 doi.org/10.52568/000719/JCSP/41.01.2019

Optimization of Zinc Ions Removal by Modified Phoenix Dactylifera L. Seeds Using Response Surface Methodology

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(Received on 21st April 2017, accepted in revised form 13th July 2018)

Summary: The current study investigates the role of Phoenix Dactylifera L. (date palm) seeds as an effective biosorbent for removing Zn^{+2}, a toxic heavy metal pollutant usually found in the waste streams of industries like fertilizer, mining and galvanizing etc. Date palm seeds were washed, dried, crushed in 170-300 um and modified by acidic treatment (0.1 $MHNO_3$). The effect of most important parameters i.e., pH (3.5-6.1), initial zinc ion concentration (5-100mg/l), biosorbent dosage (0.1-1g) and contact time (0.5-60sec) have been studied via design expert software (version 8.0.6) of response surface methodology. The Box-Bhenken Design (BBD) was used in Response Surface Methodology (RSM) for designing the experiments and a number of 29 experiments were run. The model suggested by the design expert software was quadratic as it had maximum R2- value (0.9235) which indicated that the predicted values of quadratic model were best fitted to the experimental values. The significance of the factors was indicated by Analysis of Variance (ANOVA). The results showed that the metal uptake increased by increasing initial zinc concentration and decreasing in biosorbent dosage and pH while the contact time had negligible effect on the response surface. The parameters were numerically optimized and the optimum input parameters obtained were pH = 3.52, initial zinc ion concentration = 59.11ppm, biosorbent dosage = 0.1g and contact time = 60min with a metal uptake of 26.84mg/g. Therefore, (Phoenix Dactylifera L.) seeds substantially removed zinc ions under optimum conditions.

Keywords: Biosorbent, Fertilizer, RSM, BBD, Phoenix Dactylifera.

Introduction

Access to clean water supply is an indispensible necessity for the dignity and health of all people [1]. Earth, which is a water planet, contains about 70% water but out of this only 0.75% is available for all living creatures. The world is facing an acute water scarcity owing to discharge of wastes into world's water by increased human global population [2–4]. According to the latest estimates of Pakistan Council of Research in Water Resources (PCRWR), Pakistan may run dry with less than 700 m^3 per capita water by 2025. This organization has warned the country to carry out research at diverse levels to resolve the crisis [5].

To overcome the crisis, there is a tremendous pressure in protecting the available water resources from waste water pollution throughout the world [6].With the rapid evolution of industries, large quantities of hazardous effluents such as toxic chemicals, organic pollutants and heavy metals are generated [7]. Out of these pollutants heavy metal ions contaminants (such as Cu, Cd, Ni, Cr, Pb and Zn etc.) have been prioritized as major pollutants due to their toxic effects in the environment [8, 9] Heavy metals are the wastes of many industries e.g., metal processing, paper and pulp, petrochemical, paints, leaded glass, textile and storage batteries industries etc. [10, 11]. Heavy metal ions are toxic because of their non-biodegradable and perseverance nature in the environment [12–14]. They are highly soluble in aqueous phase and can easily assimilate in living organisms [15, 16]. If the concentration of metals accumulated is beyond permissible limit, they are susceptible to cause eminent health disorders including cancer, nervous system damage, reduced growth and death in extreme cases [17-19]. Zn is a heavy metal whose major sources are galvanization, smelting, fertilizers, mining, refineries and pesticides etc. [20, 21]. High levels of Zn can cause serious health problems such as anemia, gastrointestinal distress, stomach cramps, neurological signs, skin irritation and depression [21–24]. According to Pakistan standards set by WHO, permissible limit of Zn in drinking water is 5mg/l [25, 26].

In order to pursue environmental regulations, it is a necessity to devise efficient and low cost technologies for the removal of heavy metal ions [27]. The already available techniques for the treatment of heavy metal ions are classified as physical, chemical and biological [28–30]. The physico-chemical methods such as filtration, ion-exchange, reverse osmosis,

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doi.org/10.52568/000719/JCSP/41.01.2019

chemical precipitation, etc. are not ideal for the removal heavy metals because they can neither be applied to the local conditions nor able to meet the established standards [31–34] Specially, when the concentration of heavy metal ions is <100mg/l, these treatments become extremely expensive [35]. Moreover, these technologies are not eco-friendly because they produce toxic sludge as a secondary source of pollution, disposal of which is itself a costly affair [36, 37]. Therefore, the removal of heavy metal ions in an eco-friendly and cost effective manner is of great importance [38].

Biosorption is the property of metabolically inactive biomasses, which has been proved as an effective technique for the removal of heavy metal ions, even with concentration (<100mg/l) [35, 38], [39]. It is a complex phenomenon which involves ion exchange, chelating and physico-chemi sorption between heavy metal ions and functional groups (carboxyl, hydroxyl, phosphates, etc.) [40, 41]. Biosorption has many advantages over the conventional techniques e.g., it makes use of naturally available, cheap and renewable biomass, growth independent system and capability to handle large volume of wastewater due to fast kinetics [42, 43]. Therefore, a lot of work is being done in exploring a low cost biosorbent of high capacity for the removal of different heavy metal ions.

