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Optimization of copper removal by acid-treated date palm seed using response surface methodology (RSM)

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ABSTRACT

With increasing industrialization, the problem of water pollution is also getting worse day by day. Several techniques are adopted to remove different polluting elements from water to get clean potable water. Among these techniques, biosorption is relatively a new technique in which mostly agricultural wastes are used as an agent to remove different kinds of polluting elements present in water. In this research paper, we are going to use acid-treated date palm seeds as a biosorbent to remove copper from aqueous solutions. We shall also use the technique of response surface methodology to determine simultaneous effect of four parameters: pH of the solution, initial metal concentration of the solution, biosorbent dose added to solution, and time of contact between solution and biosorbent. A R^2 value of 0.9691 was obtained, and optimum conditions for copper removal were found to be pH 6.08, initial metal concentration of 99.92 ppm, biosorbent dose of 0.12 g, and shaking time of 10.05 min to get an uptake of 61.8 mg/g. The results showed that acid-treated date palm seeds can be efficiently used for removing copper from water.

Keywords: Biosorption; Response surface methodology; Box–Behnken; ANOVA.

1. Introduction

As the population of world is increasing, it is becoming a trial to ensure that people will continue to have access to potable water in near future. It is expected that getting clean water for human beings, animals, and plants will be very much tough and burdensome task in future [1]. To get good quality of water specifically in developed cities, there must be some refinements and renovations applied on wastewater treatment procedures. Certain laws are allocated in different areas of the world related to restricting level of heavy metals in water that can be discharged into surroundings [2,3].

Many pollutants are released from industries which are polluting our environment. Different industries including fertilizers, pesticides, batteries, and pharmaceutical industries release materials resulting in environmental pollution. The pollutants emitted from various sources do not only cause pollution of surface water sources but also affect underground water resources. Some of these pollutants become a part of our food via agricultural products, aquatic food, etc., and in this way cause serious and lethal health issues affecting both human and aquatic life [4].

Pollutants present in industrial wastewater include dyes, heavy metals, etc. Several heavy metals have been found in wastewater discharged from industries including mercury

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(Hg), lead (Pb), arsenic (As), copper (Cu), etc. All the heavy metals present in the outflow of chemical industries are notably known as poisonous, noxious, and injurious to health and environment [5,6].

In our research, we have considered heavy metals pollution in water. Heavy metals are too much toxic and non-biodegradable. When these heavy metals are transported to water, they can be accumulated in aquatic organisms and ultimately human life is badly affected by these discharges. Heavy metals that are present in drinking water are injurious to human health. There are a few heavy metals that can accumulate in the human body and may cause cancer. Heavy metals occurrence in drinking water is very alarming because of their effects on plants, animals, and human life [7].

The ways that can be used for toxic metals elimination from water include chemical precipitation, ion exchange, physical separation, membrane distillation, etc., but some of these methods are too much costly and it is unfeasible and inappropriate to use these techniques in developing countries [8]. Another disadvantage of these methods is that as a result of these processes, lethal sludge is generated, and the methods adopted to discard and dump this sludge in a proper way also impose a negative impact on economics of the overall process. Therefore, it is essential to select a method, which is clean, environmentally benign, and economical as well, for removing these toxic metals from water [9].

Biosorption is a process in which dead microorganisms are used to remove pollutants, such as heavy metals. It is based on metal binding capacities of various biological materials. The biosorbent which we are going to use in our research is date palm seed, and its activity is increased by treating with nitric acid [10].

To determine in what manner different parameters are going to affect the adsorption capacity of biosorbent, there must be a proper design of experiments involving those parameters in specified ranges. Basically, response surface methodology (RSM) is an appropriate practice for studying interaction of different parameters among each other. The conventional approach which is generally used, involves 'one-variable-at-a-time'. As compared with it, RSM is more useful and practically feasible because it involves simultaneous effects of different parameters and in this way, it can be used to determine overall effects of all the variables on final response of the process. In recent past, RSM has been used for optimization of independent parameters in wastewater treatment processes. So, the purpose of our research work is to check and analyze the effect of different restricting parameters on adsorption of copper on acid-treated date palm seed. In our case, these parameters are pH, time, initial metal concentration, and biosorbent used, and we are going to check the effect of them on metal uptake [11].

