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Research Article

Optimization Study on the Removal of Cadmium Ion onto Biomass Nanoparticles using Response Surface Methodology

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Abstract

Date seeds are a by-product of the date fruit processing industry with minimal human and iron chloride used to synthesize Date Seeds-Iron Oxide Nanoparticles (DS-IONPs) using Response Sur-face Methodology (RSM) software. The effects of variable parameters of mixing ratio of iron chloride to date seeds extract (by volume), solution pH, and mixing temperature on the removal of the cadmium ion were investigated in this study. Based on the Central Composite Design (CCD), two-factor Interaction (2FI) and quadratic models were respectively employed to correlate the effect of variable parameters on the synthesis of nano adsorbents used for removal of cadmium ion from aqueous solutions. From the Analysis of vari-ance (ANOVA), the most influential factor in each experimental design response was identified. The optimum conditions for synthesis DS-IONPs from Iraqi date seeds and ferrous chloride were found as follows: mixing ratio of 2.5:1, solution pH of 2.5, and mixing temperature of 70oC. The theory and experimental percentage removal of Cd (II) were found to be 98.08 and 95.11%, re-spectively, while the percentage error between predicted and experimental results for the removal of Cd (II) was 3.03. The batch technique was used to investigate the effects of initial Cd (II) concentrations ranging from 10 to 25 mg/l and contact time using a water bath shaker. Furthermore, the experimental adsorption isotherms of Cd (II) on DS-IONPs were analyzed using Langmuir, Freundlich, and Temkin isotherm models. It was found that the Langmuir model achieved the best fit with a maximum adsorption capacity of 20.5 mg/g at 30°C.

Keywords: Optimization; Response Surface Methodology; Date Seeds; Nano Particles Adsorbents; Cadmium; Batch Adsorption

Introduction

Environmental pollution created by different pollutants as pesticides, dyes, Poly Aromatic Hydro-carbons (PAHs), Benzene Ethylene Toluene Xylene (BETX), phenols compounds, radioactive elements and heavy metals has become one of the major global concerns, threatening the ecosystem organisms and human health. Heavy metals are stable elements that tend to accumulate in bio-logical organisms. Heavy metals like cadmium are also toxic in trace amounts. Heavy metals poisoning can seriously damage the central nervous system, lungs, kidneys, and other vital organs. Moreover, the release of these contaminants into water sources will threaten the health of aquatics [1]. Cadmium ion is hazardous ions to the environment. It was used extensively in the manufacturing of compounds, alloys, pigments, and batteries. In comparison, soil pollution and human cadmium exposure have increased significantly over the last century as a result. When the body is exposed to high levels of cadmium over time, norepinephrine, acetylcholine, and serotonin levels decline. According to those tests, chronic cadmium inhalation induces pulmonary adenocarcinomas in rodent models. Adenocarcinomas may also occur as a result of systemic or direct contact [2].

Heavy metals are removed from aqueous solutions by various methods such as adsorption, ion exchange, reverse osmosis, coagulation and flocculation, advanced oxidation, and ultra-filtration. Adsorption technique method is the simple, safe, ideal, and economical option for removing metal ions from contaminated water [3]. Adsorbents of various types have been used for heavy metal adsorption, including modified clays, zeolites, clays, industrial waste peel, activated car-bons, and nano adsorbents. The various nano adsorbents used in wastewater treatment are dis-cussed categorically with an emphasis on regeneration to remove various types of contaminants using nano adsorbents [2]. In chemical engineer process and reactions, Response Surface Methodology (RSM) software is a popular optimization method employed to study the relationships between the input and output parameters and independent variables and to reach the optimum conditions. It has the advantages of high precision, low experimental cost and excellent prediction performance. RSM used to analyze the optimum conditions for removing hexavalent chromium by nanoscale zero-valent iron and established a quadratic model between temperature, pH, dosage, initial concentration and removal rate [4]. The removal of Cd (II) from aqueous solution optimized by ascorbic acid modified nanoscale zero-valent iron using RSM [5]. RSM used to analyze the effect of initial concentration, pH and dosage on the removal efficiency of malachite green dye by clay supported iron nano-particles. Overall, RSM can be used to optimize chemical processes, which can be described with a second order polynomial equation [6]. The production of dates is one of the most important agricultural activities in the world. Much agricultural waste is generated from date palms in the most desert-filled areas of the earth and in Mediterranean climates [7]. For this reason, this article seeks to study new possibilities of using date seeds extract to prepare nanoparticles adsorbent by mixing with iron chlorides under the optimum conditions.