Date palm seeds are the agricultural waste of date palm trees which are widely available in dried regions throughout the world [44]. They can be utilized to eliminate heavy metal ions as they contain carbohydrates, proteins, lipids and large amount of nutrients. The major constituents of date palm seeds are cellulose, hemicellulose and lignin on which the main functional groups are carbonyl hydroxyl and ether [45–48] The purpose of current research is to evaluate potential of acidic treated date palm (Phoenix Dactylifera L.) seeds for the removal of Zn^{+2} in aqueous solution using Response Surface Methodology (RSM). RSM is a mathematical and statistical technique for experimental design which is useful to determine the effects of varying factors and searching the optimum parameters [49–51] In this study, RSM was used to optimize the four parameters (pH, initial concentration, biosorbent dosage and contact time) and to analyze the interaction between factors affecting overall binding capacity of date palm seeds for Zn ions. Major steps involved in optimization are: performing statistical design of experiments, model fitting and predicting response.

Experimental

Biomass Preparation

Date palm seeds were collected, washed with distilled water repeatedly to take out extraneous and soluble impurities and utilized as sorbent for the removal of Zn(II) ions. The date palm seeds were collected from a juice shop in Lahore, Pakistan. Seeds were dried by putting them in sunlight for 24h and a fine powder of size range between 170-300µm was prepared. Sample was stored in clean and dry place. Screen analysis of seeds powder Table-1.

Modification of Date Palm Seeds by Acidic

The prepared date powder was modified by treating it with 0.1 M HNO3 at ambient temperature for 24h. The pH of the powder was maintained at 7 by washing it thoroughly with distilled water. After filtration it was dried under shade for 24h and stored for experimental work.

Determination of point of zero charge

The Point of zero charge is the pH of an adsorbent surface at which that surface has a net neutral charge [52]. It was determined using method mentioned in previous study by adding 0.2g of date palm seeds to 100 mL of distilled water with pH from 2 to 6 respectively and stirred in orbital shaker at 150rpm for 24h. pH of the samples were analyzed at regular intervals and change in pH was determined [53]. pHZPC for date palm seeds powder is determined as pH 3.5 Fig. 1.

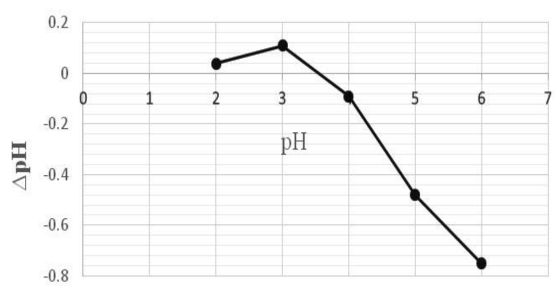

Fig. 1: Determination of Point Of Zero Charge.

Table-1: Sieve Analysis of Date Palm Seeds.

Sieve #	Diameter (mm)	Weight of Retained Soil (gm)	Percentage Retained Weight	Percentage Retained Cumulative	Percentage Passing
25	0.707	0	0.00	0.00	100.00
40	0.42	0.23	0.23	0.23	99.77
50	0.297	16.0661	16.17	16.40	83.60
60	0.25	15.107	15.20	31.60	68.40
80	0.177	58.8773	59.25	90.85	9.15
100	0.149	7.9943	8.04	98.89	1.11
Pan		1.103	1.11	100.00	0.00

Point of Precipitation

The point of precipitation was determined by adding 0.1M NaOH drop wise in the 0.1M solution of zinc chloride solution. The moment at which insoluble precipitates were formed in the solution, pH was measured which was 6.1, taken as upper limit of pH.

Selection of Ranges for Independent Variables

To perform the experimentation, the ranges of the all four parameters (pH, biosorbent dosage, initial concentration and contact time) were defined [54, 55].The lower range of pH was defined by pHZC and point of precipitation respectively [56]. The range of biosorbent dosage was selected as 0.1 to 1 gram. The lower limit of initial metal ion concentration was defined by maximum permissible limit of Zn and the upper limit was taken as per bisorption property i.e. it is suitable for even very dilute solutions <100mg/l [39]. The time range was chosen after performing preliminary experimentation. The selected ranges were given to the software so that experiments can be designed accordingly. The actual and coded values of all independent variables Table-2**.**

Table-2: Actual and Coded Values for Different Parameters Involved.

Factors	Parameters	Units	Low range	Mid	High range
A	pH	-----	3.5	4.8	6.1
B	Contact Time	Min	0.5	30.25	60
C	Biosorbent Dosage	Gm	0.1	0.55	1
D	Initial Metal ion Conc.	Ppm	5	52.5	100

Experimental

In the present work, design expert software 8.0.6. with Box-Behnken design is used for the design of experiments and to find out optimization of adsorption of Zn ions in aqueous solution as used in previous studies [57, 58]. BBD makes use of $N=2^k+2k+c$ experiments, where k is the number of factors and c is the central point. This study involves four factors and 5 central points. The four independent factors are designated as A (pH), B (biosorbent dosage), C (initial concentration) and D (contact time). Accordingly, a total of 29 experiments were run to find maximum metal uptake. The factors are adjusted at equally spaced intervals between three levels (-1, 0, +1). Different tests were investigated such as lack of fit, sum of squares and model summary statistics which help in choosing the best model for representing relation between independent variables and response.

