

Experimental Design and Response Surface Modeling for Optimization of 2-Chlorophenol Removal from Water by Nanoscale Iron and Fe Powder

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Abstract

The discharge of organic contaminants such as phenol and its derivatives emerging from the industries into water has become a critical concern. In present research, potential of nanoscale iron particle and iron powder has been tested for the removal of 2-chlorophenol from aqueous solutions. In this research, nano particles were procreated by reduction of ferric iron in presence of sodium borohydrid. The characterization of synthesized particles was carried out using SEM and XRD analysis. The effect of pH, initial concentration of chlorophenol, and contact time and sorbents dosage on 2-CP removal was investigated. A statistical experimental design based on "central composite design" was exerted for measure the effect of these variables. The results of the CCD predicted that the maximum adsorption of 2-CP (100%) by nZVI could be achieved at pH, initial concentration, time, and dosage of sorbent as 4, 5.0 mg/L, 70 min, and 1.33 g, respectively. Also, for 86.74% removal of 2-CP, initial concentration, pH, contact time and Fe powder dosage were 5.0 mg/L, 3.23, 56.92 min and 2.50 g respectively.

The results show that the nZVI can be applied for treatment of organic contaminants in water and wastewater. Also, the optimum conditions of these theoretically obtained variables are beneficial for their monitoring which can be applied at an industrial-scale process.

Keywords: Nano scale iron particle; 2-Chlorophenol; Central composite design; Powder; Potential

Introduction

Phenol and compound phenolic are one of the organic and priority pollutants amongst all industrial effluents. 2-chlorophenol is one of the derivatives for phenol which is produced during chlorination of water. This compound is the most toxic form of phenol, which imposes hazardous health effects towards humans as well as animals [1]. Chlorophenols are identified from aspects such as taste, smell, color and harmful to organisms. Also, Chlorophenols are corrosive compound for skin, eye and respiratory tract. Chlorophenols are rapidly absorbed when swallowed by the oral or respiration [2,3]. This organic pollutant accumulates mostly in the liver and kidney, muscle and brain. Chlorophenols are eliminated primarily in the urine as both free and bound forms, with lesser amounts in fecal matter. Also, these contaminants exist in the effluents of industrial, such as petroleum, plastics manufacturing, coal conversion, etc. Unfortunately, chlorophenol compounds are not desirous to biodegradation [4]. Different methods are employed for removal of Chlorophenols including chemical oxidation, adsorption, solvent extraction, reverse osmosis [5,6]. Despite these fruitful attempts, there is still a need to search a drastic matter to eradicate the menace of phenolic compound from wastewater and, hence it is envisaged to develop a systematic and exhaustive process for the removal of pollutants [7,8]. In present research, nano particle iron and iron powder were selected to investigate the optimum adsorption parameters for maximum removal of 2-chlorophenol from wastewater through batch adsorption process.

Literature survey reveals that in recent past nZVI has been successfully employed as an adsorbent for the removal of organic matters and metal ions from industrial effluents [8-10]. During recent years, the synthesis of nanoparticle Iron is of specific interest for researcher. NZVI and Fe powder are widely investigated in degradation of phenol and other organic matter [11]. These compounds can degrade contaminants in the short time than biodegradation under the same conditions [12]. Degradation of contaminants occurs on the surface of nZVI or Fe powder [13]. There are many ways to produce nanoparticles

which one of these methods synthesizes ZVI nanoparticles by dropping ferric ion solution to borohydride solution [14]. In most of researches, the particles perform best when the size is typically around 1-100 nm [15,16]. The purpose of this research was to synthesize of nanoscale iron particle by a cheap method and comparison of its efficiency with Fe powder.

The purpose of the present study is to investigate the optimum conditions for the removal of 2-chlorophenol from aqueous solutions using nZVI and Fe powder. This paper includes results on the effects of pH, temperature, contact time, sorbent dosage, and 2-chlorophenol concentration. Another prominent feature of the present paper is application of the gathered data on statistical calculations based on "Central Composite Design (CCD)" and theoretical monitoring of effects of various operating variables such as pH, sorbent dosage, and 2-chlorophenol concentration on the performance of the sorption process.