Previously copper biosorption has been studied by using different biosorbents such as orange peels, olive stones, bark of pines, pine cone shell, etc. [12–14]. In selection of biosorbent material, the first criterion is that it should be low priced. Mostly they are derived from waste materials from agriculture or industries. So, we have selected date palm seeds as biosorbent material for removal of copper. It is found in almost all regions of the world. Therefore, we can say that it can be used as an economic biosorbent. Another advantage in using date palm seeds as biosorbent is that the problem of disposing the date palm seeds by the date industries is also solved [15].

The major functional groups present in date palm seeds are cellulose, hemicellulose, and lignin. Furthermore, some amount of oil, carbohydrate, calcium, magnesium, potassium, and protein is also found. The percentage distribution of components is almost 42% cellulose, 30% hemicellulose, and 28% lignin [16].

2. Materials and methodology

2.1. Biosorbent preparation

Date palm seeds were obtained from juice shops. They were thoroughly washed with distilled water and then dried. They were crushed by grinder up to particle size of 150 microns, and this crushed material was dipped in 0.1 M of nitric acid solution for 1 d. After this, it was filtered and thoroughly washed with distilled water and then dried for 24 h under shade. And then it was stored in a jar for performing the experiments [17].

2.2. Use of design expert

First of all, the ranges of parameters were decided. The lower range of pH was decided by point of zero charge, and the upper range of pH was determined by performing preliminary experiment and checking the point of precipitation using a copper salt, that is, copper sulfate. The range of time was taken from 30 s to 60 min. The range of biosorbent per 100 mL of the solution was taken as 0.1–1 g. Finally, metal initial amount in solution was decided as 5–100 ppm. All these ranges were entered in the software named Design Expert after selecting RSM and Box–Behnken Design (Table 1). Then several experiments were designed in the software in the given range of parameters [18].

2.3. Preparation of solution

For performing these experiments, 100 mL flasks were taken and the solution of required initial concentration was prepared in distilled water. The exactly measured

Table 1
Experimental range and level of independent variables [19]

Factor ranges and levels (coded)	A (pH)	B (time [min])	C (biosorbent dose [g])	D (initial metal concentration [ppm])
–1	3.6	0.5	0.1	5
0	4.90	30.25	0.55	52.5
+1	6.2	60	1	100

stoichiometric amount of salt was added into 100 mL of water according to the experiments designed by the RSM.

2.4. Batch experimentation

In order to perform the experiments, required concentration of copper solution was prepared at first. For maintaining the pH, we had prepared 0.1 M of HNO3 and 0.1 M of NaOH solutions. By using these two solutions, required pH of solution was maintained, and then required amount of biosorbent was added to this solution after measuring on weight balance. Then this flask was put on orbital shaker and was shaken for required time on 100 rpm. After completion of shaking, this solution was immediately filtered and the filtrate was 50 times diluted with distilled water. Each experiment was done thrice as per designed by the software.

2.5. Analysis of solutions

After dilution, this diluted solution was taken to the atomic absorption spectrophotometer, and the final concentration of the solution was checked. As we had diluted the filtrate 50 times, the result from the atomic absorption spectrophotometer was multiplied with 50. The average of triplets' result was taken as the final concentration of copper in the solution after biosorption. Then uptake of the metal was calculated by following formula [20].

$$Q = \frac{V\left(C_i - C_f\right)}{S} \tag{1}$$

where Q = copper ion uptake in mg/g bio mass, V = volume of solution in liters (0.1 L), C_i = the initial amount of copper metal in solution in ppm, C_f = residual amount of copper in the solution in ppm, and S = amount of added bio sorbent on dry basis in g (Table 2).

2.6. Fourier transformation infrared spectroscopy

Fourier transformation infrared (FTIR) spectroscopy is useful for recognition of chemical composition of the sample because functional groups present in a sample absorb