Mathematical Modeling

After conducting the experimentation, the relation between independent variable and dependent variable was determined by the following equation take from ANOVA.

$$\text{Log}_{10}Y = +0.52-0.038*A+9.862E\text{-}003*B-0.46*C+0.46*D+0.11*A*C+0.24*A*D+0.14*C*D+0.29*C^2-0.35*D^2$$

where,

A= pH
B= Biosorbent dosage
C is the biosorbent dosage
D is the initial zinc ion concentration.
Y= metal uptake which is the process response

After putting experimental results in design expert software using Box–Behnken design were completely analyzed by ANOVA (analysis of variance). 3-D plots and contour plots were obtained due to the effect of two parameters. Other parameters can be changed by default. The graphs in ANOVA help to study effect of factors and their interactions on the response.

Experimental Procedure

To perform experimentation as per design expert software, the solution of required initial metal ion concentration was prepared in distilled water and its pH was maintained by using 0.1M HNO_3 and 0.1M NaOH. The solution of desired pH and metal ion concentration was poured in 100ml flask and weighted amount of biosorbent was added. The prepared sample was shaken using orbital shaker at 150rpm for the desired time. After the process of shaking, the sample was filtered and filtrate was diluted 50 times with distilled water and stored in an air tight container. Each experiment was repeated thrice.

Metal Analysis

After the experimentation was completed, the samples were analyzed in the atomic absorption spectrophotometer to determine final concentration of metal ions. The values obtained from the unit were multiplied by 50 as each sample was diluted before storage and the mean value was computed for each experiment.

The uptake of Zn^{+2} ions was determined using material balance equation i.e.

$$q_e = \frac{(Ci - Cf) * V}{W}$$

where, qe is the uptake in mg/g; Ci and Cf are is the initial and final concentration of Zn in the aqueous solution.

And the percentage of metal ion removed from samples was determined by

$$\text{Removal } \% = \frac{(Ci - Cf) * 100}{Ci}$$

where, V is the volume of solution in liters (0.1 liter) and W is the biosorbent dosage in grams.

Results and Discussions

Characteristic Study of Date Palm Seeds by FTIR Analysis

FTIR is performed to study the functional groups present on the acidic treated date palm seeds before and after the biosorption of the zinc ions as shown in the Fig-2 and Fig-3 respectively. It can be seen in the Fig-2 the strong peaks are at 869cm-1 representing =C-H group, 1007 representing ester, 1241 representing ether, 1636 which is amine group, 2323 which is phosphine, 3288 representing alcohols. By making comparison between the peaks if the two Fig it can be seen that the main functional groups which take part in the process of biosorption are =C-H, phosphine and alcohol groups.