Material and Methods

Preparation of the nZVI

In this research, nano particles were procreated by reduction of ferric iron in the presence of sodium borohydrid. These particles synthesized with 1:1 volume ratio of NaBH₄ and FeCl₃·6H₂O. The nano particles were produced each day. NaBH₄ solution (0.16 M) added drop into FeCl₃·6H₂O (0.1 M) by vigorous magnetic stirring at atmospheric

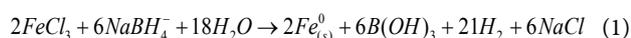
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conditions during 1 hour. Finally, fine black precipitates created and precipitated according to the following reaction:



Chemicals and batch experimental

All chemicals were procured from M/s Merk. Standard 2-chlorophenol (2CP) stock solution was prepared and all working solutions were prepared by diluting the stock solution. Experiment was done at different qualification of contact time (10, 40, 70, 100 and 130 min), phenol concentration (5, 10, 15, 20 and 25 mg/L), pH (2, 4, 6, 8 and 10), temperature (20, 30, 40, 50 and 60°C) and sorbent dosage (0.5, 1.5, 2.5, 3.5 and 4.5 g). The concentration of residual phenol was determined using the spectrophotometer DR-5000 in $\lambda_{max}=520$ nm. Also for data analysis the Response Surface Method was used. The central composite design was applied to appraisal the effect of

operating variables such as pH, sorbent dosage, and 2-chlorophenol concentration on the performance of the sorption process. Thus, for investigation the interactive influence of these independent parameters and their optimization for 2-chlorophenol biosorption process Response Surface Methodology (RSM) was applied.

Experimental design

A statistical experimental design based on “Central Composite Design (CCD)” was planned [17] and the percentage removal of 2-chlorophenol was measured for different variables such as pH, 2CP concentration, time and dosage of nZVI and Fe powder abbreviated as x1, x2, x3, x4, and x5, respectively. These variables were investigated at five levels (-2, -1, 0, 1, 2) and the dependent variable was chosen as Y. In present study, Minitab software package was used to design and evaluate these five independent variables at five levels on the responses according to the Eq. (2). The ranges for the selected levels of the five variables are shown in Table 1, while the experimental percentage removal of 2-CP for different selected levels of these variables is presented in Tables 2 and 3 for all the 30 runs carried out during the theoretical treatment.

$$Y = \beta_0 + \sum \beta_j X_j + \sum \beta_{jj} X_j^2 + \sum \beta_{jk} X_j X_k \quad (2)$$

Where, Y = response, β_0 = intercept, β_j = linear coefficients, β_{jj} = squared coefficients, β_{jk} = interaction coefficients, X_j, X_j^2, X_j, X_k = level of independent variables.

Moreover, the theoretically predicted values of yield at different experimental conditions are illustrated in Tables 2 and 3.

Results and Discussions

Characterization of nZVI

Properties of nano iron particles were determined with scanning electron microscope (SEM) and X-Ray Diffractometry (XRD). The morphology of nZVI was ascertained with the help of scanning electron microscopy (SEM) analysis. These analyses show the quantitative characteristics such as the particle size, shape/morphology and surface area of the particles. Figure 1 exhibits the SEM images of the synthesized nano particle. It is determined that nanoscale Iron particles can have several good advantages such as high specific surface, great surface reactivity and flexibility in applications [18]. The results display that the nano scale particles are some deal spherical. The result shows that these spherical particles have thread-like structures. This property increased the available and specific surfaces for more reaction.

The XRD pattern (Figure 2) displays six characteristic peaks at $2\theta = 4.4521^\circ, 16.54^\circ, 31.5378^\circ, 44.2876^\circ, 57.6486^\circ$ and 71.4737° in crystalline structure and corroborates the presence of Lepidocrocite ($Fe^{+3}O(OH)$) in the nZVI.