Table 2
List of experiments performed and their results

No. of experiment	pH	Time (min)	Biosorbent dose (g)	Initial metal concentration (ppm)	Metal uptake (mg/g)
1	6.20	0.50	0.55	52.50	7.69697
2	3.60	60.00	0.55	52.50	2.86667
3	6.20	30.25	1.00	52.50	2.417
4	4.90	0.50	0.55	100.00	2.37
5	4.90	0.50	1.00	52.50	3.32833
6	4.90	60.00	0.55	5.00	0.0121212
7	3.60	30.25	0.55	5.00	0.106061
8	3.60	30.25	1.00	52.50	2.485
9	3.60	30.25	0.10	52.50	10.4
10	4.90	30.25	0.55	52.50	3.9
11	4.90	30.25	0.55	52.50	3.8
12	6.20	30.25	0.55	100.00	15.7578
13	4.90	30.25	0.10	100.00	35.9333
14	4.90	30.25	0.55	52.50	4.1
15	3.60	0.50	0.55	52.50	0.5727
16	3.60	30.25	0.55	100.00	2.7364
17	6.20	30.25	0.55	5.00	0.3727
18	6.20	30.25	0.10	52.50	47.4
19	4.90	0.50	0.10	52.50	26.2333
20	4.90	0.50	0.55	5.00	0.166
21	4.90	60.00	0.55	100.00	4.02
22	4.90	60.00	0.10	52.50	19.85
23	4.90	30.25	0.55	52.50	3.83
24	4.90	30.25	0.10	5.00	1.8
25	6.20	60.00	0.55	52.50	7.81
26	4.90	30.25	0.55	52.50	4.05
27	4.90	30.25	1.00	100.00	1.74167
28	4.90	30.25	1.00	5.00	0.105
29	4.90	60.00	1.00	52.50	0.56833

radiations having unique frequencies. Samples composition can be determined by comparing it with some reference, that is, some similar materials' spectra [21].

The FTIR analysis of biosorbent before and after adsorption is given in Figs. 1 and 2.

The comparison of both figures shows that differences in peaks are at 804.11, 2,323.16, and 3,288.82 cm^{-1}. So, we can conclude that main groups involved in adsorption are alkene bending, phosphine group, and alcohol group.

3. Results and discussion

3.1. Box–Cox transformation

In statistical analysis, some transformations may be applied to improve the distribution of data points. Design Expert software has an option of Box–Cox transformation in which some power transformation is recommended after entering actual response values. This transformation suggests a suitable exponent which is called lambda which represents the power to which all actual response values are raised. The recommended transformation is square root transformation in our case.

3.2. Analysis of variance

Analysis of variance (ANOVA) is observed to check whether model is significant or not [22]. If the p values are less than 0.005, it shows that that term is significant. Table 3 shows response surface quadratic model.

R^2 value was obtained 0.9691 after performing ANOVA. This shows that our model can be used to correlate independent variables and response that is uptake. Value of adjusted R^2 is 0.9382, and it shows that this model cannot clarify variation less than 7%.

Signal-to-noise ratio is determined by precision, and its ratio must come larger than 4. Our ratio of 23.148 designates an acceptable signal. Therefore, design space can be steered by this model.

Fianl equation in terms of coded factors is as follows:

$$\begin{aligned}\text{Sqrt}\left(\text{Metal uptake}\right) =\; & +1.98+0.78\text{A}-0.051\text{B}-1.64\text{C}+1.11\text{D} \\ & -0.23\text{AB}-0.92\text{AC}+0.51\text{AD}-0.10\text{BC} \\ & +0.19\text{BD}-0.91\text{CD}+0.28\text{A2}-0.17\text{B2} \\ & +1.10\text{C2}-0.75\text{D2}\end{aligned} \tag{2}$$

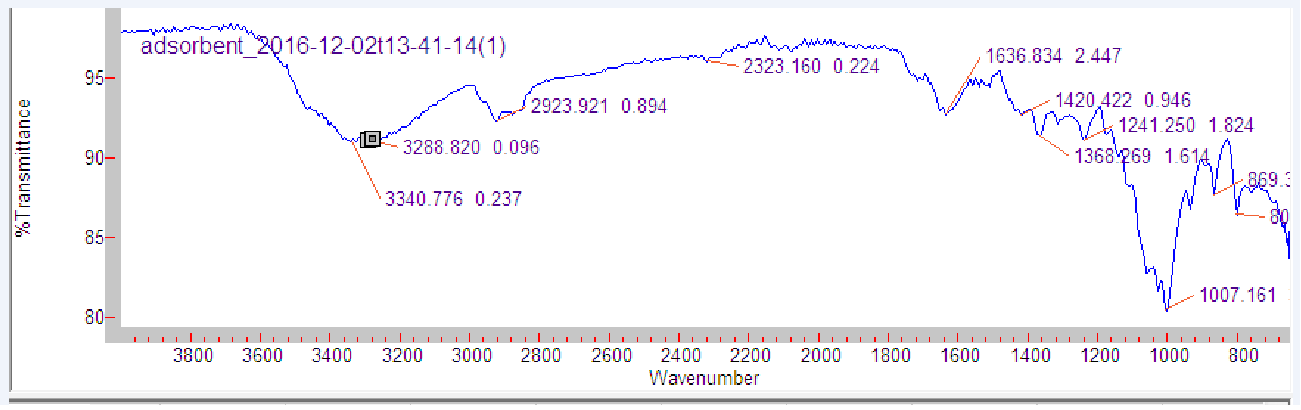

Fig. 1. FTIR analysis of biosorbent before biosorption.