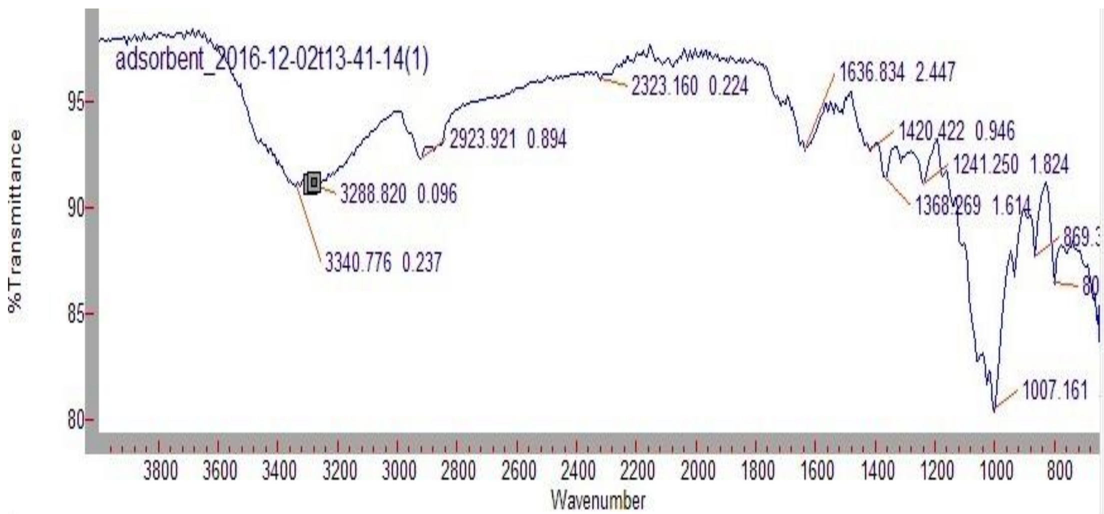

Fig 2: FTIR Analysis of Modified Date Palm Seeds before Biosorption

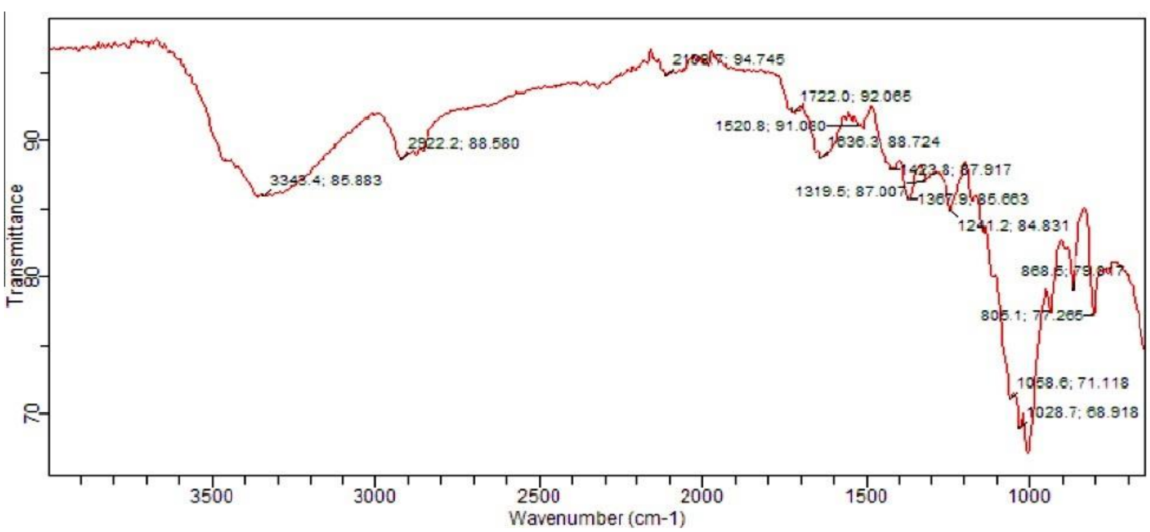

Fig. 3: FTIR Analysis of Modified Date Palm Seeds after Biosorption.

Results of Box-Bheneken Design Experiments

The experiments designed by the design expert were performed and results obtained were entered in the software to evaluate the response surface Table-3.

Table-3: Results of Box-Bheneken Design Experiments.

Run	A pH	B Contact time (min)	C Biosorbent dosage (g)	D Initial metal ion concentration (ppm)	Response (Metal uptake) mg/g
1	4.8	0.5	0.55	5	0.886
2	4.8	30.25	0.55	52.5	4.072
3	4.8	60	1	52.5	2.361
4	3.5	30.25	0.55	100	4.740
5	6.1	30.25	0.1	52.5	20.116
6	4.8	0.5	0.1	52.5	14.11
7	6.1	30.25	1	52.5	2.2678
8	4.8	30.25	0.1	5	4.945
9	3.5	30.25	1	52.5	1.104
10	4.8	30.25	0.55	52.5	3.27
11	4.8	30.25	0.55	52.5	2.957
12	3.5	0.5	0.55	52.5	3.960
13	6.1	60	0.55	52.5	5.725
14	6.1	30.25	0.55	5	0.138
15	4.8	0.5	0.55	100	2.819
16	4.8	30.25	0.1	100	14.062
17	3.5	30.25	0.55	5	0.7684
18	4.8	60	0.55	5	0.347
19	3.5	30.25	0.1	52.5	27.765
20	6.1	30.25	0.55	100	7.427
21	4.8	60	0.55	100	4.098
22	6.1	0.5	0.55	52.5	1.946
23	4.8	30.25	1	5	0.402
24	4.8	30.25	1	100	4.212
25	4.8	30.25	0.55	52.5	3.378
26	4.8	60	0.1	52.5	14.083
27	4.8	0.5	1	52.5	2.584
28	3.5	60	0.55	52.5	3.405
29	4.8	30.25	0.55	52.5	3.726

Statistical Analysis

ANOVA: Analysis of Variance

ANOVA for Response Surface Quadratic Model

The accuracy of the model can also be verified by correlation coefficient (R^2), adjusted R^2 and predicted R^2 [59] as shown in the Table-4. Value of R^2 close to 1 indicates that the experimental data points estimated by the model perfectly match the actual data points [60, 61]. The quadratic model used here gives value of R^2 value is 0.9235, predicted R^2 is 0.7534 and adjusted R^2 value is 0.8872. It means that at least 0.08 % of the experimental results cannot be explained by the proposed model. The difference in predicted R^2 and adjusted R^2 is 0.133 which indicates the value of R^2 is in close agreement with predicted R^2. The table shows the value of Adeq precision to be 19.553. Adequate precision i.e. signal to noise ratio >4 is desirable [61]. The present value supports the fitness of the model because it is well above the desired value.

The lack of fit for the quadratic model has a p-value equal to 0.004 due to which it is found to be significant which shows that linear regression model does not fit the data adequately [62]. Table-5 shows the model selected for the zinc removal by date palm seeds. It can be clearly seen that that the quadratic model is selected because it fits the experimental data well.

Table-4: ANOVA for Response Surface Quadratic Model.

Std. Dev.	0.18	R^2	0.9235
Mean	0.49	Adj. R^2	0.8872
C.V. %	35.55	Predicted R^2	0.7534
PRESS	1.89	Adeq. Precision	19.553

Diagnostic plots

Actual VS Predicted Graph

Fig. 4 shows the plot of the actual VS predicted value. It is observed that data points are distributed close to the straight line which indicates that quadratic model can be considered to be a significant model for predicting response of the independent variables.

