

Assessment of Phenol Removal Efficiency by Synthesized Zero Iron Nanoparticles and Fe Powder Using the Response Surface Methodology

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ABSTRACT: *The purpose of this study was the investigation of the removal of phenol with nanoparticles zero valent iron and iron powder. The effect of various parameters such as initial concentration, pH, contact time, and dosage of NZVI and Fe powder were examined, and a Central Composite Design (CCD) was then applied to appraisal the effect of these variables. The chemical and physical characteristics of NZVI were studied with Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) analysis. The results displayed that the adequate initial concentration for phenol sorption, pH, contact time, and sorbent dosage were 5 mg/L, pH 2, 54.75 min and 1.40 g in the case of NZVI and 5 mg/L, pH 2, 55.84 min and 2.5 g in the case of Fe powder. The Central Composite Design (CCD) showed that the fundamental parameters were pH and initial phenol concentration had the main effect on phenol removal.*

KEYWORDS: *Zero valent iron; Phenol; Central composite design; Sorption; Nanoparticles; Dosage.*

INTRODUCTION

Phenol and phenolic compounds are ubiquitous pollutants which come to the natural water resources from the effluents of a range of chemical industrial such as coal refineries, phenol manufacturing, pharmaceuticals and industries of resin paints, dyeing, textile wood,

petrochemical, pulp mill, etc [1]. Therefore, aquatic organisms are subjected to these pollutants. These aromatic compounds induce ecological problems such as taste and smell in the presence of chlorine compounds [2]. US EPA nominated phenol among the priority pollutants;

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1021-9986/2017/2/137-146

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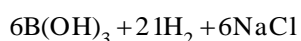
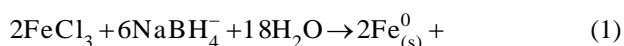
thus, phenol and its derivatives concentration in drinking water should be under the order of $\mu\text{g/L}$ [1]. A variety of techniques have been utilized to remove phenol from water and wastewater such as biosorption, chemical oxidation with ozone, adsorption, ion exchange, photodegradation, membrane separation, active carbon, etc [3]. Most of these methods can appear costly and might produce sludge, whose disposal is challenging [4].

During recent years, the synthesis of nanoparticle Iron is of specific interest for researcher. Iron nanoparticles and Iron powder are widely investigated in the removal of phenol and other organic matter [5]. NZVI was also used in the elimination of Cr (VI) [6], Malathion [7], aromatic compounds [8] and arsenic [9]. In rather comparable conditions, such process allows contaminants removal in a short time compared to a conventional process like biodegradation. Elimination of contaminants occurs on the surface of NZVI or Fe powder [10]. There are many ways to produce nanoparticles, including the synthesis of ZVI nanoparticles by dropping ferric on solution to borohydride solution. In most researches, the particles perform best when the size is typically around 1-100 nm [11,12]. The purpose of this research was therefore the synthesis of nanoscale iron particle by ferric ion into borohydride solution that is a cheap method and the comparison of its efficiency with Fe powder for the removal of phenol.

EXPERIMENTAL SECTION

Preparation of the NZVI

In this research, nanoparticles were generated by reduction of ferric iron in the presence of sodium borohydride. These particles were synthesized with 1:1 volume ratio of NaBH_4 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. NaBH_4 solution (0.16 M) was added dropwise into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1M) under vigorous magnetic stirring in atmospheric conditions during 1 hour. Finally, fine black particles were obtained and precipitated according to the following reaction:



Chemicals and Batch experiments

The stock solution containing 1000 mg/L of phenol was provided by dissolving phenol into deionized water.

Batch experiments were performed by adding NZVI in 250 mL bottles containing phenol and the following parameters were examined: the contact time (10, 40, 70, 100 and 130 min), the phenol concentration (5, 10, 15, 20 and 25 mg/L), the pH (2, 4, 6, 8 and 10), and the sorbent dosage (0.5, 1.5, 2.5, 3.5 and 4.5 g). The concentration of residual phenol was spectrophotometrically determined (DR-5000 spectrophotometer model number LZV485).

The Response Surface Method was used to analyze data. For this purpose, a central composite design was applied to appraisal the effect of the operating variables such as pH, sorbent dosage, contact time, and phenol concentration on the performance of the sorption process. Thus, to optimize the parameters and investigate the interactions between these independent parameters for phenol sorption Response Surface Methodology (RSM) was applied.