Theoretical treatment for deriving optimum conditions

The experimental results represent that the maximum adsorption of 2-CP (100%) by nZVI could be achieved at pH, initial concentration, time, and dosage of sorbent as 4, 5.0 mg/L, 70 min, and 1.33 g, respectively. Also, for maximum removal of 2-CP (86.74%), concentration, pH, time, and dosage were 5.0 mg/L, 3.23, 56.92 min, and 2.50 g, respectively. The optimum conditions of these variables obtained theoretically were used to monitoring them, which can be applied to an industrial-scale process.

Following second-order polynomial equation is proposed for the prediction of percentage removal of 2-CP as a function of different variables [17].

Independent variables	Levels				
	+ α^a	1	0	-1	- α
initial concentration (mg/L)	45	35	25	15	5
pH	10	8	6	4	2
time (min)	85	65	45	25	5
Dosage (g)	2.5	2.0	1.5	1.0	0.5

^a $\alpha=2$, calculated by Minitab software

Table 1: Range of Values of Central Composite Design.

Run	2-CP concentration (mg/L)	pH	Time(min)	Dosage(g)	Observed Yield (%)	Predicted Yield (%)
1	15	4	25	1.0	73.70	72.0796
2	35	4	25	1.0	67.80	67.0275
3	15	8	25	1.0	38.32	38.4075
4	35	8	25	1.0	38.90	39.5879
5	15	4	65	1.0	86.40	84.7275
6	35	4	65	1.0	73.30	72.5679
7	15	8	65	1.0	52.20	52.9379
8	35	8	65	1.0	47.15	47.0108
9	15	4	25	2.0	90.70	89.9942
10	35	4	25	2.0	76.90	74.9096
11	15	8	25	2.0	47.60	47.0796
12	35	8	25	2.0	37.40	38.2275
13	15	4	65	2.0	100.00	98.0596
14	35	4	65	2.0	76.80	75.8675
15	15	8	65	2.0	57.10	57.0275
16	35	8	65	2.0	40.70	41.0679
17	5	6	45	1.5	83.40	85.2046
18	45	6	45	1.5	63.90	64.1929
19	25	2	45	1.5	68.30	72.4346
20	25	10	45	1.5	6.00	3.9629
21	25	6	5	1.5	55.00	55.9546
22	25	6	85	1.5	70.30	71.4429
23	25	6	45	0.5	65.90	66.5629
24	25	6	45	2.5	77.10	78.5346
25	25	6	45	1.5	70.40	70.7000
26	25	6	45	1.5	70.80	70.7000
27	25	6	45	1.5	71.00	70.7000
28	25	6	45	1.5	70.50	70.7000
29	25	6	45	1.5	70.70	70.7000
30	25	6	45	1.5	70.90	70.7000
31	25	6	45	1.5	70.60	70.7000

Table 2: Theoretically Predicted Values of Percentage Removal of 2-CP by nZVI for the Different Selected Levels of Variables.

$$Y = 70.70 - 5.2529 C_{cp} - 17.1179 pH + 3.8721 t + 2.9929 D_{nZVI} + 0.9997 C_{cp}^2 - 8.1253 pH^2 - 1.70503 t^2 + 1.5581 pH \times C_{cp} - 1.7769 C_{cp} \times t - 2.5081 C_{cp} \times D_{nZVI} - 2.3106 pH \times D_{nZVI} - 1.1456 t \times D_{nZVI} \quad (3)$$

$$Y = 49.5143 - 3.6783 C_{cp} - 11.9833 pH + 2.7100 t + 2.0975 D_{Fe} + 0.6943 C_{cp}^2 - 5.6932 pH^2 - 1.2307 t^2 + 1.0888 pH \times C_{cp} - 1.2462 C_{cp} \times t - 1.7562 C_{cp} \times D_{Fe} - 1.6163 pH \times D_{Fe} - 0.8013 t \times D_{Fe} \quad (4)$$

T = temperature, P= pH, C_{cp} = 2-CP concentration, t= time, and D= dosage of adsorbent.