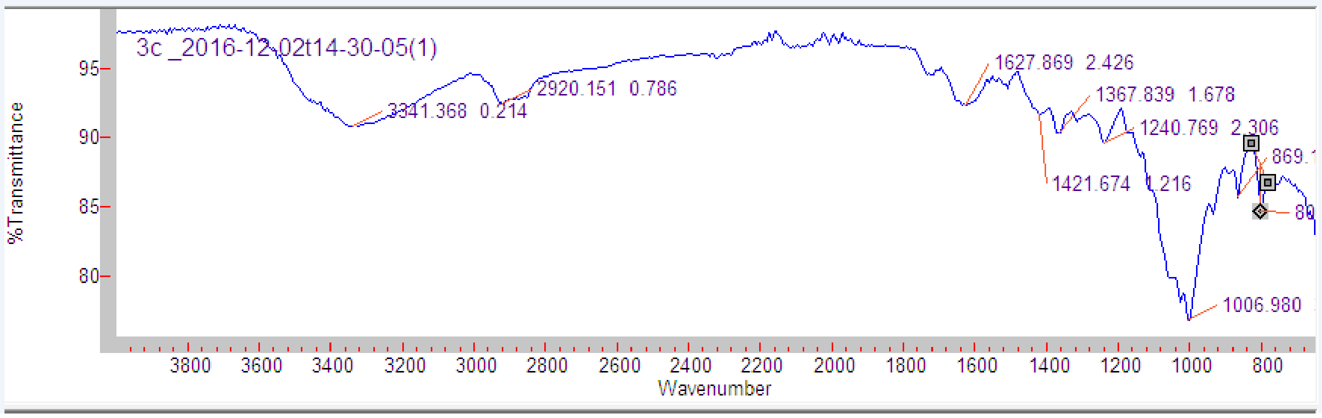

Fig. 2. FTIR analysis of biosorbent after biosorption.

Table 3
Response surface reduced quadratic model

Source	Sum of squares	df	Mean square	*F* value	*p* value (probability > *F*)
Model	77.38	14	5.53	31.36	<0.0001
A (pH)	7.30	1	7.30	41.40	<0.0001
B (time)	0.031	1	0.031	0.18	0.6802
C (biosorbent dose)	32.24	1	32.24	182.93	<0.0001
D (initial concentration)	14.88	1	14.88	84.43	<0.0001
AB	0.21	1	0.21	1.19	0.2937
AC	3.39	1	3.39	19.23	0.0006
AD	1.03	1	1.03	5.85	0.0298
BC	0.041	1	0.041	0.23	0.6379
BD	0.15	1	0.15	0.83	0.3790
CD	3.34	1	3.34	18.97	0.0007
A^2	0.50	1	0.50	2.81	0.1156
B^2	0.19	1	0.19	1.08	0.3162
C^2	7.79	1	7.79	44.22	<0.0001
D^2	3.66	1	3.66	20.74	0.0005
Residual	2.47	14	0.18		
Lack of fit	2.46	10	0.25	219.48	<0.0001
Pure error	4.489E – 003	4	1.122E – 003		
Corrected total	79.85	28			

Final equation in form of actual parameters is as follows:

$$
\begin{aligned}
\text{Sqrt}\,(\text{metal uptake}) = {} & +0.19204 - 0.39102(\text{pH}) + 0.036078(\text{time}) \\
& +0.58635(\text{biosorbent dose}) \\
& +0.037538(\text{initial conc.}) - 5.92151\text{E-}003(\text{pH})(\text{time}) \\
& -1.5733(\text{pH})(\text{biosorbent dose}) + 8.22098\text{E-}003(\text{pH})(\text{initial conc.}) \\
& -7.54403\text{E-}003(\text{time})(\text{biosorbent dose}) \\
& +1.34958\text{E-}004(\text{time})(\text{initial conc.}) \\
& -0.042773(\text{biosorbent dose})(\text{initial conc.}) + 0.16364(\text{pH})2 \\
& -1.93605\text{E-}004(\text{time})2 + 5.41289(\text{biosorbent dose})2 \\
& -3.32704\text{E-}004(\text{initial conc.})
\end{aligned}
\tag{3}
$$

Fig. 3 represents the relation between actual and predicted values of response. Ideally, this graph should be a straight line showing actual values are equal to values predicted by model equation.

