the design process is very important. For a packed-bed tubular reactor, the design equation can be written as follows[16]:

$$(-R_A) = -q\frac{dC_A}{dW} \tag{3}$$

Where q is the volumetric flow rate of fluid in batch-recirculated reactor, W is the mass catalyst contained in the reactor, CA is the substrate concentration and $-R_A$ is the rate of reaction.

After the integration of Eq. (3), we obtain:

$$\int_{C_2}^{C_1}\frac{dC}{-R_A} = \int_0^W \frac{dW}{q} \tag{4}$$

The kinetics of the removal of organic pollutants from a photocatalytic process such as UV/H_2O_2 /Catalyst were reported pseudo-first-order [17]:

$$(-R_A) = k_2 C_A \tag{5}$$

Where k_2 is pseudo-first-order reaction rate constant for packed-bed photoreactor.

By substituting equation 5 into equation 4 and integration, we will have:

$$C_1 = C_2 e^{\left(-\frac{Wk_2}{q}\right)} \tag{6}$$

This equation correlates outlet concentration for photoreactor (C1) to inlet concentration (C2). The CSTR

Table 3: Estimated effects and coefficients for k2

Ter	Effect × 10^{-3}	Coef × 10^{-3}	SE Coef × 10^{-5}	T value	P value	VIF
Constant	-	2.063	1.7	118.41	0.000	
pH	-1.070	-0.535	2.0	-26.20	0.000	1.00
Resorcinol	-0.667	-0.333	2.0	-16.32	0.000	1.00
H_2O_2	1.046	0.523	2.0	25.60	0.000	1.00
Resorcinol × pH	-0.278	-0.139	2.0	-6.80	0.002	1.00
H_2O_2 × pH	-0.130	-0.065	2.0	-3.18	0.034	1.00
Resorcinol × H_2O_2	-0.307	-0.154	2.0	-7.52	0.002	1.00
R^2=99.77%, Pred R^2=92.01%, Adj R^2=99.42%						

operates under unsteady stated conditions. The mass balance of substrate for the CSTR with V1 volume is represented by the following equation:

$$V_1 \frac{dC_2}{dt} = qC_1 - qC_2 \quad (7)$$

$$\frac{dC_2}{dt} = \frac{q}{V_1}\left(C_1 - C_2\right) \quad (8)$$

By substituting equation 4 into equation 6 the following equation will be obtained:

$$-\frac{dC_2}{dt} = \frac{q}{V_1}\left[1 - e^{\left(-\frac{Wk_2}{q}\right)}\right]C_2 \quad (9)$$

By comparing equation 7 with pseudo-first-order reaction rate, we can write k_1 as follows:

$$k_1 = \frac{q}{V_1}\left[1 - e^{\left(-\frac{Wk_2}{q}\right)}\right] \quad (10)$$

While k_2 may be empirically related to the effective parameters with full factorial experimental design analysis.

The statistical analysis for modeling of k

In Table 3, the estimated effects and coefficients for (k_2) have been listed. In this table, correlation coefficient pried R-squared and adjusted R-squared values were also reported. The square of the correlation coefficient for each response was computed as the coefficient of determination (R^2). The accuracy and variability of the model can be evaluated by R^2. The R^2 value is always between 0 and 1. The closer the R^2 value to 1, the stronger the model is and the better the model predicts the response (k_2). R^2 value was reported to be 0.9971 in this paper. The "pried R-squared" of 0.9201 is in reasonable agreement with the "adj R-squared" of 0.9942, confirming good predictability of the model. In this way, the effects of the variables, interaction was reported in Table 3. It is vital to note that P values have been assessed considering α=0.05. Table 4 depicts the results of ANOVA. The effect on the response was increased by increasing the value of F parameter and decreasing P parameter. For main effects (with 3 degrees of freedom) including the initial concentration of Resorcinol, pH and H_2O_2 concentration, F and P values have obtained.

Resorcinol decomposition rate constant was determined from the chart of $\ln COD_0/COD$ according to time; the slope of the line is k_2. Mathematical model representing Resorcinol photocatalytic degradation in the range studied can be expressed by the following equation:

$$k_2 = 2.063\times10^{-3} - 5.35\times10^{-4}\left[pH\right] - 3.33\times10^{-4}\left[Res\right] + 5.23\times10^{-4}\left[H_2O_2\right] - 1.39\times10^{-4}\left[Res\times pH\right] - 6.5\times10^{-5}\left[pH\times H_2O_2\right] - 1.54\times10^{-4}\left[Res\times H_2O_2\right] \quad (11)$$

In Fig. 5, the plots of the main effects have been shown. These plots indicate that of three main effects, only the variable of the initial concentration of Resorcinol has a negative effect on response (k_2); the effects of other variables on response were positive. By substituting Eq (11) into Eq (10) the final equation will be obtained as

Table 4: ANOVA results.