Run	2-CP concentration (mg/L)	pH	Time(min)	Dosage(g)	Observed Yield (%)	Predicted Yield (%)
1	15	4	25	1.0	51.60	50.4596
2	35	4	25	1.0	47.46	46.9304
3	15	8	25	1.0	26.82	26.8804
4	35	8	25	1.0	27.23	27.7063
5	15	4	65	1.0	60.48	59.3071
6	35	4	65	1.0	51.31	50.7929
7	15	8	65	1.0	36.54	37.0629
8	35	8	65	1.0	33.00	32.9038
9	15	4	25	2.0	63.50	63.0021
10	35	4	25	2.0	53.85	52.4479
11	15	8	25	2.0	33.32	32.9579
12	35	8	25	2.0	26.18	26.7588
13	15	4	65	2.0	70.00	68.6446
14	35	4	65	2.0	53.76	53.1054
15	15	8	65	2.0	40.00	39.9354
16	35	8	65	2.0	28.49	28.7513
17	5	6	45	1.5	58.38	59.6483
18	45	6	45	1.5	44.73	44.9350
19	25	2	45	1.5	47.81	50.7083
20	25	10	45	1.5	4.20	2.7750
21	25	6	5	1.5	38.50	39.1717
22	25	6	85	1.5	49.21	50.0117
23	25	6	45	0.5	46.13	46.5917
24	25	6	45	2.5	53.97	54.9817
25	25	6	45	1.5	49.28	49.5143
26	25	6	45	1.5	49.60	49.5143
27	25	6	45	1.5	49.70	49.5143
28	25	6	45	1.5	49.40	49.5143
29	25	6	45	1.5	49.50	49.5143
30	25	6	45	1.5	49.65	49.5143
31	25	6	45	1.5	49.47	49.5143

Table 3: Theoretically Predicted Values of Percentage Removal of 2-CP by Fe powder for the Different Selected Levels of Variables.

The obtained response surface model from an experimental design was evaluated using ANOVA and analysis of residuals was performed. The results of the statistical analyses include the estimated regression coefficients; t-test and p-values of the sorption are tabulated in Tables 4 and 5. The regression coefficient (R²) adjusted of the sorption was found close to unity, which indicates that the developed models is able to fully predict the percentage removal of 2-CP. The linear regression coefficient of the sorption was also found as 0.9956, which shows good performance of the model on the experimentally observed as well as theoretically predicted percentage of 2-CP removal.

Tables 4 and 5 exhibits that larger the t-value and the smaller the p-value, the more significant is the corresponding coefficient. Based on the statistical results (ANOVA) with confidence level of 95%, the effect of each term in the models could be significant provided that its p-value is smaller than 0.05 (p-value<0.05) [19].

Variables affecting

The effect of the 2-CP concentration and pH: Figures 3 and 4 exhibit that by increasing the 2-Chlorophenol concentration a decrease in the percentage removal of this compound sorption is observable and maximum sorption (100 and 87.74%) was predicted at 5.0 mg/L 2-CP concentration with nZVI and Fe powder, respectively. The initial concentration was 5, 15, 25, 35 and 45 mg/L. Initial concentration of contaminant is a main agent for efficiency of Fe particles. According to the results, with the initial 2-CP concentration increase, the degradation efficiency decreased. The results show that the reaction time for the further degradation of 2-CP extended with increase in initial 2-CP concentration. With increase in 2-CP concentration, this organic contaminant molecules can be adsorbed on the reactive surface of iron particles and these ions can be occupy greater number of active sites on the particle surface [20]. Thus, at lower concentration, large number of pores on the sorbent surface was available for reaction. Then, the pore sites on the surface became occupied by 2-CP molecules and