Experimental design

A statistical experimental design based on "Central Composite Design (CCD)" was planned [13] and the yield was measured for different variables such as phenol concentration, pH, time, and sorbent dosage coded as x_1 , x_2 , x_3 , and x_4 respectively. These variables were investigated at five levels (-2, -1, 0, 1, 2) and the dependent variable was Y. The Minitab software package (version 16.2) was used to design and evaluate these five independent variables at five levels on the responses according to Eq. (2). The ranges for the selected levels of the four variables are shown in Table 1. The experimental yield for different selected levels of variables is shown in Tables 2 and 3 for 30 runs.

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

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

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

RESULTS AND DISCUSSION

Characterization of NZVI particles

Synthesized iron nanoparticles were analyzed to confirm their nanosize and zero valence Characterization. Therefore, SEM was used to investigate the morphology

Table 1: Range of values for the central composite design.

	$-\alpha^*$	-1	0	1	$+\alpha$
Phenol concentration (mg/L)	5	15	25	35	45
pH	2	4	6	8	10
time (min)	5	25	45	65	85
Dosage of NZVI / Fe (g)	0.5	1.0	1.5	2.0	2.5

* $\alpha=2$, calculated by Minitab software**Table 2: Theoretically predicted values of percentage removal of phenol by NZVI for the different selected levels of variables.**

Run	Phenol concentration (mg/L)	pH	Time(min)	Dosage of NZVI(g)	Observed Yield (%)	Predicted Yield (%)
1	15	4	25	1.0	68.34	66.5211
2	35	4	25	1.0	60.20	57.7277
3	15	8	25	1.0	28.30	27.6028
4	35	8	25	1.0	26.40	27.8944
5	15	4	65	1.0	78.80	77.7611
6	35	4	65	1.0	66.45	66.2277
7	15	8	65	1.0	33.10	35.1028
8	35	8	65	1.0	30.50	32.6544
9	15	4	25	2.0	85.00	81.9861
10	35	4	25	2.0	66.50	64.0277
11	15	8	25	2.0	35.80	35.5528
12	35	8	25	2.0	26.50	26.6794
13	15	4	65	2.0	93.50	91.5361
14	35	4	65	2.0	71.00	70.8377
15	15	8	65	2.0	39.75	41.3628
16	35	8	65	2.0	28.40	29.7494
17	25	6	45	1.5	58.80	59.9790
18	25	6	45	1.5	59.00	59.9790
19	25	6	45	1.5	59.20	59.9790
20	25	6	45	1.5	57.60	59.9790
21	5	6	45	1.5	63.30	65.2178
22	45	6	45	1.5	45.40	44.8112
23	25	2	45	1.5	72.00	77.9178
24	25	10	45	1.5	2.50	-2.0888
25	25	6	5	1.5	30.50	34.3595
26	25	6	85	1.5	51.20	48.6695
27	25	6	45	0.5	47.80	47.4345
28	25	6	45	2.5	58.30	59.9945
29	25	6	45	1.5	57.80	54.9420
30	25	6	45	1.5	57.40	54.9420

Table 3: Theoretically predicted values of percentage removal of phenol by Fe powder for the different selected levels of variables.

Run	Phenol concentration (mg/L)	pH	Time(min)	Dosage of Fe powder(g)	Observed Yield (%)	Predicted Yield (%)
1	15	4	25	1.0	56.10	52.1690
2	35	4	25	1.0	46.90	46.9440
3	15	8	25	1.0	22.60	21.1973
4	35	8	25	1.0	19.80	20.9723
5	15	4	65	1.0	63.80	64.1773
6	35	4	65	1.0	56.40	55.4523
7	15	8	65	1.0	28.40	29.6557
8	35	8	65	1.0	22.10	25.9307
9	15	4	25	2.0	68.10	65.2773
10	35	4	25	2.0	59.30	56.4023
11	15	8	25	2.0	26.80	26.1057
12	35	8	25	2.0	21.60	22.2307
13	15	4	65	2.0	78.90	76.0857
14	35	4	65	2.0	61.30	63.7107
15	15	8	65	2.0	32.40	33.3640
16	35	8	65	2.0	23.70	25.9890
17	25	6	45	1.5	50.80	51.4090
18	25	6	45	1.5	50.40	51.4090
19	25	6	45	1.5	51.00	51.4090
20	25	6	45	1.5	50.90	51.4090
21	5	6	45	1.5	55.60	59.8170
22	45	6	45	1.5	50.80	47.2170
23	25	2	45	1.5	59.88	64.8537
24	25	10	45	1.5	0.50	-3.8397
25	25	6	5	1.5	22.50	27.1337
26	25	6	85	1.5	46.90	42.9003
27	25	6	45	0.5	38.60	38.0837
28	25	6	45	2.5	50.10	51.2503
29	25	6	45	1.5	50.70	49.4820
30	25	6	45	1.5	50.80	49.4820