In the last decade, iron oxides (Fe_2O_3) have drawn a lot of attention due to their catalytic prop-erties to address environmental issues [8]. Ferrites are magnetic compounds whose main constituent is iron oxide. Easy separation and recovery is one of the most essential advantages of these compounds in water and wastewater treatments. Biomass extract suggested mixing with iron oxides for the purpose of water treatment processes due to its non-toxicity, high phase resistance, visible light absorption, low cost, insolubility in water, and light corrosion resistance [2]. This study conducted in synthesis Date Seeds Iron Oxide Nanoparticles (DS-IONPs) by mixing Date Seeds (DS) extract and ferrous chloride ($FeCl_2$) solution using Response Surface Methodology (RSM) software to optimize the preparation parameters (mixing ratio, solution pH and mix-ing temperature) with the removal of Cd (II) from the synthesis aqueous solution.

Materials and Methods

Cadmium

Technical grade of cadmium ion Cd(II) supplied by Scharlaw Chiemi, Spain, was used as ad-sorbate. Distilled water was used for the purpose of preparation the solutions.

Preparation of (DS-IONPs)

First of all 0.1 M $FeCl_2$ prepared by dissolve 12.7gm of ferrous chloride in 1000ml of distilled water, mixed for 20 minutes by a magnetic stirrer and stored at 20^{o}C until use. Date seeds extract was considered as good substance for reducing iron chlorides to their oxides. Date seeds are a by-product of the date fruit processing industry with minimal human use; however, they are a rich source of polyphenols with a range of potential biological properties, so it used for the preparation of nano particles material at the optimum conditions of mixing ratio, solution pH and mixing temperature. Iron oxide nanoparticles were prepared by adding 0.1 M FeCl2 solution to date seeds extract at (2.5:1) volume ratio. The mixture was stirred for 60 min and then allowed to stand at room temperature for another 30 min to obtain colloidal suspension. Mixture was centrifuged at 16000 rpm, then, the precipitate were washed several times with ethanol and then dried at 45°C under vacuum to obtain the mixture of Fe_2O_3 –NPs and Fe_3O_4 -NPs. Date seeds extract have the best reduction capability against ferric chloride that is observed by the external color change. The DS-IONPs were prepared by mixing of 0.1 M of $FeCl_2$ with date seeds extract in volume ratio 2.5:1 on acidic solution pH at 2.5 at mixing temperature of 50^{o}C.

Batch adsorption studies

Batch adsorption tests of cadmium solutions onto prepared date seeds iron oxide nanoparticles (DS-IONPs) which prepared at the optimum conditions according to the RSM software. The adsorption experiments were determined using set of 250ml of Erlenmeyer flasks. 200ml of Cd (II) solutions with initial concentrations of the range of 10-25mg/l. 0.30 g of (DS-IONPs) was added to each flask using bath shaker at speed of 110 rpm and 30°C. The cadmium concentra-tions at the maximum wavelength of 477 nm were determined using an atomic absorption spec-trophotometer (AAS). Equation (1) used to determine the amount of cadmium adsorbed at equi-librium, qe (mg/g), while Equation (2) used to determine the percentage removal of Cd (II).

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\% \mathrm{Re}\,moval = \frac{(C_o - C_e)}{C_O} \times 100 \quad (2)$$

Where Co and Ce (mg/l) are the liquid-phase concentrations of Cd (II) at initial and equilibrium conditions, respectively; V (l) the volume of the solution and W (g) the mass of dry adsorbent used. The adsorption quantity at time t, qt (mg/g), was calculated using Equation (3):

$$q_t = \frac{(C_c - C_t)V}{M} \quad (3)$$

Where Ct (mg/l) is the concentrations of Cd (II) at any time t.

The predicted error of experimental and predicted results for Cd (II) removal calculated using Equation (4):

Predicted Error = $\frac{(Predicted\ value - Expermental\ value)}{predicted\ value}$ (4)

Adsorption isotherm models

Langmuir, Freundlich, and Temkin isotherm models were used to describe the experimental re-sults. The form of the Langmuir isotherm [9] is given by Equation (5):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where qm (mg/g) is the monolayer adsorption capacity, and KL (l/mg) is the equilibrium adsorp-tion constant.

The nonlinear form of the Freundlich isotherm [10] is given by Equation (6)

$$q_e = K_F C_e^{1/n} \quad (6)$$

where KF (l/g) and n are Freundlich constants.

The Temkin isotherm [11], is commonly used in the form given in Equation (7).

$$q_e = B \ln(AC_e) \quad (7)$$

where B = RT/b and b (J/mol) is the Temkin constant related to the heat of adsorption; A (l/g) is also a Temkin isotherm constant, R (8.314 J/mol K) the gas constant, and T (K) the absolute temperature [12].