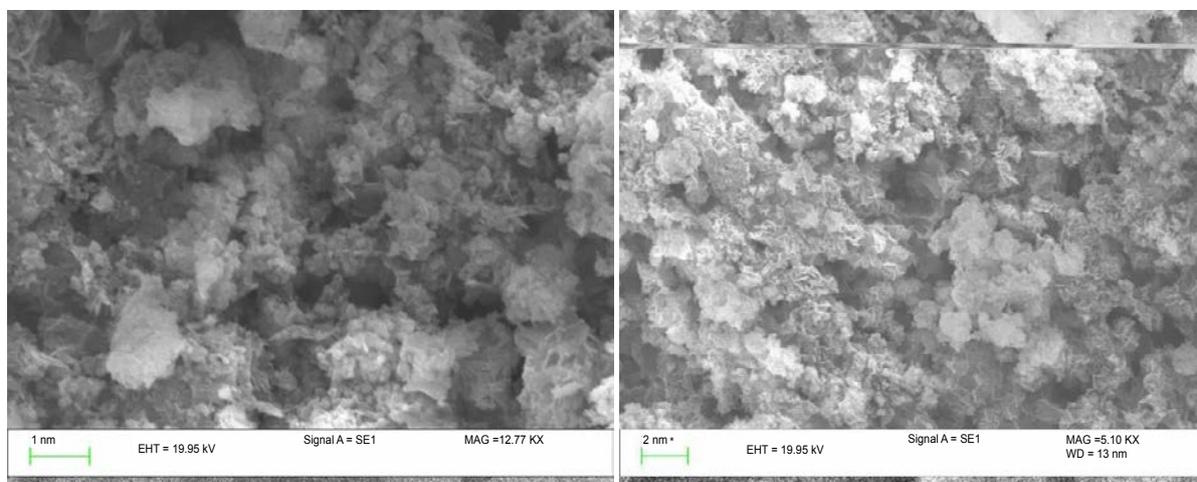


Figure 1: SEM images of nano zero valent iron particle.

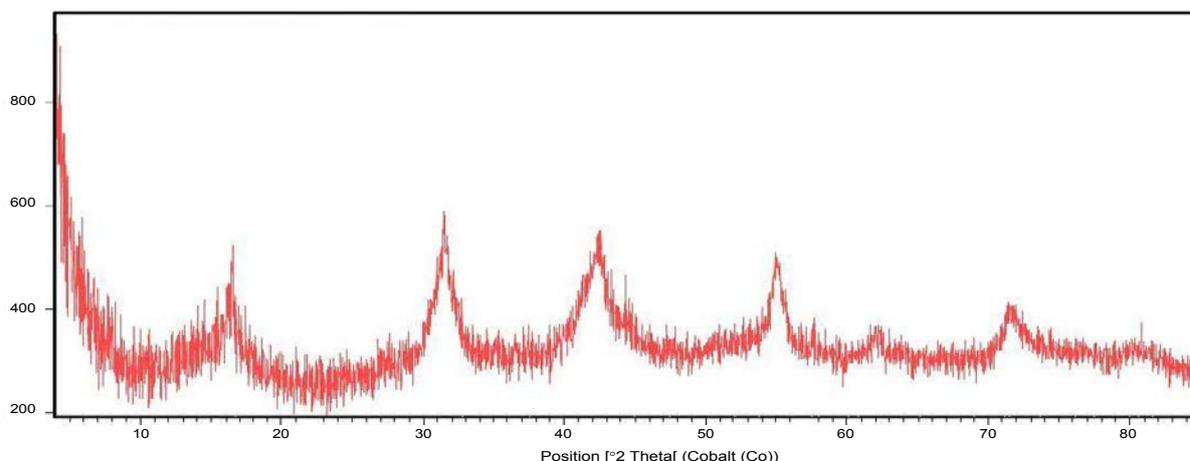


Figure 2: X-ray Diffraction Pattern of nano zero valent iron particles.

