Statistical analysis of the removal of Chromium(VI)by Iron Oxide Nanoparticle (Fe_3O_4)

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ABSTRACT

Investigation of the adsorption of Chromium (VI) on Fe_3O_4 is carried out using batch scale experiments according to statistical design using a software program minitab17 (Box-Behnken design). Experiments were carried out as per Box-Behnken design with four input parameters such as pH (2-8), initial concentration (50–150mg/L), adsorbent dosage (0.05–0.3 g) and time of adsorption (10–60min). The better conditions were showed at pH: 2; contact time: 60 min; chromium concentration: 50 mg/L and magnetite dosage: 0.3 g for maximum Chromium (VI) removal of (98.95%) with an error of 1.08%. The three models (Freundlich, Langmuir, and Temkin) were fitted to experimental data, Langmuir isotherm has better described the adsorption process. Whereas, the kinetics results of the adsorption process obeyed the pseudo-second-order.

Keyword: Chromium (VI), Adsorption, Design of experiments, Iron Oxide Nanoparticle (Fe_3O_4).

التحليل الإحصائي لإزالة كروم السداسي بواسطة مادة النانو المازة (أوكسيد الحديد)

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الخلاصة

يتم التحقيق في امتزاز الكروم السداسي على أوكسيد الحديد(Fe_3O_4) بها باستخدام تجارب النمط الدفعي (batch experiment) وفقا للتصميم الإحصائي باستخدام برنامج حاسوبي(Minitab17)(Box-Behnken design) . اجريت التجارب وفقا للتصميم box-Behnken مع اربعة عوامل كمدخلات مثل درجة الحموضة (2-8) , تركيز الابتدائي (50-150 mg/l), جرعة المادة المازه (0.05-0.3 g), والوقت من الامتزاز (10-60 min) . وافيد ان الظروف المثلى لتكون 2 درجة الحموضة 0.3 g من المادة المازه مع جرعه 50 mg/l تركيز الابتدائي وزمن 1 hr، وكانت الإزالة في هذه الظروف 98.95% مع نسبة خطا قليلة 1.08%. تم تحليل النتائج باستخدام موديلات(Freundlich, Langmuir and Temkin) , موديل لانكماير يمثل أفضل وصف لعملية الامتزاز . في حين تم دراسة حركية الامتزاز بالاعتماد على موديل الدرجة الثانية لأنها مثلت اعلى معامل ارتباط .

الكلمات الرئيسية : الكروم السداسي، الامتزاز، تصميم التجارب، مادة النانو اوكسيد الحديد.

1.INTRODUCTION

As human needs increase and civilization changes, more and more finished products of different types are required. A large number of industries are born and grown in every country and industry plays an important role in economic development of the world. It improves the economic welfare of citizens and supplies the material goods they consume. The way in which society will develop in the future is largely dependent on how the growth which industry generates is distributed. The industry is also a major consumer of natural resources and a major contributor to the overall pollution load. Process waste streams contain heavy metals at concentrations exceeding the local discharge limits, **Belachew, 2015**.

Heavy metals are very important that are used in several manufacturing processes such as electroplating industry, petrochemical industries, paint, pigments, sugar mills, distilleries, leather processing industries, paper mill, agrochemicals, mining, plumbing, ammunition, fuel additives, use in pesticides manufacturing industries, pharmaceutical industries, X-ray shielding, crystal glass production and PVC plastics. All these industries effluent have a lot of heavy metals that have to be treated before being discharged to the environment**, Mohammed, 2014**.

Metallic elements have been excessively released into the environment due to rapid industrialization and have created a major global concern, **Ngah,** and **Hanafiah, 2008**. Hexavalent chromium, Cr(VI) is highly mobile and is considered acutely toxic, carcinogenic and mutagenic to living organisms, and hence more hazardous than other heavy metals, **Gupta,** and **Babu, 2010**. Contact with chromium can result in severe health problems ranging from simple skin irritation to lung carcinoma**, Shen, et al., 2009**, therefore it should not be present in the leather fabrics. Hexavalent chromium usually exists in wastewater as oxyanions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) and does not precipitate easily using conventional precipitation methods**, Amin, et al., 2010**.

Different technologies have been used for removal of chromium compound from an aquatic system which includes chemical precipitation, ion exchange, and adsorption, use of membrane technology, evaporation recovery and reverse osmosis. However, the conventional treatment technologies require expensive equipment, high energy and generate enormous quantity of sludge. Adsorption processes are one of the most important methods for metals' removal and attract much attention because of inexpensive, efficient and simple methods**, Aftabtalab,** and **Sadabadi, 2015**.

The use of magnetic nanoparticles for separation and treatment of waste water is new methodology that is faster and simpler. Magnetite nanoparticles (Fe_3O_4) have been widely studied because of structural and functional elements have various novel applications**, Yeary, et al., 2005**. Magnetism is a unique physical property that independently helps in water purification by influencing the physical properties of contaminants in water. Adsorption process combined with magnetic separation has therefore been used extensively in environmental cleanup and water treatment. Iron oxide NMs are promising for industrial scale wastewater treatment, due to their little cost, strong adsorption capacity, easy separation and enhanced stability**, Xu, et al., 2012**. Magnetite nanoparticles received considerable attention not only in the fields of medical applications, including radiofrequency hyperthermia, photo magnetics, magnetic resonance imaging (MRI), medical diagnostics, cancer therapy, but also in the field of waste water treatment**, El Ghandoor, et al., 2012,** and **Aftabtalab, et al., 2013**.

Investigating the process parameters and modeling its response is of vital or essential part of a process analysis. For controlling the adsorption independent variables, the factorial experimental design method can be used because it reduces the number of experiments, material resources and time by simple statistical design of experiments, **Chilab, 2016.** In this research Chromium concentration, time, adsorbent loading and pH are selected as most important process factors to be study. Models based on regressions, are used in a constrained optimization to get the best fit of experimental data and optimum conditions for highest removal efficiency. Using classical method to optimize the parameters could be made by changing one variable but keeping all factors constant in the same time. This may be effective in some cases, but it needs extra time, material and large number of trials. Also, the combined effect of factors cannot be fixed and due to all these limitations, analysis and investigation can be efficiently made using statistical experimental design.