Table-5: Selection of adequate model for Zn removal.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	< 0.0001	0.0004	0.6080	0.4749	
2FI	0.6318	0.0003	0.5796	0.1091	
Quadratic	0.0001	0.0036	0.8888	0.6834	Suggested
Cubic	0.0085	0.0389	0.9793	0.4854	Aliased

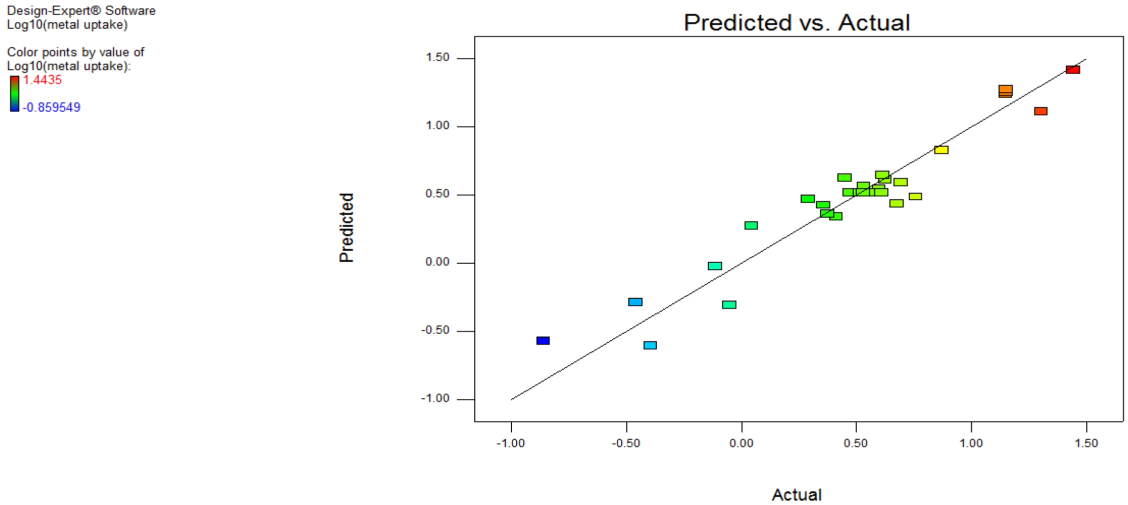

Fig. 4: Actual VS Predicted Graph.

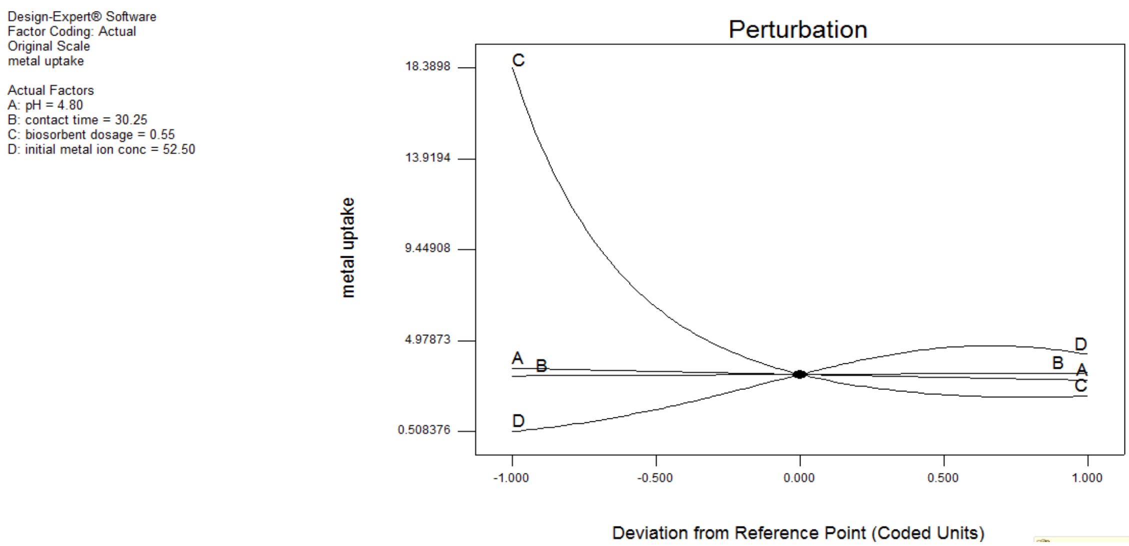

Fig. 5: Perturbation Plot.

Perturbation Plot

Fig. 5 shows perturbation curve indicating the influence of different factors on the response. Change in response range with deviation from reference point highlights the influence of response on that factor in the graph. It is observed that out of four factors biosorbent dosage and initial metal ion concentration are more sensitive towards response. When these factors are disturbed, the response is changed notably. The graph shows that metal uptake is high at low biosorbent dosage and high initial metal ion concentration.