Term	Regression coefficients	t-value	p-value
Constant	70.7000	108.708	0.000
C_{cp} (mg/L)	-5.2529	-14.955	0.000
pH	-17.1179	-46.736	0.000
t (min)	3.8721	11.024	0.000
D (g)	2.9929	8.521	0.000
C_{cp}^2 (mg/L) ²	0.9997	3.107	0.007
pH ²	-8.1253	-25.251	0.000
t ² (min) ²	-1.7503	-5.440	0.000
D ² (g) ²	0.4622	1.436	0.170
pH × C_{cp} (mg/L)	1.5581	3.622	0.002
C_{cp} (mg/L) × t (min)	-1.7769	-4.131	0.001
C_{cp} (mg/L) × D (g)	-2.5081	-5.830	0.000
pH × t (min)	0.4706	1.094	0.290
pH × D (g)	-1.8787	-5.371	0.000
t (min) × D (g)	-1.1456	-2.663	0.017

Table 4: Observed Regression Coefficients, t-Test, and p-Values for 2-CP removal by nZVI.

Term	Regression coefficients	t-value	p-value
Constant	49.5143	108.708	0.000
C_{cp} (mg/L)	-3.6783	-14.933	0.000
pH	-11.9833	-48.651	0.000
t (min)	2.7100	11.002	0.000
D (g)	2.0975	8.516	0.000
C_{cp}^2 (mg/L) ²	0.6943	3.077	0.007
pH ²	-5.6932	-25.229	0.000
t ² (min) ²	-1.2307	-5.454	0.000
D ² (g) ²	0.3181	1.410	0.178
pH × C_{cp} (mg/L)	1.0888	3.609	0.002
C_{cp} (mg/L) × t (min)	-1.2462	-4.131	0.001
C_{cp} (mg/L) × D (g)	-1.7562	-5.822	0.000
pH × t (min)	0.3338	1.106	0.285
pH × D (g)	-1.6163	-5.358	0.000
t (min) × D (g)	-0.8013	-2.656	0.017

Table 5: Observed Regression Coefficients, t-Test, and p-Values for 2-CP removal by Fe powder.

efficiency decreased [21]. The decrease in percentage of adsorption at higher concentration is mainly due to unavailability of sorption sites at the sorbent for larger number of adsorbing 2-CP ions. Usually, surface

atoms/ or ions, particularly atoms at border of nano particle iron, has a high activity in chemical reaction with contaminants. On the other hand, these atoms/or ions are reactive, active and available sites of sorbents surface [22]. Therefore, at the first stage 2-CP Molecules were adsorbed by these sites on the nanoscale surface, and the concentration of 2-CP decreased. Subsequently, some of the adsorbed these molecules reacted with the surface atoms of Fe particle [22]. In conclusion, the decrease of 2-CP molecules were the result of both sorption and degradation processes, and the initial concentration of 2,4-DCP also influenced adsorption process.

The effects of pH (2-10) and initial 2-chlorophenol concentration (5-45 mg/L) on the adsorption of 2-CP over nZVI and Fe powder were simultaneously monitored at removal efficiency and presented in Figures 3 and 4. The pH of the solution was adjusted using 0.1M HCl and 0.1 M NaOH.

As results demonstrated, acidic conditions were more idealistic for removal of 2-CP and efficiency decreased when pH was greater than 4 and 3.23. Most of the organic contaminants were reduced effectively at lower pH values in the nZVI-water system since reduced function of nZVI under acidic conditions [23]. Also, pH may be affected in the mechanisms of the nZVI oxidative degradation. The results also display that the tendency and static traction between the 2-CP and nZVI/ and Fe powder meliorated at lower pH, thus 2-CP could be adsorbed onto the Fe particles surface more easily. At alkaline condition, iron is converted to insoluble forms (ferrous hydroxide). These precipitations impose on the iron surface and the mass transfer is limited. Thus, 2-CP degradation is reduced. In alkaline conditions, 2-CP and Fe particles are negatively charged, thus this phenomenon is causing repulsive forces between phenoxide ion and Fe(III)-O⁻ groups [24]. In addition, with pH increase, electrostatic repulsive force becomes operative, which thereby retards diffusion and adsorption.

In alkaline conditions, Iron ions are produced in solution. Then, the hydroxyl ion collided with Fe particles surface and ferrous ions dissolved in surface. Therefore, ferrous hydroxide produced in this reaction and precipitated on the iron surface. These precipitations occupy the available and active sites on the particles surface to hinder the repercussion. Also, at high pH nZVI surface is negative (Fe(III)-O⁻) electrostatic repulsive force becomes operative.