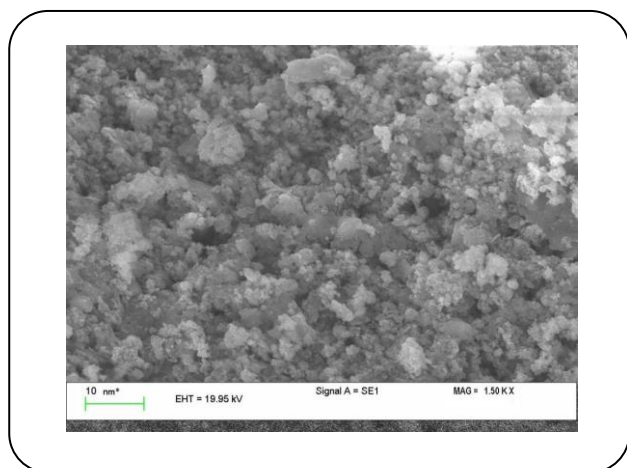


Fig. 1: SEM images of nano zero valent iron particles.

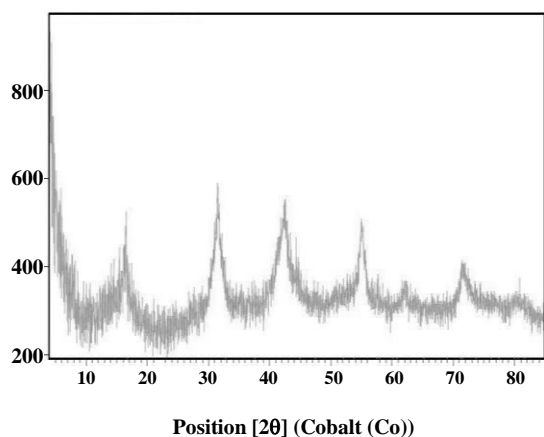


Fig. 2: X-ray Diffraction Pattern of nano zero valent iron particles.

and the size diffusion of synthesized NZVI. Fig. 1 shows a SEM micrograph of these pristine samples. Synthesized NZVI particle was in the size range of 20-50 nm. This micrograph showed that these particles are not disjoint and that the synthesized NZVI particles are almost spherical. As shown in Fig.1, on the spherical particles there were string-like structures. These structures increased the active and available surface area of reaction [14].

Fig. 2 shows the X-ray diffraction pattern of the NZVI sample. The XRD pattern displays six characteristic peaks at $2\theta = 4.4521^\circ, 16.5409^\circ, 31.5378^\circ, 44.2876^\circ, 57.6486^\circ$ and 71.4737° in crystalline structure. These peaks indicate the presence of Iron Crystals in the surface area.

Optimum conditions

For total phenol removal, initial phenol concentration, pH, time, and sorbent dosage were 5.0 mg/L, 2, 54.75 min, and 1.4 g in the case of NZVI and 5.0 mg/L, 2, 55.84 min, and 2.5 g in the case of Fe powder. The optimum conditions might provide the design basis for an industrial-scale process. A second-order polynomial equation is proposed for the prediction of the yield for NZVI (Eq. (3)) and Fe powder (Eq. (4)) as a function of the different variables as follows [13, 15]:

$$Y = 57.4605 - 5.1017C_p - 20.0017pH + 3.5775t + 3.1400D_{NZVI} - 4.2569pH^2 - 3.3569t^2 + 2.2712pH \times C_p - 2.2913C_p \times D_{NZVI} - 1.8787pH \times D_{NZVI} \quad (3)$$

$$Y = 50.4455 - 3.150C_p - 17.1733pH + 3.9417t + 3.2917D_{Fe} - 4.7437pH^2 - 3.6163t^2 + 2.2712pH \times C_p - 2.0500pH \times D_{Fe} \quad (4)$$