2-D Contour Plots

Fig. 6 shows 2-D contour plots. The effect of factors C (biosorbent dosage) VS D (initial zinc ion concentration) is indicated by gradual color changes from blue to green. Blue and green colors indicates low and high uptake respectively. It is shown in the plot that metal uptake increases by decreasing biosorbent dosage as the amount of zinc ions adsorbed per unit weight of biosorbent is high and increasing initial metal ion concentration.

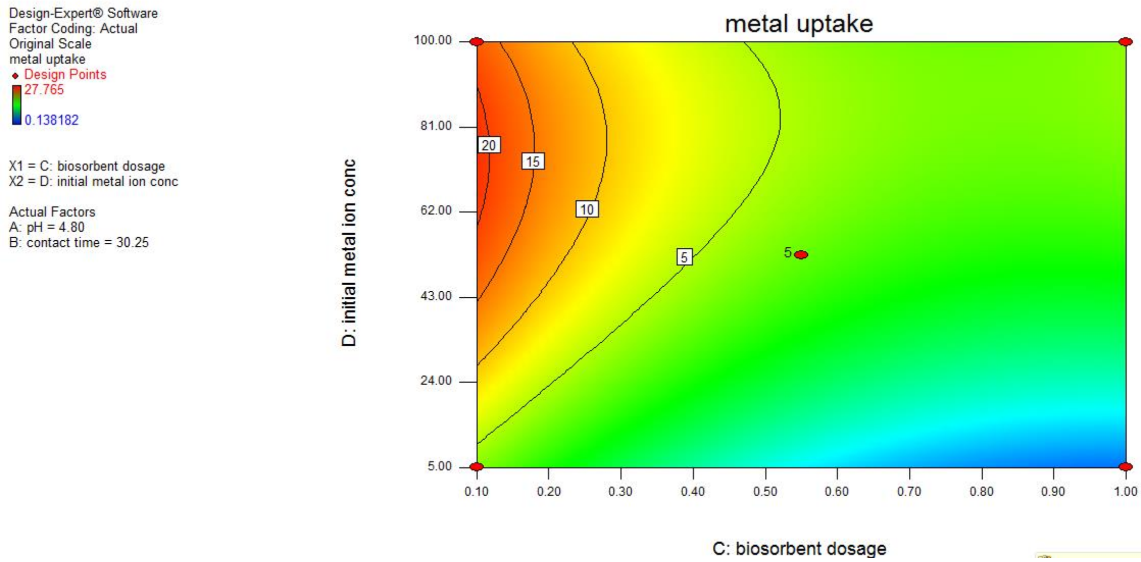

Fig. 6: 2-D Contour Plots between Biosorbent Dosage and Initial Zinc Ion Concentration.

3D surface plots

Effect of pH and biosorbent dosage on the uptake of zinc ions by date palm seeds

The effect of pH and biosorbent dosage is shown in the Fig. 7. In this study, experimentation was done in acidic medium because of the limits defined by point of zero charge and point of precipitation. The Fig shows that maximum metal uptake was 27.765mg/g for date palm seeds at low pH 3.5. This is due to the fact that the biomass contains large amount of polysaccharides (cellulose, hemicellulose, lignin etc.) whose surface is enriched with a number of functional groups like amine, alcohol, phenol and phosphate groups). The process of biosorption mainly depends upon protonation and deprotonating of the functional groups. The ions present in the solution and charges on surface are dependent upon pH of the solution. The amines, phosphates and related functional groups favor protonation at low pH which helps metal ions binding as anionic species [63]. Greater metal uptake at low pH is also observed in several studies. Kumar et al removed fluoride from aqueous solution using several raw materials and observed higher bio sorption at low pH on commercially available activated carbon, sawdust raw and activated bagasse carbon [63]. Esmaeili et al observed the similar trend in his study on the removal of heavy metals using chitosan nanoparticles [55]. Misbah et al used Mangifera indica for the bio sorption of chromium ions from aqueous solution and observed similar trend for pH [64].

Fig. 7 also shows the effect of bisorbent dosage on metal uptake. Metal ion uptake is maximum at low value of bisorbent dosage i.e. 0.1 gm. The reason of high metal uptake at low biosorbent dosage is that for a fixed metal ion concentration at low dosage, the amount of zinc ions adsorbed per unit weight of biosorbent is high. The metal uptake lessens when the dosage in increased because of low adsorbent to binding site ratio, where ions are adsorbed onto greater surface area with more binding sites. Similar results are reported in several studies where metal uptake is decreased when biosorbent dosage is increased [55-66].

Effect of biosorbent dosage and initial concentration of zinc on the uptake of zinc ions by date palm seeds

The combined effect of biosorbent dosage and initial zinc ion concentration has been shown in the 3D graph Fig-8**.** The results indicate that the metal uptake increase with the increase in zinc ion concentration and decrease in biosorbent dosage. The metal uptake is maximum at high initial zinc ion concentration because it acts as a driving force to overcome the resistance of mass transfer between biosorbent and biosorbent medium.

Effect of contact time and biosorbent dosage on the uptake of zinc ions by date palm seeds

The combined effect of contact time and biosorbent dosage has been shown in the 3D graph Fig. 9. The results indicate that the metal uptake increases with the decrease in biosorbent dosage but contact time has negligible effect on metal uptake so it is not a significant parameter for the removal of zinc ions by date palm seeds.