This paper describes the use of magnetite nanoparticles Fe_3O_4 for removal of Chromium (VI) from aqueous solutions. The adsorption of Chromium (VI) was investigated as a function of pH, contact time, concentration of chromium (VI) and Fe_3O_4 dose by using Response Surface Methodology (RSM) using Minitab software. Isotherms and kinetics studies had been performed to describe the process

2. EXPERIMENTAL WORK

2.1 Materials and Methods

2.1.1 Adsorbate

Potassium dichromate supplied by SIGMA Aldrich, was chosen in this study. Chemical and physical properties of potassium dichromate are shown in **Table 1**.

2.1.2 Adsorbent

Prepared Nano-Magnetite (Fe_3O_4) was used as adsorbent. Magnetite nanoparticles were synthesized according to, **Parsons, et al., 2014**. One liter of a 30 mM solution of $FeCl_2$ was prepared from deionized water and $FeCl_2.4H_2O$. The solution was then titrated with NaOH solution at a rate about 1mL/min. The solution kept on constant mixing to attain a well-mixed blend. Then the Fe(OH)x was put in the Teflon container and heated in a programmable electrical furnace. The particles were heated at constant temperature of 100ºC for 60 min and consequently cooled to room temperature and then filtered using Buckner funnel with the aid of a vacuum pump and washed twice with deionized water and then dried in oven for 24 hours at 100 °C. **Fig.1** shows XRD pattern of prepared Fe_3O_4. **Table 2** shows the characterization of nano Fe_3O_4.

2.1.3 Procedure of adsorption

The ability of iron oxide magnetite to remove chromium (VI) solution was determined under batch mode conditions. 50 ml of chromium (VI) solutions with different initial concentrations (50,100,150 mg/l) were mixed with Fe_3O_4 at adsorbent dose (0.05, 0.175, 0.3 g). The mixture was added to 50 ml Erlenmeyer flasks, and the flask were shaken at 120 rpm and 25±5 °C. After that, the samples were separated by using centrifuge for 10 min at 2000 rpm and the concentration of chromium(VI) were measured using Atomic Absorption Spectrophotometer, (AAS) at wave length (375.9 nm) for chromium(VI). The uptake of chromium (VI) at equilibrium, qe (mg/g) was calculated by the following expression.

$$qe = \frac{(\mathrm{Co-Ce})\mathrm{V}}{\mathrm{W}} \tag{1}$$

3. EXPERIMENTAL DESIGNUSING BOX-BEHNKEN DESIGN

A standard response surface methodology (RSM) design known as Box-Behnken experimental design was used to study the parameter for adsorption of chromium(VI) on Fe_3O_4, and was used to create a set of designed experiments by MINITAB software (version 17). In this work, four independent variables were study for the chromium (VI) adsorption; x_1= pH, and x_2=concentration of chromium (VI) (ppm), x_3= Fe_3O_4 dosage (g), x_4= time (min).

Box-Behnken experimental design is applied to investigate and validate adsorption process parameters, which affect the removal of Cr (VI) ions onto magnetic nano-adsorbents. **Table 3** represents a 27-trial experimental design, where each variable was tested in three different coded levels: low (-1), middle (0) and high (+1). The coded values correspond toX1: -1(2), 0(5), +1(8), X2: -1(50 mgl-1), 0(100 mgl-1), +1(150 mgl-1) for X3: -1(0.05g), 0(0.175g), +1(0.3g), and for X4: -1(10), 0(35), +1(60). The all set of experiments was performed in triplicate and mean response was used for analysis. A second order polynomial equation was then fitted to the data using the Minitab for the regression and graphical analysis of the data obtained. The reliability of the fitted model was justified through and the coefficient of R^2, The p-value of less than 0.05 indicates that the model is significant for 95% probability, **Ahmad,** and **Hameed, 2009**.

4. RESULTS AND DISCUSSION

4.1Adsorption isotherms

The adsorption isotherm is the most important information, where the equilibrium amount adsorbed qe (mg/g) is related to the equilibrium concentration Ce (mg/L) indicating how adsorbate molecules are distributed between the liquid phase and solid phase as the process reach equilibrium**, Huo, et al., 1996.** The adsorption process was performed at initial concentrations (50, 100, 150 ppm). Three most common isotherm equations namely, Langmuir, Freundlich and Temkin were tested in this work to describe the equilibrium adsorption. **Table 4** lists the four isotherms along with the constants of the linear plots studied in this work.

By examining **Table 4**, the results gave a different linearity calculated by the correlation coefficient (R^2) which ranges between 0.994 and 0.997, so, based on R^2, the adsorption of Chromium(VI) is best fitted in the Langmuir isotherm indicating the homogeneous nature**, Yuan, et al., 2010, and Bhaumik, et al., 2011.**

The values of (1/n) ranging between 0 and 1 in Freundlich isotherm is an indication of surface heterogeneity, and the closer to zero, the more heterogeneous is the surface. It is clear from **Table3** that value of 1/n was less than 1 confirming the heterogeneity of the surface of adsorbent.

4.2 Kinetics Analysis

In this section, the adsorption rate is investigated. The pseudo first-order and pseudo second order models were adapted to the test experiment data.

The results, as shown in **Table 4**, indicate that the adsorption of Chromium (VI) perfectly complies with pseudo 2^{nd} order reaction based on the correlation coefficient. Similar results were reported **Bhaumik, et al., 2011,** and **Parsons, et al., 2014.**

4.3 Modeling Using Minitab Software

In this study, the relationship between the response and variable is examined by regression.

The predicted removal efficiency of Chromium (VI) or the response of surface methodology (Y) is given in Eq. (2).

$$Y = 68.88 + 2.760\ X_1 + 0.0723\ X_2 + 34.4\ X_3 + 0.5115\ X4 - 0.3778\ X_1^2 - 0.000151X_2^2 - 43.6\ X_3^2 - 0.002169\ X_4^2 - 0.00982\ X_1X_2 - 1.780\ X_1X_3 - 0.01607\ X_1X_4 - 0.0276\ X_2X_3 - 0.000550\ X_2X_4 + 0.070\ X_3X_4 \qquad (2)$$

The predicted values versus the experimental values for Chromium (VI) removal can be seen in **Fig. 7** Results reveal that the developed model successfully captured the relation between the variables to the responses within the range of the studied variables.

4.4 Effects of Variables and Their Interactions

A hypothesis was assumed that this relationship is statistically significant, for a p-value coefficient. This probability was set as 95 % of the observation is significant or 5% is rejected.