Where C_p is the Phenol concentration, t is contact the time, and D the sorbent dosage. The response surface model which was obtained from an experimental design was evaluated using ANOVA and analysis of residuals. The results of the statistical analysis including the estimated regression coefficients, t-test, and p-values of the yield were tabulated in Tables 4 and 5. The obtained R^2 were 0.9738 and 0.9573 for NZVI and Fe powder, respectively, showing the accuracy of the developed models to fully predict the yield. The linear regression coefficients, R^2 for NZVI and Fe powder for the yield was also 0.9874 and 0.9794 which shows good performance of the model based on the observed and predicted yields. The value of significance of each coefficient determined by t-test and p-values are listed in Tables 4 and 5. The 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 being smaller than 0.05 (p-value < 0.05).

Effect of the different parameters

Effects of the Phenol concentration and the pH

The adsorption of phenol was also monitored in the concentration range 5 to 45 mg/L. Figs. 3a and 3b show

Table 4: Observed regression coefficients, t-Test, and p-Values for phenol removal by NZVI.

	t-value	p-value
Constant	42.088	0.000
C _p (mg/L)	-7.566	0.000
pH	-29.665	0.000
t (min)	5.306	0.000
D (g)	4.657	0.000
C _p ² (mg/L) ²	0.029	0.977
pH ²	-6.749	0.000
t ² (min) ²	-5.322	0.000
D ² (g) ²	-0.487	0.634
pH × C _p (mg/L)	2.750	0.016
C _p (mg/L) × t (min)	-0.830	0.421
C _p (mg/L) × D (g)	-2.775	0.015
pH × t (min)	-1.132	0.277
pH × D (g)	-2.275	0.039
t (min) × D (g)	-0.512	0.617

Table 5: Observed regression coefficients, t-Test, and p-Values for phenol removal by Fe powder.

	t-value	p-value
Constant	32.999	0.000
C _p (mg/L)	1.345	0.001
pH	-4.172	0.000
t (min)	-22.747	0.000
D (g)	5.221	0.001
C _p ² (mg/L) ²	4.360	0.175
pH ²	1.428	0.000
t ² (min) ²	-6.717	0.000
D ² (g) ²	-5.121	0.110
pH × C _p (mg/L)	-1.705	0.198
C _p (mg/L) × t (min)	-0.946	0.360
C _p (mg/L) × D (g)	-0.987	0.340
pH × t (min)	-0.960	0.353
pH × D (g)	-2.217	0.044
t (min) × D (g)	-0.324	0.750

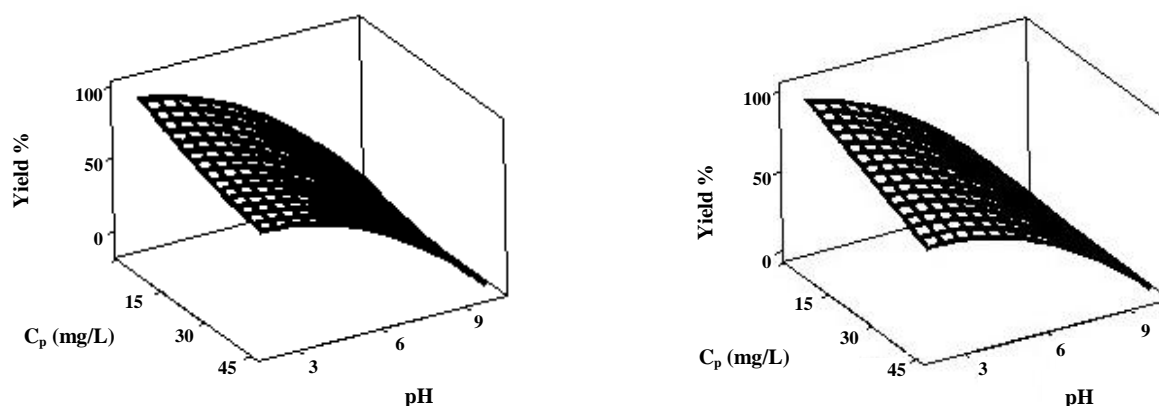


Fig. 3: Response Surface of the Percentage Sorption of phenol ions versus pH and initial concentration by NZVI (a) and Fe powder (b).