Design of experiments for preparation of (DS-IONPs)

The nano adsorbent preparation parameters were studied with a standard response surface meth-odology (RSM) design called a Central Composite Design (CCD). This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum num-ber of experiments, and also to analyze the interaction between the parameters [13]. Generally, the CCD consists of a 2n factorial runs with 2n axial runs and nc center runs (six replicates). The biosynthesis of date seeds iron oxide nanoparticles (DS-IONPs) by mixing of 0.1 M of $FeCl_2$ with date seeds extract in various volume ratio at different solution pH and different mixing temperatures. The nano adsorbent prepared by varying the preparation variables using the CCD. The preparation variables studied were (i) x1, mixing volume ratio; (ii) x2, solution pH and (iii) x3, mixing temperature. These three variables together with their respective ranges were chosen based on the literature and preliminary studies. The number of experimental runs from the central composite design (CCD) for the three variables consists of eight factorial points, six axial points and six replicates at the centre points indicating that altogether 20 experiments were required, as calculated from Equation 8:

$$N = 2n + 2n + nc = 23 + 2 \times 3 + 6 = 20 \quad (8)$$

where N is the total number of experiments required and n is the number of process variables.

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The response (Y) was cadmium removal. The response was used to develop an empirical model which correlated the response to the three preparation process variables using a second degree polynomial equation [14] as given by Equation 9:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (9)$$

Where Y is the predicted cadmium removal response, the constant coefficient, bi the linear co-efficients, bij the interaction coefficients, bii the quadratic coefficients and xi, xj are the coded values of the nan adsorbent preparation or cadmium removal variables.

The parameters involved in the preparation were varied using the response surface methodology (RSM). The three variables studied were:

x1, Mixing volume ratio (FeCl2 solution/date seeds extract)

x2, Solution pH

x3, Mixing temperature.

These three variables together with their respective ranges were chosen based on the literature and the results obtained from the preliminary studies, while the responses considered in this study was:

Y, Cd (II) removal

The predicted error of experimental and predicted results for Cd (II) removal calculated on the following equation:

$$\%\text{Prediction Error} = \frac{(predicted - expermental)}{predicted} \times 100 \quad (10)$$

Results and Discussion

Cadmium removal onto Prepared DS-IONPs using DOE

The complete design matrix for the removal of Cd (II) from the experimental works are presented in Table 1. Runs 15-20 at the center point were conducted to determine the experimental error and the reproducibility of the data.

Table 1: Preparation of (DS-IONPs) experimental design matrix and results for cadmium removal.

Run	Type	Ratio	pH	Temperature°C	Removal %
1	Fact	1.00	2.50	30.00	85
2	Fact	3.00	2.50	30.00	88
3	Fact	1.00	6.50	30.00	85
4	Fact	3.00	6.50	30.00	82
5	Fact	1.00	2.50	70.00	97
6	Fact	3.00	2.50	70.00	99
7	Fact	1.00	6.50	70.00	93
8	Fact	3.00	6.50	70.00	95
9	Axial	0.32	4.50	50.00	81
10	Axial	3.68	4.50	50.00	86
11	Axial	2.00	1.14	50.00	94
12	Axial	2.00	7.86	50.00	89
13	Axial	2.00	4.50	16.36	80
14	Axial	2.00	4.50	83.64	91
15	Center	2.00	4.50	50.00	92
16	Center	2.00	4.50	50.00	92
17	Center	2.00	4.50	50.00	92
18	Center	2.00	4.50	50.00	92
19	Center	2.00	4.50	50.00	92
20	Center	2.00	4.50	50.00	92

The final empirical model in terms of coded factors (parameters) after excluding the insignificant terms for Cd (II) removal (Y) is given in below Equation.

Y =91.87 +0.91X1–1.64 X2 +4.58 X3 –2.17 X12 +0.66 X22 –1.46 X32 –0.75 X1X2 +0.50 X1X3 –0.25 X2X3 (11)

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value. The closer the R2 value to unity, the better the model will be as this will give predicted values which are closer to the actual value for the response. The R2 value was consid-ered relatively high, indicating that there was agreement between the experimental and the pre-dicted in the removal of cadmium from this model. The adequacy of the models was further justified through analysis of variance (ANOVA). The ANOVA results for Cd (II) removal (Y) onto (DS-IONPs) is listed in Table 2. The model F-value of 455.53 implied that this model was significant. Values of Prob > F of less than 0.05 indicate that the model terms were significant. In this case, x2, x3 and x12 were significant model terms whereas x1, x22, x32, x1x2, x1x3 and x2x3 were insignificant to the Cd (II) removal response. The experimental observation for both the pH and mixing temperature revealed that they have significant effects on the response of Cd (II) removal onto prepared nano adsorbent, whereas mixing ratio showed the least effect on this response. The quadratic effect of mixing ratio was also higher compared to the quadratic effects of pH and mixing temperature on the same re-sponse. The interaction effect between mixing ratio, pH and mixing temperature on the response of Cd (II) removal were found to moderate. The interaction effects between mixing ratio, pH and mixing temperature on the removal of Cd (II) represented in three-dimensional response as showing in Figures (1-3).