The Final equation is:

$$Y=87.63-8.622X_1-1.549X_2+1.239X_3+5.915X_4-3.4X_1^2-0.682X_3^2-1.355X_4^2-1.472X_1X_2-1.205X_1X_4 \qquad (3)$$

It can be deduced from **Table 5** that the effect of pH, dosage and concentration were more pronounced than time based on the F-values of 1797.71 (pH), 58.05 (concentration), 37.14 (weight of adsorbent) and 846.12 (time). The quadratic effects of pH, weight of adsorbent and time were meaningful having (F-value of 124.29), (F-value of 5.00) and (F-value of 19.74) respectively.

The following important binary interactions were found as follows:

- pH(x1) and concentration(x2) , where x1x2 got high F-value of 17.48 and low P-value of 0.002.
- pH(x1) with time(x4), where x1x4 got high F-value of 11.71 and low P-value of 0.007.

4.5 Main Effects and Interaction Effects Plot for Chromium (VI) Removal Efficiency

The main effects plot **Fig. 8** was developed based on **Table 5** in which the un-coded values of the test variables and the Chromium (VI) removal efficiencies obtained experimentally are shown. The main effects of all parameters on percentage chromium (VI) removal were determined and shown in **Fig. 8**. The effect of pH on Chromium (VI) removal was studied in the range of pH 2-8. It is apparent from the **Fig.8** that efficiency removal was increased with decreased pH. At high pH values electrostatic repulsion between Chromium (VI) and Fe_3O_4 might result lower removal efficiencies whereas at lower pH conditions Fe_3O_4 electrostatic attraction between Fe_3O_4 and acidic Chromium (VI) may be resulted in higher efficiencies**, Yuan, et al., 2010.** The percentage removal of Chromium (VI) decreased slightly up to the concentration of 150ppm as shown in figure. The reason for decreasing the removal in higher concentration media is by increasing the initial concentration from 50 ppm to 150 ppm, the removal decreased. On this basis, it can be explored that, for the given adsorbent dose, the available sites for adsorption become less at higher concentrations, and hence, the percentage adsorption of Cr (VI) decreases**, Lasheen, et al., 2013**. Percentage removal of chromium (VI) was increased with time up to 60 min. This might be due to the fact that increased time allowed the particles to reach equilibrium hence, removal percentage was increased**, Parsons, et al., 2014**. It is noticed from the **Fig.8** that efficiency removal of Chromium (VI) has increased significantly with increased adsorbent dosage. This means that the toxic ions can be removed effectively from the contaminated water with the proper amount of adsorbent, due to the fact that intensely activated surface of Fe_3O_4 nanoparticles substantially possess more adsorption sites available for metal ions uptake from the solution. This is in accordance with the reports available on other Chromium (VI) removal processes**, Shen, et al., 2009**

Fig. 9 is the surface plot showing the combined effect of both pH and concentration using (0.3g) of Fe_3O_4 after 1hour. From **Fig.9** it can be seen an increase in the percentage Chromium (VI) removal can be observed with decrease in pH from 8 to 2 as well as there is an decrease in concentration from about 50 to 150 ppm. The dramatic increase of the Chromium (VI) uptake with the decrease of pH values was mainly due to that higher pH values made the surface of magnetite more negatively charged, which greatly enhanced the electrostatic repulsion between magnetite and Chromium (VI) anions, leading to a release of the adsorbed Chromium (VI) species from the magnetite surface**, Bhaumik, et al., 2011.** The reason for decreasing the removal in higher concentration media is by increasing the initial concentration from 50 ppm to 150 ppm, the removal decreased. On this basis, it can be shown that, for the given adsorbent dose, the available sites for adsorption become less at higher concentrations, and hence, the percentage adsorption of Cr (VI) decrease**s, Ilankoon, 2014.**

Fig.10 shows the combined effect of pH and time for Chromium (VI) removal on Fe_3O_4. From these figures it can be seen an increase in the percentage Chromium (VI) removal can be observed with decrease in pH from 8 to 2 as well as there is an increase in time from about 10 to 60 min, contact time and removal rate are important factors for selection a design of economical adsorbent for wastewater treatment. The removal efficiency increased with the contact time increased, the contact time was reach to saturation within 60 min for adsorbents that mean the saturation time was independent of adsorbent nature. This relation is found significant in similar work of, **Srivastava,** and **Sharma, 2014.**

4.6 Optimization of Operating Parameters

So, the optimum conditions were one of the objectives of the experimental design so that the high Chromium (VI) removal can be achieved. The optimum conditions of chromium (VI) removal by Fe_3O_4 was achieved at pH, weight of Fe_3O_4 , initial Chromium (VI) concentration and time of 2, 0.3g, 50 ppm and 1hr, respectively. At these conditions, chromium (VI) removal was 98.95%.**Table 6** shows the model validation were the predicted and experimental values of the responses for chromium (VI) are presented. The predicted and experimental values obtained at optimum conditions was 100% and 98.95%, showing good agreement between the experimental values and predicted from the model, with relatively small error which was only 1.08%. Model desirability approaching unity and with low error value displays the applicability of the model towards the responses. Relatively small errors were obtained for the predicted and the actual values indicate that the models are suitable in predicting the responses efficiently.

5 CONCLUSIONS

Chromium (VI) was successfully removed from aqueous solutions onto Fe_3O_4 nanoparticles. The obtained data for the adsorption is best fitted with the Langmuir isotherm. The adsorption complies with pseudo second order reaction. The statistical approach, response surface Box-Behnken experimental design was successfully employed for

experimental design and analysis of results, to study the linear, quadratic and interaction effects between the variables and also to optimize those variables for maximum removal of Chromium (VI).

The experimental results showed, percentage Chromium(VI) removal in permeate increased with decreasing in pH from 8 to 2, increasing time from 10 to 60 min, decreasing initial concentration from 150 to 50 mg/L , increasing adsorbent dosage from 0.05 to 0.3 g.

Appropriate regression model was developed for predicting the removal for Chromium (VI) and satisfactorily predicted the experimental values. Graphical surface response plots were used to obtain the optimum points. The best conditions for maximum Chromium (VI) removal (98.95%) were obtained at pH: 2; Chromium (VI) concentration: 50mg/L; contact time: 1hr and Fe_3O_4 dosage: 0.3g. Optimum values were confirmed by validation experiments.