Source	Degree of freedom	Adj SS × 10^{-6}	Adj MS × 10^{-6}	F value	P value
Model	6	6	1	286.830	0.000
Linear	3	5	2	536.02	0.000
pH	1	2	2	686.45	0.000
Resorcinol	1	1	1	266.22	0.000
H_2O_2	1	2	2	655.40	0.000
2-Way Interactions	3	0	0	37.63	0.002
Resorcinol × pH	1	0	0	46.26	0.002
H_2O_2 × pH	1	0	0	10.10	0.034
Resorcinol × H_2O_2	1	0	0	56.53	0.002
Error	4	0	0		
Lack of Fit	2	0	0	1745.53	0.001
Pure Error	2	0	0		
Total	10	6			

Table 5: Residual values.

Exp. No.	k_2 × 10^{-3}	Fit × 10^{-3}	Residual (k_2–Fit) × 10^{-5}	St Resid
1	2.097	2.050	4.608	1.99767
2	1.360	1.388	-2.794	-1.21030
3	1.941	1.969	-2.790	-1.21030
4	0.797	0.7509	4.607	1.99767
5	3.506	3.534	-2.792	-1.21030
6	2.657	2.611	4.603	1.99767
7	2.884	2.838	4.602	1.99767
8	1.332	1.359	-2.794	-1.21030
9	2.036	2.063	-2.616	-0.47569
10	2.038	2.063	-2.403	-0.43703
11	2.040	2.063	-2.226	-0.40481

follows:

$$k_1 = \frac{q}{V_1}\left[1 - e^{\left(\frac{W}{q}\times 10^{-4}\right)(Y)}\right] \quad (12)$$

That where on

Y=0.2063-5.35[pH]-.33[Res]+5.23[H_2O_2]-1.39[Res×pH]-6.5[pH×H2O2]-1.54[Res×H_2O_2]

n order to evaluate Eq (12) in predicting k_1 at different conditions, a comparison between experimental and calculated k1 for the decomposition of Resorcinol is shown in Fig. 6.

CONCLUSIONS

The results revealed that:

1. $ZnFe_2O_4$ Nanoparticles(NPs) had been successfully synthesized and supported on the surface of CS with no decrease of NPs photocatalytic efficiency and chemical change of CS which are indicative of being effective this supporting method.

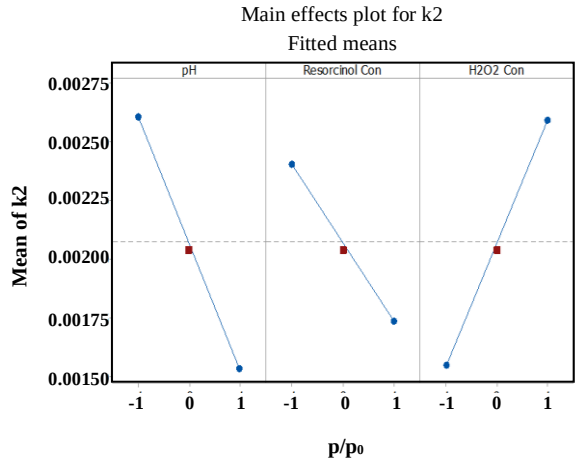


Fig. 5: the plots of main effects.

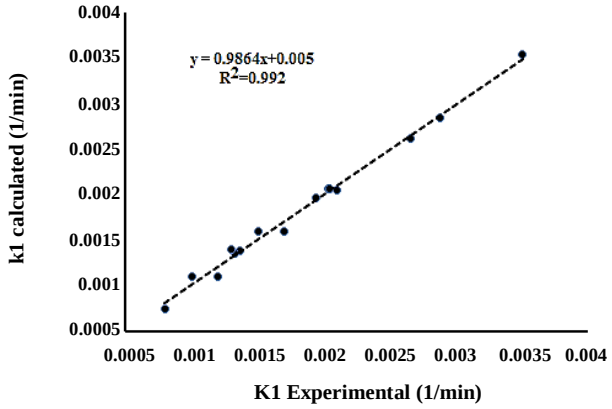


Fig 6: Comparison between experimental and calculated k1 for removal of Resorcinol in batch -recirculated packed bed photoreacto.

2. While supporting $ZnFe_2O_4$ NPs on the surface of CS help to enhance the catalyst separation from the mixture.

3. The statistical analysis results indicated that the model used in this paper is significantly reliable and valid.

4. In the process of the Resorcinol photocatalytic degradation using $ZnFe_2O_4$/CS, the three parameters of pH, the initial concentration of Resorcinol and H_2O_2 concentration are effective on k_2. If the interaction effects of variables are ignored, only the initial concentration of Resorcinol has a negative effect on the k_2.

5. The mathematical model of the rate constant for Resorcinol photocatalytic degradation in the range studied can be obtained with full factorial experimental design analysis.

6. The results showed that pH=5, the initial concentration of Resorcinol=50 ppm and H_2O_2 initial concentration=40 ppm had the best performance for Resorcinol degradation in aqueous solution.

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