Table 2: Analysis of variance (ANOVA) response surface quadratic model for Cd (II) removal.

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob > F
Model	455.53	9	49.50	6.60	0.0034
X_1	11.28	1	11.28	1.50	0.2483
X_2	36.77	1	36.77	4.90	0.0500

X_3	286.03	1	286.03	38.13	0.0001
X_1^2	67.57	1	67.57	9.01	0.0133
X_2^2	6.34	1	6.34	0.84	0.3787
X_3^2	30.64	1	30.64	4.08	0.0709
X_1X_2	4.50	1	4.50	0.60	0.4566
X_1X_3	2.00	1	2.00	0.27	0.6169
X_2X_3	0.50	1	0.50	0.067	0.8015
Residual	75.02	10	75.02		

Figure 1, show the effects of mixing temperature and mixing ratio on the removal of Cd (II) at solution pH of 2.5, Figure 2, show the effects of mixing ratio and solution pH on the removal of Cd (II) at mixing temperature of 70°C., while Figure 3 show the effects of mixing temperature and solution pH on the removal of Cd (II) at mixing ratio of 2.5:1. It was observed from these figures that the removal of Cd (II) onto prepared DS-IONPs generally increased with increasing mixing temperature and mixing ratio. This is due to the formation of nano structure which caused by an increase in the mixing temperature and the nano particles added from the increasing of mixing ratio of iron chloride to the date seeds extract [2].

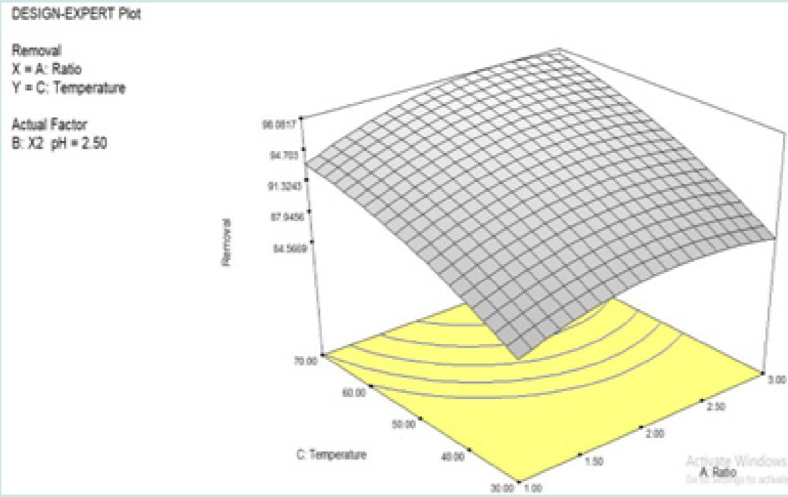

Figure 1: Three-dimensional response surface plot of cadmium removal onto DS-IONPs (effect of mixing ratio and mixing temperature) at pH of 2.5.

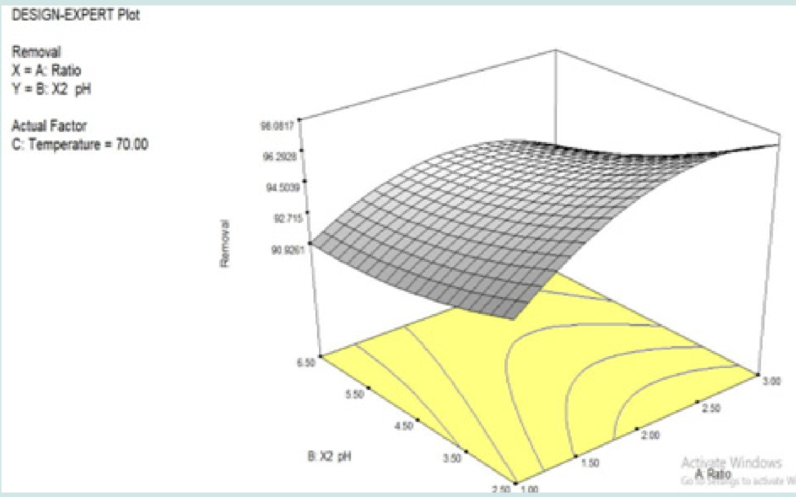

Figure 2: Three-dimensional response surface plot of cadmium removal onto DS-IONPs (effect of pH and mixing ratio) at mixing temperature of 70Oc.