NOMENCLATURE

Ce: Equilibrium concentrations of chromium (VI) solution (mg/L)

Co: Initial concentrations of chromium (VI) solution (mg/L)

Ct: Concentration of chromium (VI) at time t (mg/L)

K1: First order kinetic model constant (1/min)

K2: Second order kinetic model constant (g/mg.min)

KF: Freundlich isotherm equation constant ((mg/g).(L/mg)1/n)

KL: Langmuir isotherm equation constant (L/mg)

M: Mass of adsorbent used (g).

V: Volume of solution (L)

n: Freundlich isotherm equation constant

qe: Uptake of chromium(VI) at equilibrium (mg/g)

q_L: Langmuir maximum uptake of chromium(VI) per unit mass of Fe_3O_4 (mg/g)

qt: Uptake of chromium(VI) at time t (mg/g)

R^2: Correlation coefficient

DF: Degree of Freedom

S: Standard error of the regression

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Table 1. Chemical and physical properties of Potassium dichromate

Chemical formula	$K_2 Cr_2 O_7$
Molar mass	294.185 g/mol
Appearance	red-orange crystalline solid
Odor	Odorless
Purity	99%

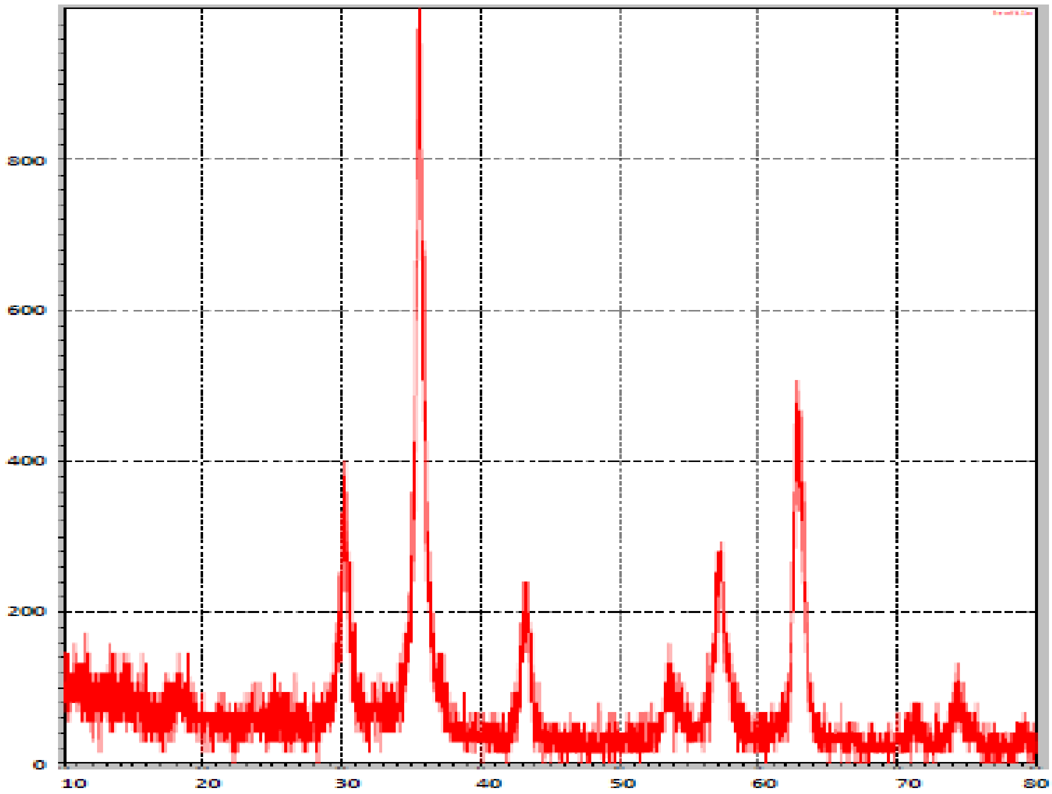

Figure 1. XRD pattern of prepared Fe_3O_4.

Table 2. The characterization of nano Fe_3O_4.

Property	**Value**
surface area, m^2/g	85.97
pore volume, cm^3/g	0.1566
average particles diameter, nm	75.92

Table 3. Design of Experiments.

Run	levels				adsorption variables				AFD removal %	
	X1	X2	X3	X4	pH	Dosage G	Conc. Ppm	Time hr	Exp.	Pred.
1	0	-1	0	-1	5	0.05	100	10	79.890	78.6564
2	0	0	1	0	5	0.175	100	35	87.630	87.6300
3	-1	0	1	0	2	0.175	150	35	93.520	92.3979
4	0	-1	1	1	5	0.05	100	60	91.200	90.0512
5	-1	0	-1	0	2	0.175	50	35	93.120	92.5514
6	1	0	-1	1	8	0.175	50	35	79.100	78.2530
7	1	1	0	-1	5	0.3	100	10	81.520	80.6997
8	1	0	1	0	8	0.175	150	35	73.610	72.2095
9	0	1	0	1	5	0.3	100	60	93.700	92.9645
10	0	0	-1	-1	5	0.175	50	10	81.691	80.8452
11	0	0	0	0	5	0.175	100	35	87.630	87.6300
12	-1	-1	0	0	2	0.05	100	35	90.120	90.2628
13	1	-1	0	0	8	0.05	100	35	74.000	74.3545
14	-1	1	0	0	2	0.3	100	35	94.620	94.0762

15	1	1	0	0	8	0.3	100	35	75.830	75.4978
16	0	0	1	-1	5	0.175	150	10	79.240	79.1212
17	0	0	1	1	5	0.175	150	60	88.920	89.5765
18	0	0	-1	1	5	0.175	50	60	94.120	94.0495
19	-1	-0	0	-1	2	0.175	100	10	82.900	84.3760
20	0	1	1	0	5	0.3	150	35	84.960	86.0891
21	0	-1	0	0	5	0.05	50	35	85.680	86.7093
22	1	0	0	1	8	0.175	100	60	78.280	78.9625
23	0	1	-1	0	5	0.3	50	35	88.230	89.5326
24	-1	0	0	1	2	0.175	100	60	98.000	98.6158
25	0	0	0	0	5	0.175	100	35	87.630	87.6300
26	1	0	0	-1	8	0.175	100	10	68.000	69.5426
27	0	-1	1	0	5	0.05	150	35	83.100	83.9558

Table 4. Isotherm parameters for removal Chromium (VI) by Fe_3O_4 .