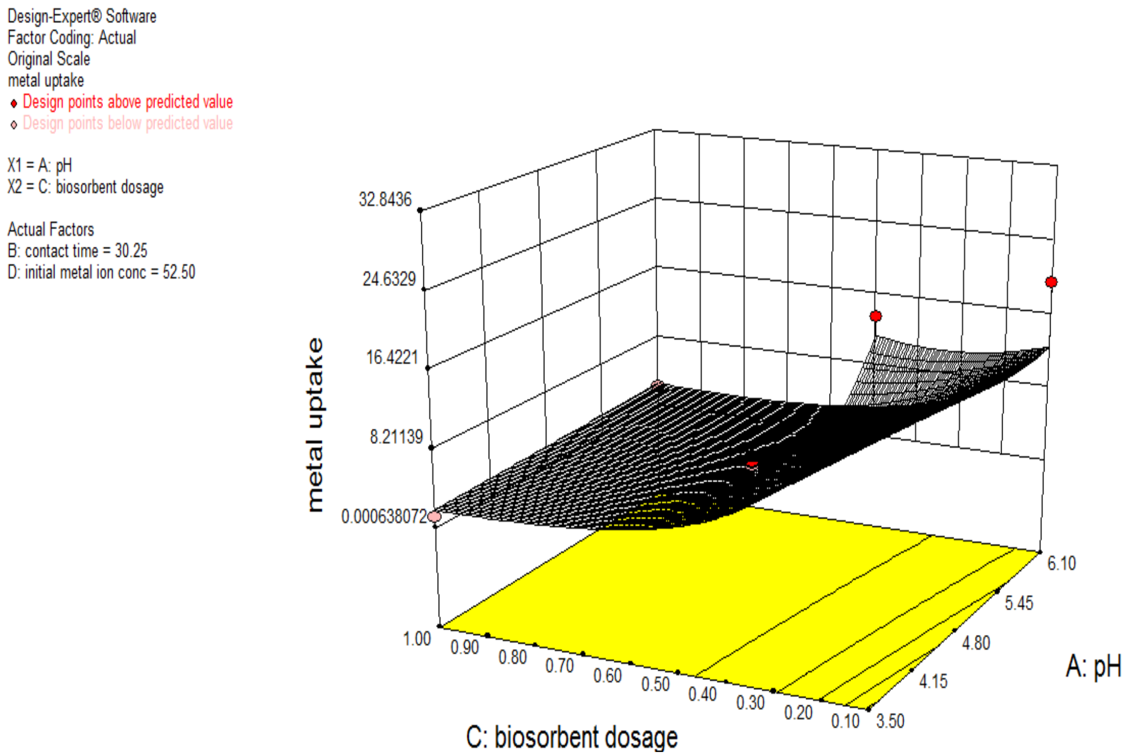

Fig. 7: 3D Surface Plots between pH and Bisorbent Dosage.

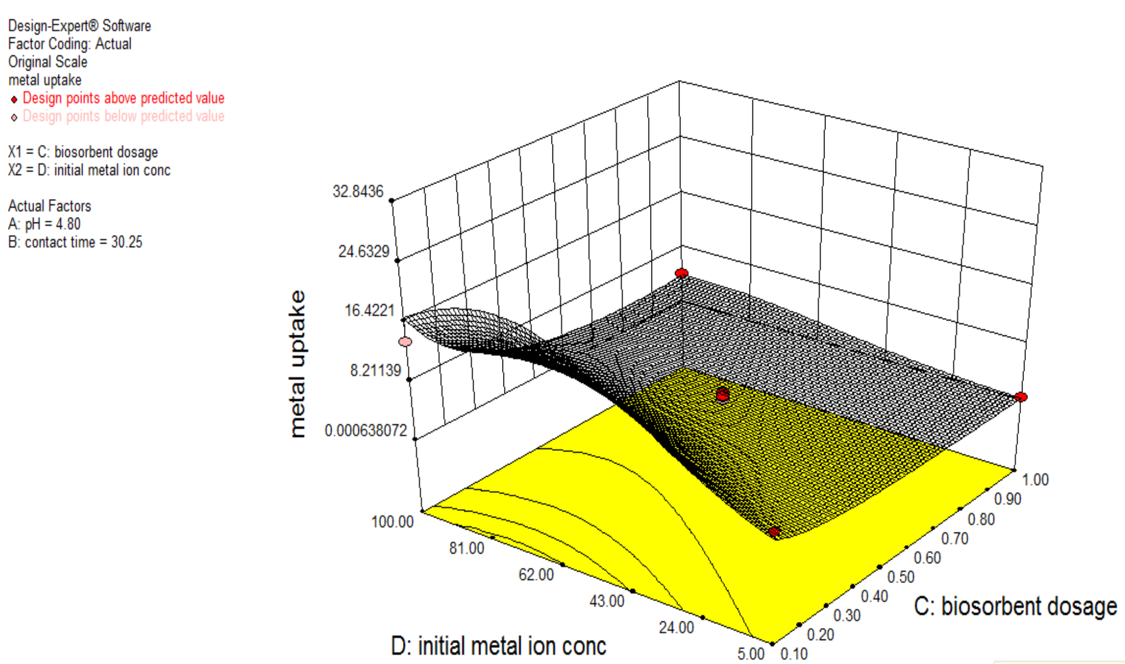

Fig. 8: 3D Surface Plots between Biosorbent Dosage and Initial Concentration of Zinc.