On the other hand, at acidic conditions is done acid washing on

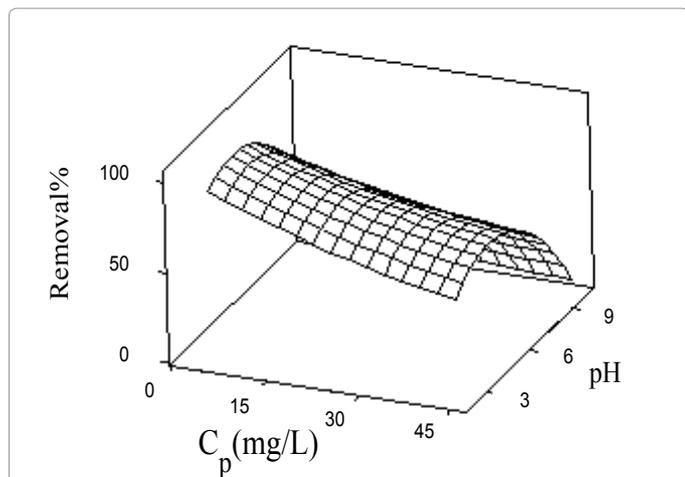


Figure 3: Response Surface of the Percentage Sorption of 2-CP ions versus pH and initial concentration by nZVI.

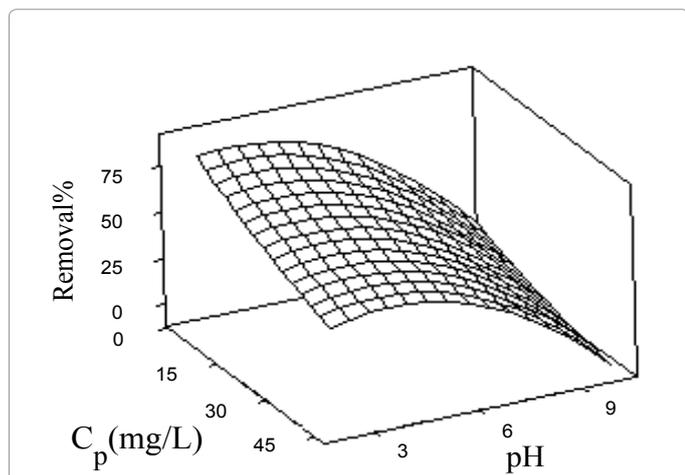


Figure 4: Response Surface of the Percentage Sorption of 2-CP ions versus pH and initial concentration by Fe powder.

metallic surfaces, broadly. These reactions, reduces passivation of Fe particles and metallic surfaces with Facilitating solvability of these hydroxides [25]. This is evidence that the degradation/or adsorption reduction of 2-CP with Fe particles is idealistic in lower pH. Moreover, at low pH, Iron particles have positive charge. These positive charges absorb ionized species of phenol and chlorophenol which has negative charges. Also, chlorophenol compounds known as proton donor. Therefore, removal of this compound in alkaline pH decreases due to the repulsive forces between negative groups ($\text{Fe}^{+3}\text{-O}^-$) and ions phenoxide. In this research, the p-value is used to determine the effect of each parameter. To prove the correctness of the parameters, the p-value should be less than 0.05. The impact parameters is omitted if p-value is greater than 0.05. ANOVA statistical test shows that there was no statistically significant difference between the removal efficiency and these variables (p-value <0/05).

The effect of contact time and dosage nZVI/Fe powder

Removal efficiency for 2-CP at contact time of 5-85 min was investigated. The result showed that the optimum time for 2-CP removal by nZVI and Fe powder were obtained in 70 min and 56.92

min, respectively. Therefore, the 2-CP adsorption was found to increase with increase in time as shown in Figures 5 and 6. The 2-chlorophenol sorption in mentioned time was attributed to the surface junction between active surface groups and phenol ion. Also, the further sorption at the described times can be illustrated with an increased availability in the active bounding sites on the sorbent surface area [26,27].