Langmuir constants	**k*L* (L/mg)**	**q*L(mg/g)***	**R2**
$qe = \frac{q_L \mathrm{KLCe}}{1 + \mathrm{KLCe}}$	0.695	31.25	0.997
Freundlich constants	**log k*F***	**1/n**	
$qe = \mathrm{KF}\ Ce^{1/n}$	1.065	0.505	0.995
Temkin constants	**Kt**	**B1**	

$qe = B_1 \, lnK_t + B_1 \, ln(Ce)$	5.567	7.401	0.994

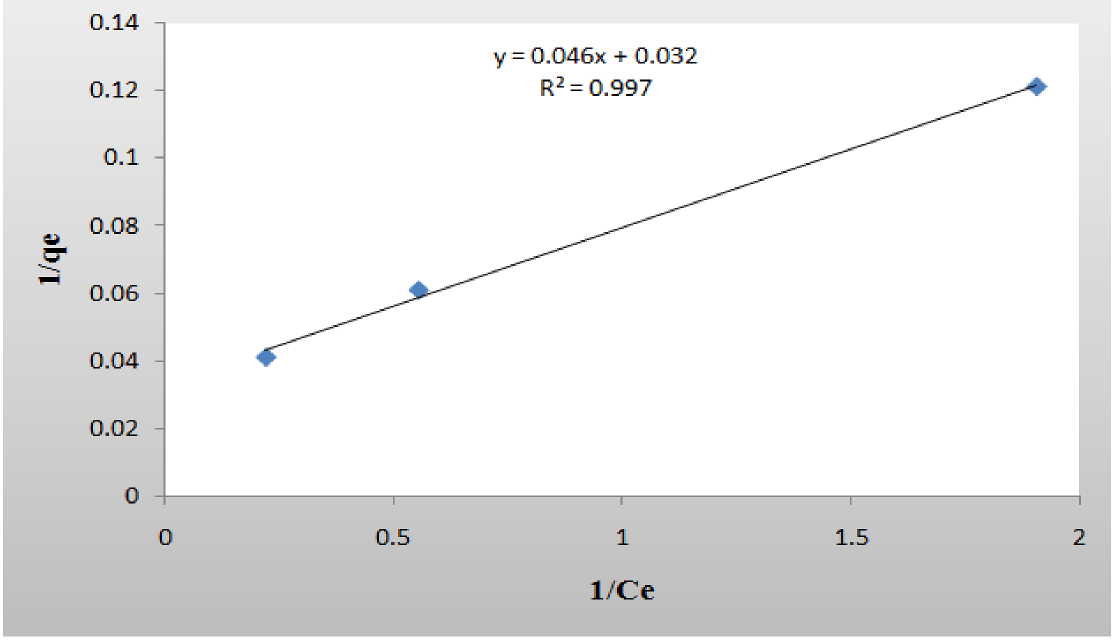

Figure 2. Langmuir adsorption isotherm of Chromium (VI) on Fe_3O_4.

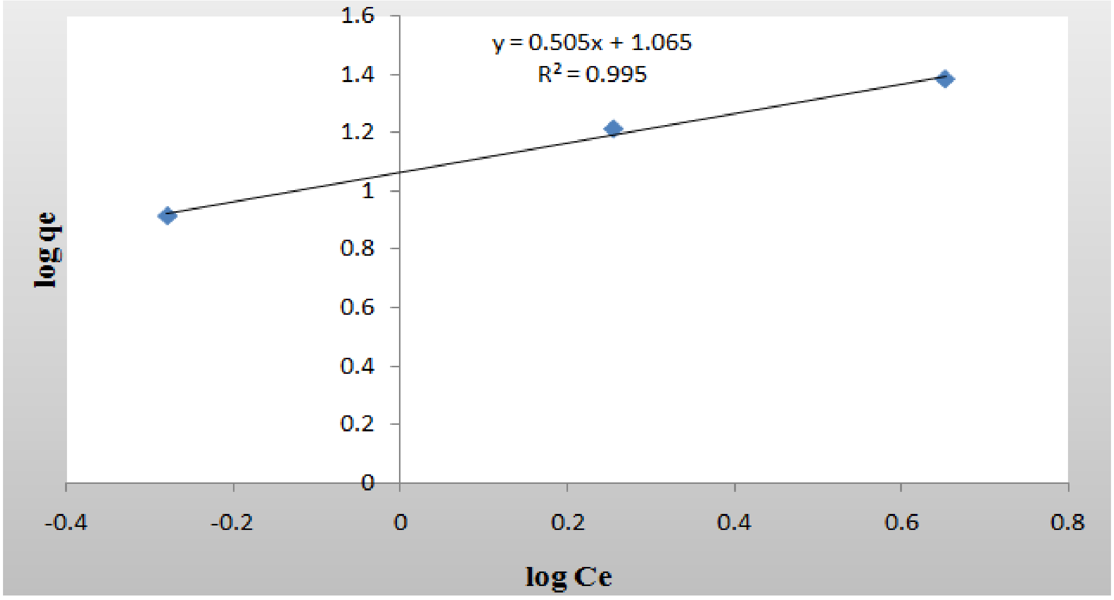

Figure 3. Freundlich adsorption isotherm of Chromium (VI) on Fe_3O_4.