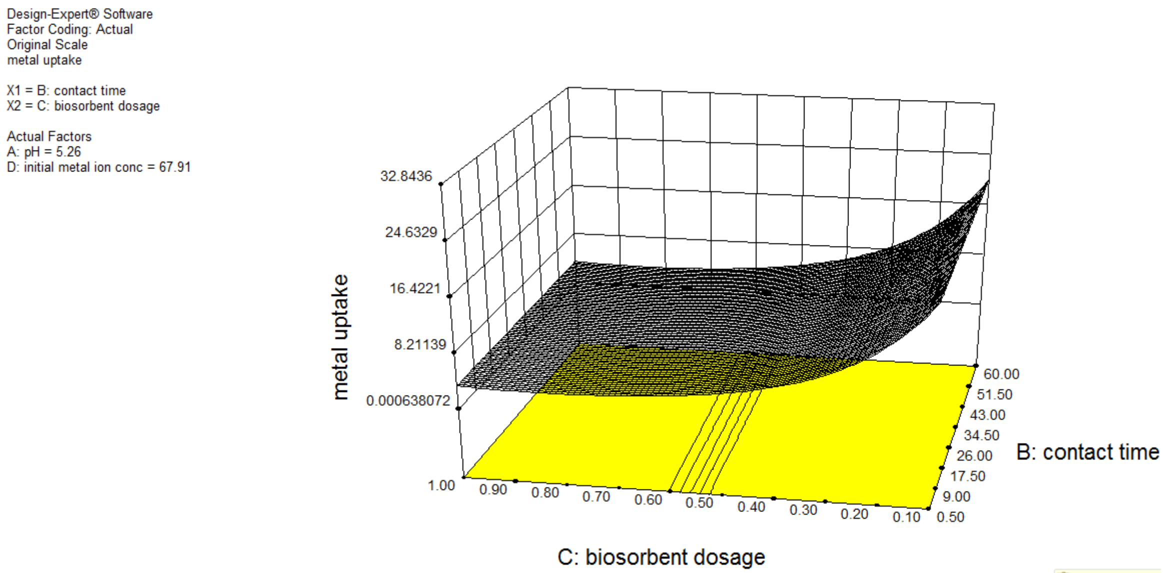

Fig. 9: 3D Surface Plots between Biosorbent Dosage and Contact Time.

Table-6: Numerical Optimization Table.

			Constraints			
Description	**Goal**	**Lower limit**	**Upper limit**	**Lower weight**	**Upper weight**	**Importance**
pH	**Range**	**3.5**	**6.1**	**1**	**1**	**3**
Contact time	**Range**	**0.5**	**60**	**1**	**1**	**3**
Biosorbent dosage	**Range**	**0.1**	**1**	**1**	**1**	**3**
Initial metal conc.	**Range**	**5**	**100**	**1**	**1**	**3**
Metal uptake	**Max**	**0.138182**	**27.765**	**1**	**1**	**3**

Table-7: Solutions of the Numerical Optimization Table.

pH	**Contact time (min)**	**Biosorbent dosage (gram)**	**Initial metal ion conc. (ppm)**	**Metal uptake (mg/g)**
3.52	**60**	**0.1**	**59.11**	**26.84**

Optimization of the Process Parameters

Optimization of the process variables was carried out by using numerical optimization in design expert software. Various ranges were taken for each parameter as presented in Table-6. The readings attained from statistical software are also listed in Table-7. Table-9 shows that optimum value of the uptake is obtained at pH=3.52, contact time=60, biosorbent dosage=0.1, and initial metal ion concentration=59.11. And the optimum value of the metal uptake obtained is 26.84mg/g.

Conclusions

The batch experimental study was performed for the adsorption of zinc ions from aqueous solution. The purpose of the current study was to determine the optimum conditions for the Zn^{+2} ions remediation by date palm seeds using response surface methodology. The use of BBD in RSM significantly decreased the number of experiments. The correlation coefficient (R2=0.923) indicated that the experimental values perfectly fitted the values predicted by the quadratic model. By Analysis of Variance (ANOVA) was utilized to analyze the individual, overall and interactive influences of factors in biosorption phenomena. Various plots indicated the model fitting and trends of factors effecting the biosorption of Zn^{+2} ions. The plots present in the ANOVA showed that the metal uptake increased with the increase in initial zinc concentration and pH and with the decrease in bisorbent dosage while the contact time had negligible effect on the response surface. The optimum conditions of the input parameters obtained were pH = 3.52, initial zinc ion concentration = 59.11ppm, biosorbent dosage = 0.1g and contact time = 60 min with a metal uptake of 26.84mg/g. Therefore, (Phoenix Dactylifera L.) seeds substantially removed zinc ions under optimum conditions.

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