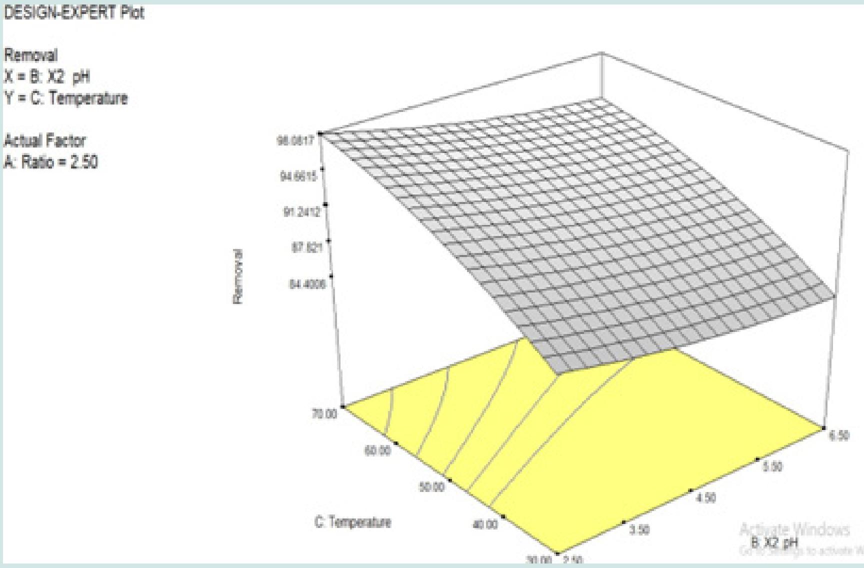

Figure 3: Three-dimensional response surface plot of cadmium removal onto DS-IONPs (effect of pH and mixing tempera- ture) at mixing ratio of 2.5:1.

Process optimization

The preparation of adsorbent for the purpose of removal pollutants should have a high removal ability. Therefore, when Design Expert software (DOE) using for optimize the adsorbent prepa-ration conditions, the experimental conditions with the highest desirability were selected to be verified. The predicted and experimental results of DS-IONPs preparation and Cd (II) removal obtained at optimum condition are listed in Table 3. It can be found that the error between predicted and experimental results for Cd (II) removal using the optimum conditions obtained by (DOE) soft-ware is (3.03) which is within the accepted values.

Table 3: The predicted and experimental results of Cd (II) removal.

Parameter	RSM software results	Experimental results	Error
Mixing temperature (°C)	70	70	
Solution pH	2.5	2.5	
Mixing ratio	2.5	2.5	
Cd (II) removal (%)	98.08	95.11	3.03

Table 4: Langmuir, Freundlich and Temkin isotherm models results for adsorption of Cd (II) onto DS-IONPs at 30°C.

Isotherm model	Parameter	Value
Langmuir	q_m (mg/g)	20.5
	K_L (l/mg)	1.787
	R^2	0.982
Freundlich	n	2.249
	K_F (l/g)	6.904
	R^2	0.910
Temkin	A (l/g)	2.718
	B (J/mol)	4.28
	R^2	0.952

Adsorption isotherm models

The adsorption Langmuir, Freundlich, and Temkin isotherm models' parameters obtained are pre-sented in Table 3. The maximum adsorption capacity obtained is 20.5 mg/g at 30°C, with R2 = 0.982 value further confirming the suitability of the Langmuir model in describing the equilib-rium data [28].

Conclusion

The nanoparticles prepared (DS-IONPs) are a promising adsorbent for the adsorption of the heavy metals (cadmium), from an aqueous solution. In this study Response, Surface Methodology (RSM) software proved to be a powerful tool for optimizing the operational conditions to prepare date seeds iron oxide nano particles (DS-IONPs) for the purpose of removal Cd (II) from aqueous solution. The optimum preparation conditions were mixing ratio 2.5:1, pH 2.5 mixing tempera-ture 70°C. The removal of Cd (II) was 95.11% under optimal conditions. Batch adsorption equilibrium data were fitted to three isotherm models: Langmuir, Freundlich, and Temkin models, the results showed that Langmuir isotherm model was the best fitting to describe the experimental data with a maximum adsorption capacity of 20.5 mg/g at 30°C. The results demonstrated that DS-IONPs have much practical potential as an efficient adsorbent for Cd (II).

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