3.3. 3D graphs

Fig. 4 represents initial metal concentration and pH effects on uptake of metal. It can be concluded from the figure that both these variables have a reasonable effect on uptake of metal. With the increasing pH, the uptake of the metal also increases. It can be explained as available sites present on biosorbent increase by increasing solution pH. At lower pH, there is a competition between protons and metal ions to occupy available spots. At higher pH, more vacant sites are available for metal ions as compared with sites available for protons. Thus, the metal binding capacity increases. Similarly, when

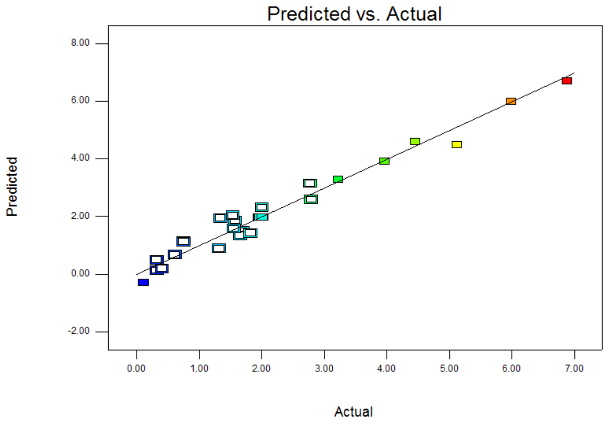

Fig. 3. Relation between actual and predicted values.

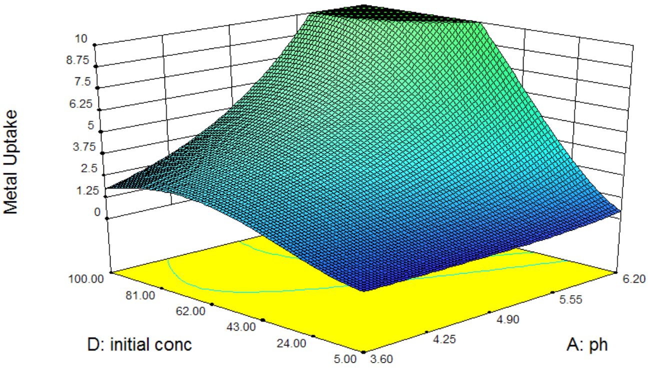

Fig. 4. Effect of initial concentration and pH on metal uptake.

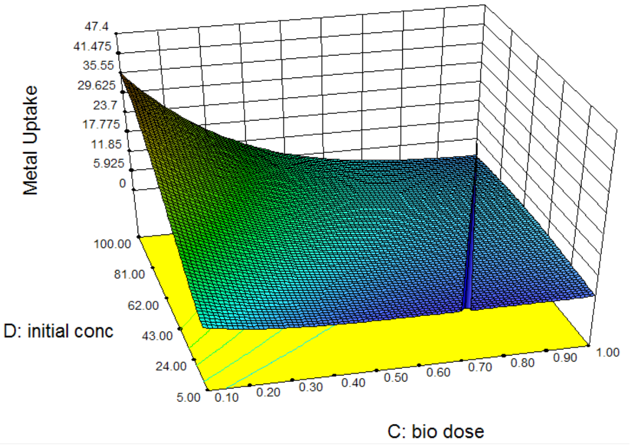

Fig. 5. Effect of biosorbent dose and initial concentration on metal uptake.

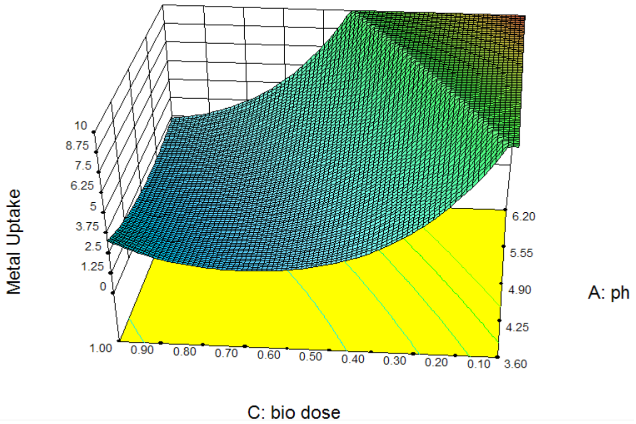

Fig. 6. Effect of biosorbent dose and solution pH.