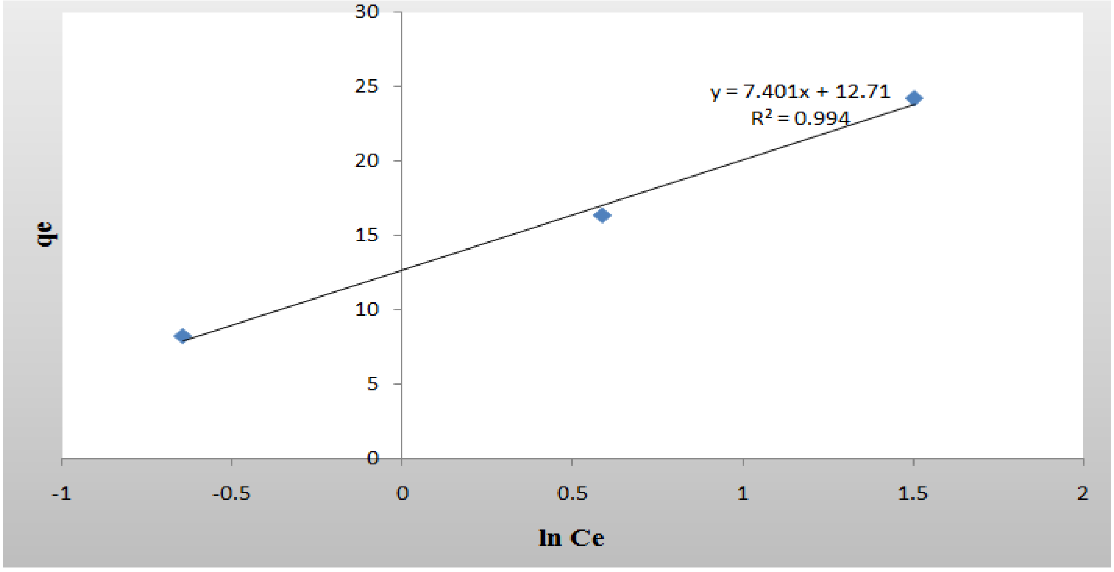

Figure 4. Temkin adsorption isotherm of Chromium (VI) on Fe_3O_4.

Table 4. Kinetic parameter for Chromium (VI) adsorption on Fe_3O_4.

Pseudo-first order	**k1 (L min-1)**	**R2**
$ln(qe - qt) = lnqe - k_1 t$	0.0368	0.986
Pseudo-second order	**k2(g/mg min)**	
$\frac{t}{qe} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{qe}\right) t$	0.049	0.999

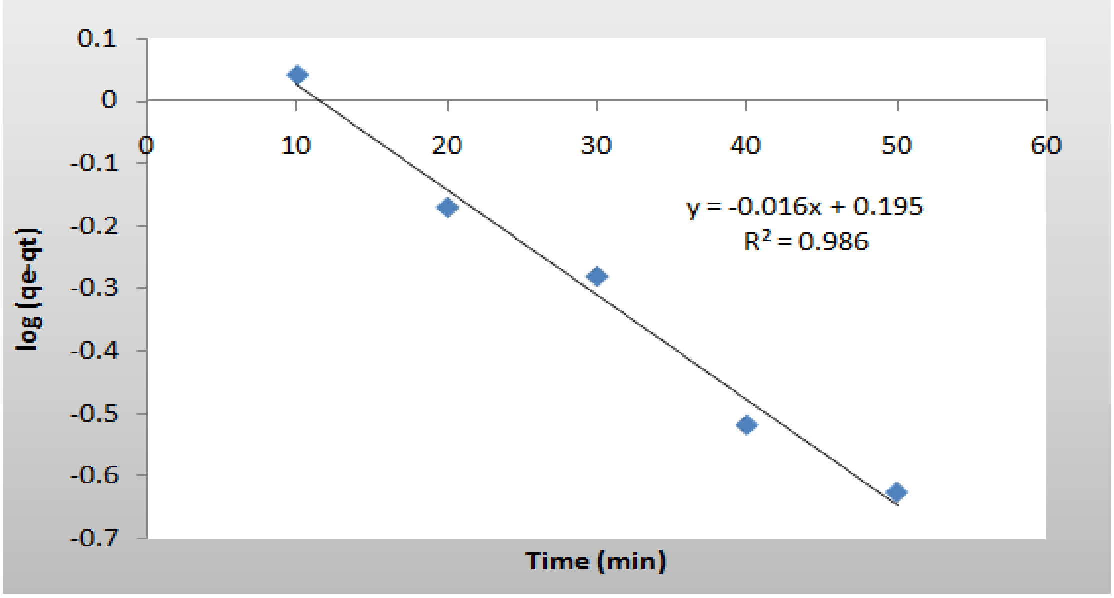

Figure 5. Pseudo- first order kinetic for Chromium (VI) on Fe_3O_4.

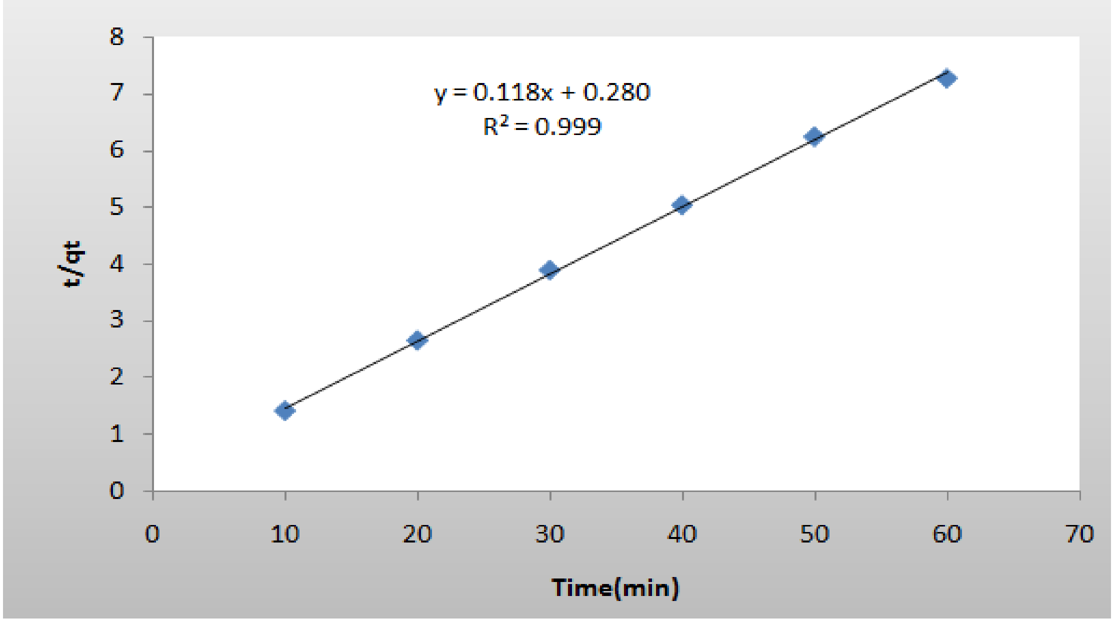

Figure 6. Pseudo- second order kinetic for Chromium (VI) on Fe_3O_4.