As shown in Figures 5 and 6, when the Fe particles dosage increased, the removal efficiency increased. The reactivity of organic contaminants with Fe particles is relevant to the dosage of these particles. Usually, the reduction of chlorinated organic pollutants with iron particles is a surface function. Consequently, the removal of organic compounds such as 2-Chlorophenol by nZVI or Fe powder implicates direct contact between the organic matter and reactive parts on the iron particle surface. Chlorophenol may be eliminated as follows: In the first stages, the chlorophenol ions pervade through the solution to the sorbent surface, where these contaminants adsorb onto the reactive parts. Secondly, electrons are transferred from ZVI to the CP ions and produce a solution with lesser contaminants and various oxides on the surface [28]. Batch studies prove that the process of demolition of 2-CP consists sorption, dechlorination and cleavage and also precipitation [29]. Adsorption process includes agglomeration of the 2-CP ions

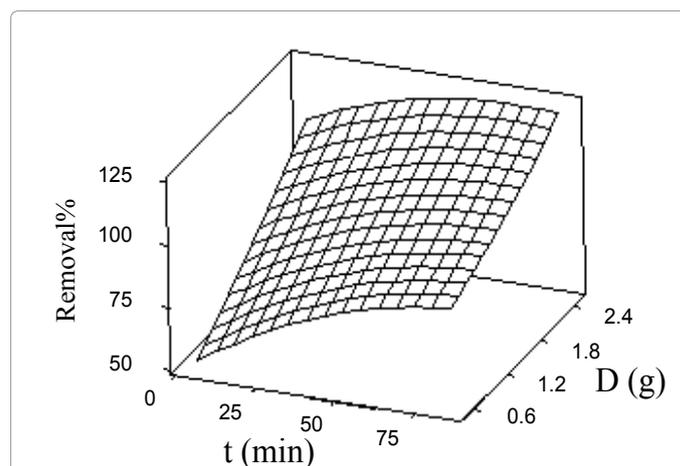


Figure 5: Response Surface of the Percentage Sorption of 2-CP ions versus time and dosage of nZVI.

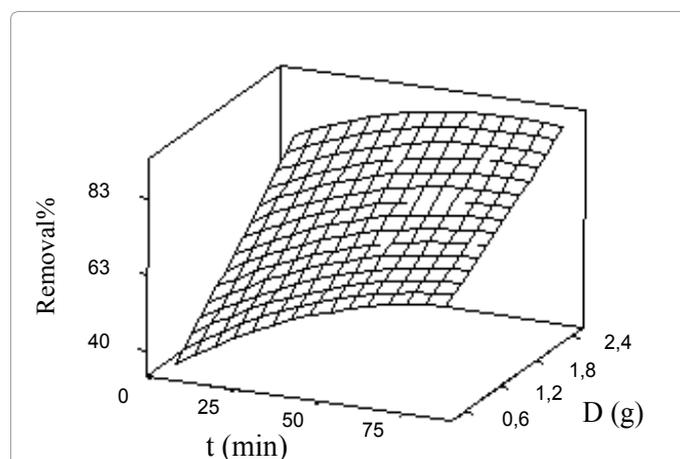


Figure 6: Response Surface of the Percentage Sorption of 2-CP ions versus time and dosage of Fe powder.

by adsorption or complex formation. Dechlorination process is demolition and formation of some intermediate compounds. Also, precipitation is consisted of insoluble compounds or removal of the contaminant ions via Trapping in the precipitates or on the ZVI surface [30,31]. Nano iron particle due to their high specific surface and high reactivity has an immense capability of sorption pollutants. The Fe ions of and 2-CP ions would supplant when Fe particles dripped into the liquid. Then, the Fe ions distributed into the solution. Thereafter, molecules of contaminant was adsorbed on the reactive surface of Fe particles and reacted with these particles. Therefore, with iron particles increase dosage, the active, adsorptive and reactive sorbent sites increased, thus led to the acceleration of the oxidation of 2-CP [32].

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