that increasing the phenol concentration led to a decrease in the sorption percentage. According to the results, the degradation efficiency decreased when the initial phenol concentration increased, leading to a total removal (100%) for the lowest phenol concentration (5.0 mg/L) with nanoparticle iron and Fe powder. The removal of phenol by iron nanoparticle depends direct contact between the organic contaminant and reactive site on the iron nanoparticle surface. This organic contaminant first diffuse through the solution to the NZVI surface and then adsorb on the reactive surface of iron particles and occupies a greater number of active sites on the particle surface [16], until saturation of the available sites at high initial phenol concentration leading to a decrease of the efficiency [17]; while at low concentration, the number of available pores on the sorbent surface is in excess. Usually, surface atoms/ or ions, particularly atoms at the border of nanoparticles iron, has a high activity in reaction with contaminants [18]. Electrons are transferred from iron particles to the contaminant molecules and produce lesser toxic compounds and various oxides on the surface. Therefore, at the first stage phenol molecules were absorbed by these sites on the nanoscale surface, and the concentration of phenol decreased. Subsequently, some of the adsorbed molecules reacted with the surface atoms of Fe particle [19]. In conclusion, the decrease of phenol molecules was the result of both sorption and degradation processes.

The effect of pH (2 – 10) was also shown in Figs. 3a and b; the pH of the solution was adjusted using dilute

HCl and NaOH. Removal was optimal at acidic pH and efficiency decreased when pH was greater than 2. Usually, organic pollutants were efficiently reduced at acidic pH values in the Fe particle-water system. Acidic condition redounds to the reduced function of Fe particles in this oxidation-reduction reaction [15]. The pollutant could be adsorbed onto the Fe particles surface more easily at acidic pH. In alkaline conditions, iron is converted to insoluble forms (ferrous hydroxide); which pervade on the reactive sites leading to a decrease of phenol removal. In alkaline conditions, phenoxide and Fe particles are negatively charged; this phenomenon induces repulsive forces between phenoxide ion and Fe(III)-O⁻ groups [10]. In addition, with pH increase, electrostatic repulsive force becomes operative, which thereby retards diffusion and adsorption. Also, at high pH, iron ions are produced in aqueous solution. Then, hydroxyl ion bopped with Fe particles surface and dissolved ferrous ions; the produced ferrous hydroxide deposited on the iron surface, and these precipitates occupy the available and active sites on the surface area and hence hinder pollutant adsorption. In addition, at high pH NZVI surface is negative (Fe(III)-O⁻) and hence electrostatic repulsive force becomes operative. On the other hand, acidic conditions promote the washing of metallic surfaces. These acts, reduces passivation of Fe particles and also facilitate solvability of these hydroxides [20]. From this, degradation and/or adsorption reduction of phenol with Fe particles is improved at low pH. Moreover at low pH, Iron particles have positive charge.

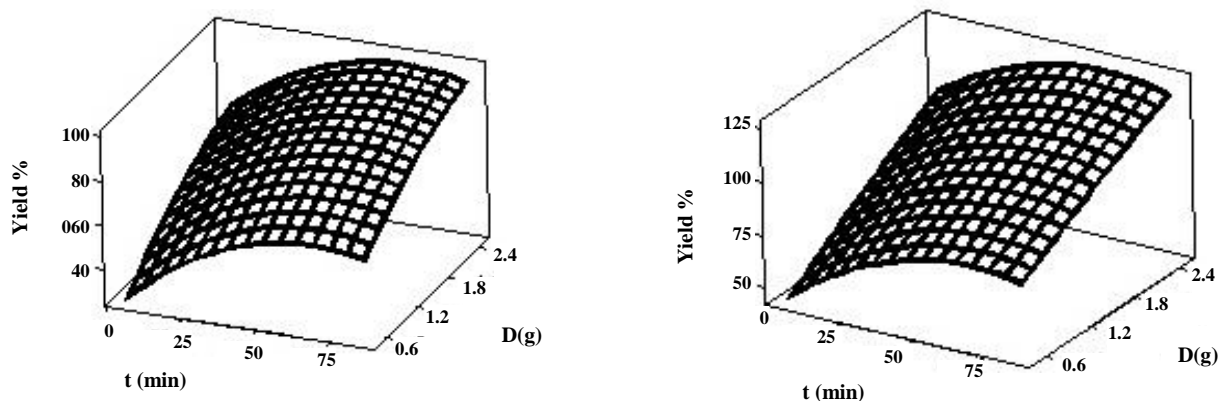


Fig. 4: Response Surface of the Percentage Sorption of phenol ions versus time and dosage of NZVI (a) and Fe powder (b).