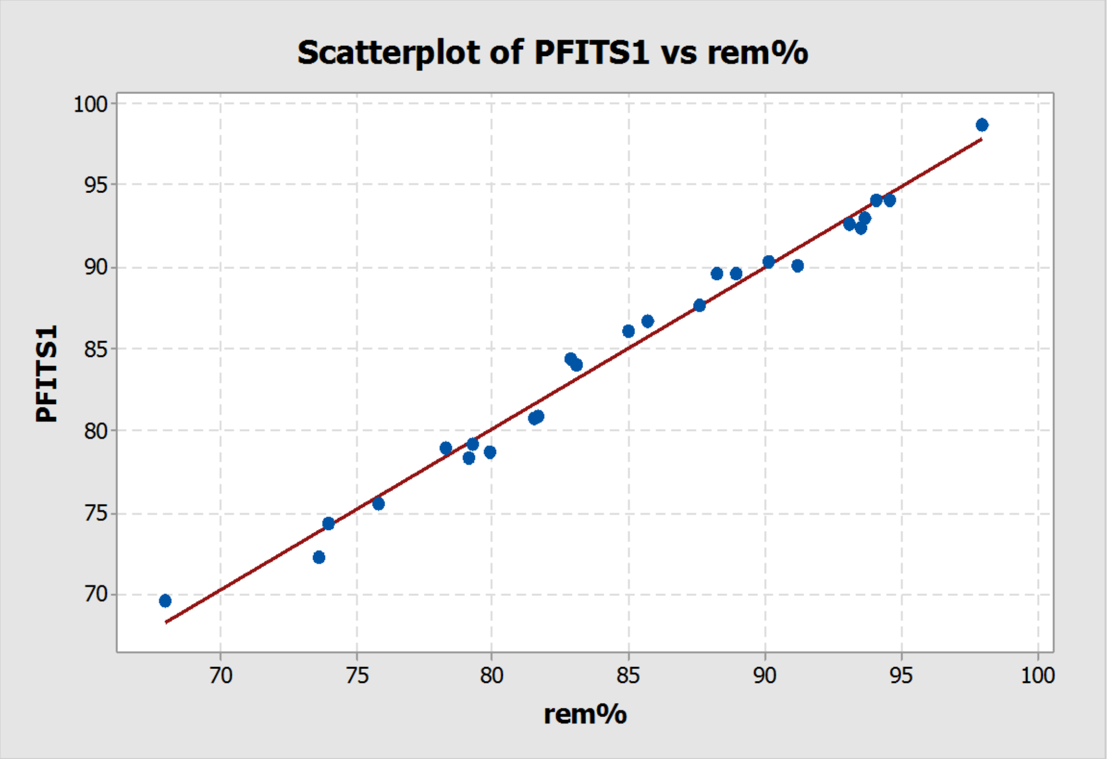

Figure 7. Relationship between predicted and experimental data for Chromium (VI) removal.

Table 5. Analysis of variance (Response Surface Regression).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model					
X1	1	892.00	891.998	1797.71	0.000
X2	1	28.80	28.802	58.05	0.000
X3	1	18.43	18.426	37.14	0.000
X4	1	419.83	419.835	846.12	0.000
X1*x1	1	61.67	61.670	124.29	0.000
X2*x2	1	0.76	0.756	1.52	0.245
X3*x3	1	2.48	2.479	5.00	0.049
X4*x4	1	9.80	9.797	19.74	0.001
X1*x2	1	8.67	8.673	17.48	0.002
X1*x3	1	1.782	1.782	3.59	0.087
X1*x4	1	5.81	5.808	11.71	0.007
X2*x3	1	0.12	0.119	0.24	0.635
X2*x4	1	1.89	1.889	3.81	0.080
X3*x4	1	0.19	0.189	0.38	0.551
Error	10	4.96	4.96	0.496	
Total	26	1464.70			
Model Summary					
	R-sq	R-sq(adj)			
	99.66%	99.12%			

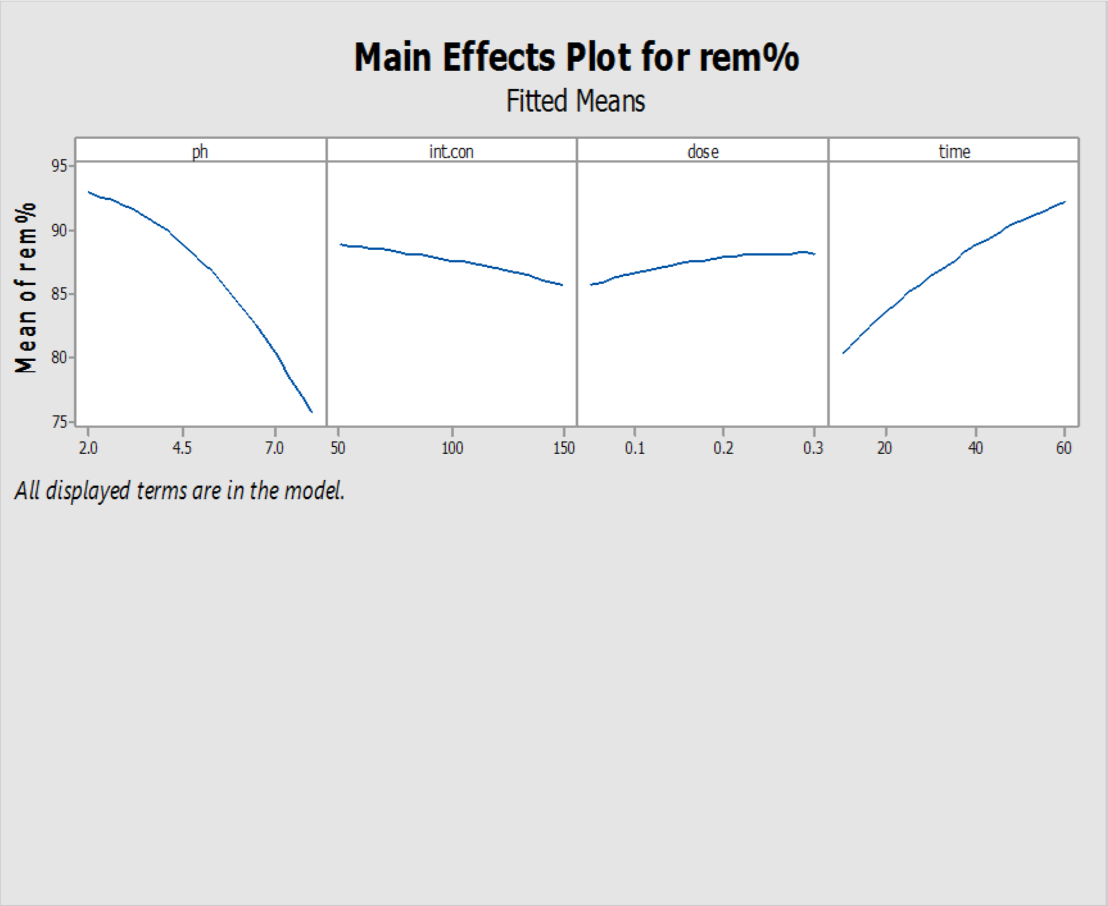

Figure 8. Main Effect Plot for Chromium (VI) removal efficiencies.