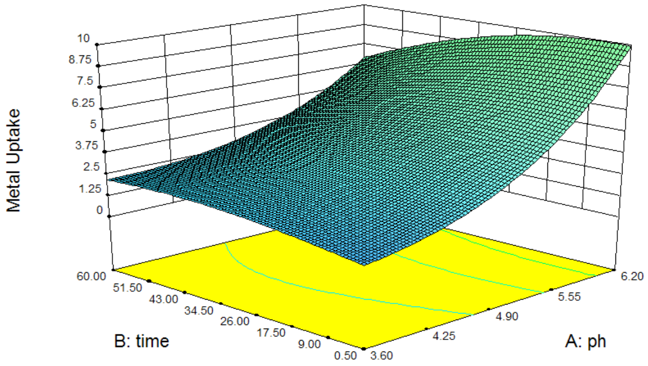

Fig. 7. Effect of time and solution pH on metal uptake.

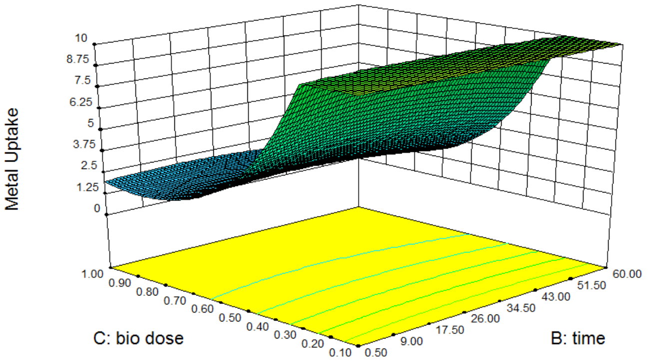

Fig. 8. Effect of time and biosorbent dose on metal uptake.

initial metal concentration of solution is higher, that is, close to 100 ppm, the biosorption efficiency is higher. It means that a higher concentration is reduced to a relatively lower concentration more efficiently as compared with already lower concentrations to be reduced to very low concentrations. The reason behind this may be that at higher initial concentrations mass transfer rate of metal ions toward biosorbents sites is higher. Because of which the efficiency of biosorbent to bind metal ions on its active sites is increased [23].

Fig. 5 represents acceptance of copper due to initial metal concentration and biosorbent dose. Biosorbent dose has most prominent effect on the uptake of metal. The increased biosorbent dosage results in decreased metal uptake. The reason behind it is that when we add a small amount of biosorbent, there are a smaller number of active sites available so that most of those active sites are occupied by metal ions. When a larger amount of biosorbent is added, there are larger number of active sites available. So, the competition among active sites is comparatively low resulting in lower uptake [23].

Fig. 6 illustrates simultaneous effect of biosorbent dose and solution pH added to solution on the uptake of copper.

Fig. 7 represents effect of time and solution pH on metal uptake. Contact time between the solution and biosorbent is a variable that affects the uptake of the copper slightly. The uptake of metal slightly increases with time initially and then it decreases. So, we may predict that after some time desorption of metal gets started [23].

Fig. 8 represents the effect of time and biosorbent dose on metal uptake. And among four factors under consideration, biosorbent dose has a maximum effect and time has a minimum effect on metal uptake.

3.4. Optimum conditions for uptake

Now by using the optimization option in software, we tried to maximize the uptake in the given ranges of four independent variables. It was shown in the results that at 6.08 pH, initial concentration of 99.92 ppm, bisorbent dose of 0.12 g, and shaking time of 10.05 min, we can get maximum uptake of copper.

4. Conclusion

Objective of this work is to enhance copper removal efficiency by using date palm seeds. Date palm seeds can also be used for removal of other toxic metals by the process of biosorption. The efficiency of acid-treated date palm seed to remove copper from water was studied using RSM. Parameters such as metal ions concentration, pH, metal uptake, amount of biosorbent, and time were optimized with a minimum number of experiments. The results showed that the best operating condition to get maximum copper uptake of 61.8 mg/g is at pH of 6.08, initial metal concentration of

99.92 ppm, biosorbent dose of 0.12 g, and shaking time of 10.05 min. The obtained results showed that date palm seeds are useful for eliminating copper metal from solution when treated with nitric acid.

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