These positive charges adsorb ionized species of phenol which has negative charges.

The p-value is used to determine the effect of each parameter; it should be less than 0.05. ANOVA statistical test shows that there was statistically significant difference between the removal efficiency by pH and concentration (p-value < 0/05).

The effect of contact time and NZVI / Fe powder dosage

Regarding contact time, the results showed that the optimal times to remove phenol by nano particles iron and Fe particles were 54.75 min and 55.84 min, respectively; and phenol removal was found to increase with time, and then a plateau is reached up to 85 min as shown in Figs. 4a and 4b. The phenol removal in mentioned time was attributed to the site junction between active surface groups and phenol ion. Also, the further sorption at the above times can be explained with an increased availability in the active bounding sites on the sorbent surface area [21].

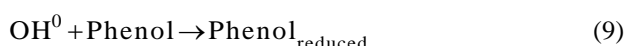
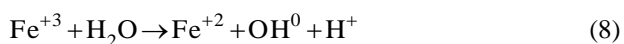
As shown in Figs. 4a and b, when the Fe particles and nano scale iron dosage increased, the removal efficiency increased. The reactivity of these aromatic contaminants with Fe particles is dependent on the dosage of these particles. Usually, the reduction of organic contaminants with Fe particles is a surface function. Consequently, the removal of organic compounds such as phenol by nanoparticle iron or Fe powder implicates direct contact between the contaminants and the reactive parts on the iron particle surface. Also, phenol may be eliminated as follows: In the first stages, the phenol ions percolate

through the solution to the Fe particles surface, where these ions adsorb onto the reactive parts. Secondly, electrons are transferred from Fe particles to the phenol ions and produce a solution with less contaminant and various oxides on the surface [22]. Batch studies prove that the process of phenol elimination consists in sorption, cleavage and also precipitation [23]. Adsorption process includes aggregation of the phenol ions in the Fe particle surface area and complex formation; cleavage process consists in the degradation and the formation of other compounds. Also, precipitation of insoluble compounds is also involved through the removal of the contaminant ions via trapping in the precipitates or on the Fe particles surface [24, 25]. Due to their high specific surface and high reactivity nano iron particle has a remarkable capability for sorption of organic ions. The Fe particles and phenolic salts would substitute when these particles dripped into the liquid; then, the Fe ions distributed into the solution. In other words, molecules of phenol were sited on the reactive surfaces and reacted with Fe particles. Therefore, with increasing dosage of Fe particles, the active, adsorptive and reactive sorbent sites increased, leading to the acceleration of phenol oxidation [26].

So for pluralization, the removal of phenol by zero iron particles depends on the direct contact between phenol and reactive site of nanoparticles. Zero iron, as an electron donor, can quickly get oxidized to +2 and +3 oxidation states and in the process reduce other as well as inorganic impurities [27]. This is demonstrated by Equations (5)-(9)

Table 6: Comparison of NZVI and Fe powder for maximum phenol removal.

Parameters	Phenol concentration	pH	Contact time	Dosage
NZVI	5	2	54.75	1.4
Fe powder	5	2	55.84	2.5



The comparison between NZVI and Fe powder for all of the parameters tested for maximum removal as shown in Table 6.

CONCLUSIONS

Nanoscale iron and Fe powder can be used to remove organic pollutants in water, under reduction reactions, adsorption and precipitation process. Due to its quick reaction, low cost and convenience-to-obtain, this material has gained interest for removal of pollutants in environment. The theoretical treatment by central composite design gave interactive influence of various parameters on the efficiency of phenol removal. Thus on the basis of experimental and theoretical data it can be safely concluded that iron powder can be efficiently used as a low cost suitable sorbent for the removal of phenol.

Acknowledgements

The authors are most grateful to the laboratory staff of the Department of Environmental Health Engineering, School of Public Health, for the financial support and their collaboration in this research.

Received : May 13, 2015 ; Accepted : May 2, 2016

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