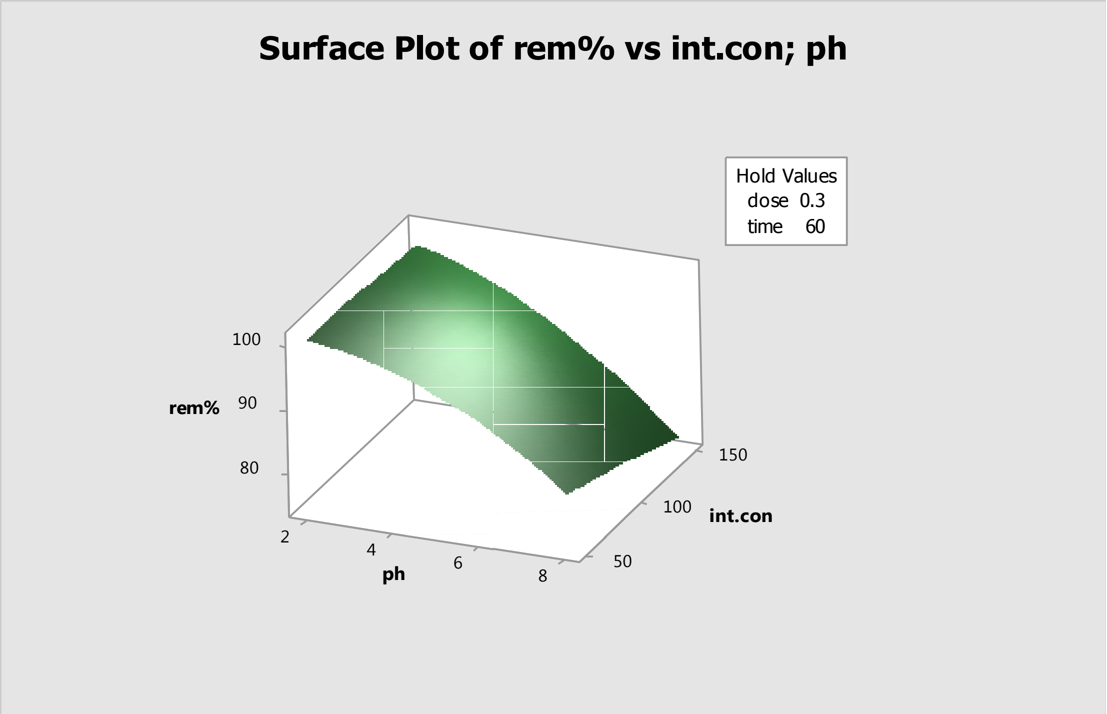

Figure 9. The effect of pH and concentration on the removal of Chromium (VI).

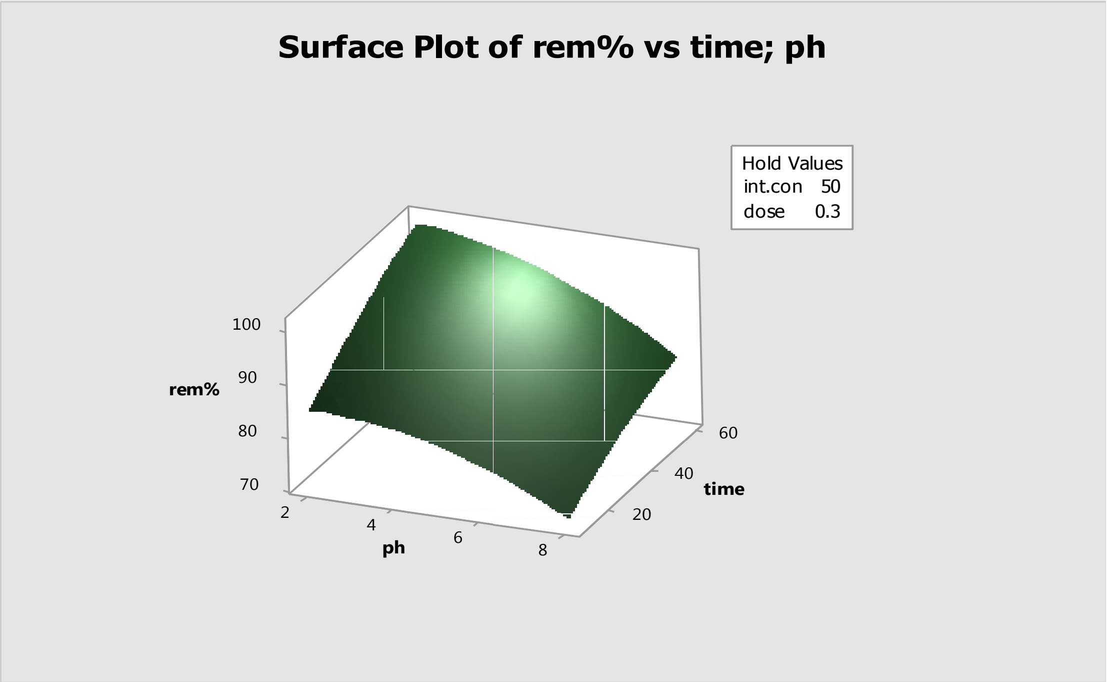

Figure 10. The effect of pH and Time on the removal of Chromium (VI).

Table 6. Model validation for AFD removal by Fe_3O_4.

Model Desirability	pH	Conc.	Weight of Adsorbent	Time	%Removal Predicted	% Removal Experimental	% Error
1	2	50	0.3	1	100	98.95	1.08