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Response surface modeling and optimization of Cu (II) removal from waste water using custard apple peel powder

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ABSTRACT

The potential use of custard apple peel powder for the removal of Cu (II) from waste water has been investigated in batch mode experiments. Influences of parameters like initial Cu (II) concentration (20-60 mg/l), pH (5-7), and biomass dosage (25-35 g/l) on Cu (II) adsorption were examined using response surface methodology. The Box-Behnken experimental design in response surface methodology was used for designing the experiments as well as for full response surface estimation and 15 trials as per the model were run. The optimum conditions for maximum removal of Cu (II) from an aqueous solution of 20 mg/l were as follows: adsorbent dosage (28.139 g/l), pH (6.40213) and initial Cu (II) concentration (17.6572 mg/l). The high correlation coefficient (R^2 =0.991) between the model and the experimental data showed that the model was able to predict the removal of Cu (II) from waste water using Custard apple peel powder efficiently.

Introduction

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment [1]. Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals [2, 3]. Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity [4, 5]. Among these heavy metals, copper is considered as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and painting bath etc. The excessive intake of copper may cause renal and hepatic damage, severe mucosal, irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver. World health organization (WHO) has recommended that maximum acceptable limit for Cu (II) concentration in drinking water should be 1.5 mg/l [6]. Consequently, it is essential that the potable water should be given some treatment before domestic supply.

Several methods are used to remove copper from the industrial wastewater. These include reduction followed by chemical precipitation [7], ion exchange [8], reduction [9], electrochemical precipitation [10], solvent extraction [11], membrane separation [12], evaporation [13] and foam separation [14]. Above cited conventional heavy metal elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption.

In this work, it has been reported the results obtained through the batch experimentations on removal of Cu (II) from waste water by Custard apple peel powder. The influence of several operating parameters, such as initial Cu (II) concentration, pH, and adsorbent dosage were investigated in batch mode. The conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved [15]. The conventional technique for the optimization of a multivariable system usually defines one-factor at a time. Such a technique needs to perform a lot of experiments and could not reveal the alternative effects between components. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable. Recently many statistical experimental design methods have been employed in chemical process optimization. Experimental design technique is a very useful tool for this purpose as it provides statistical models, which helps in understanding the interactions among parameters that have been optimized [15]. These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one suitable method utilized in many fields. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [16]. Table 1 gives the applications of Box-

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Behnken design for the removal of heavy metals by different biosorbents in separation technology.

In the present investigation, batch experimental studies [26] were carried out for the removal of Cu (II) from waste water using Custard apple peel powder. The experimental data points were used to obtain experimental model from Box-Behnken design. The input parameters for the percentage removal of Cu (II) are initial Cu (II) concentration, adsorbent dosage and pH. The process optimization has been carried out using BBD to optimize the input parameters to the process for maximum Cu (II) removal.

Materials and Methods

Chemicals

Copper (II) sulfate, $CuSO_4.5H_2O$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck. Stock solution of Copper (II) sulfate having concentration of about 1000 mg/l was prepared by using double distilled water. Various concentrations of test solution of Cu (II) ranging from 20-100 mg/l were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 6, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

Preparation of the adsorbent

The Custard apple peel was obtained from local market; washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 63 to 125 μm.

Batch mode adsorption studies [26]

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration (20-100 mg/l), adsorbent dosage (0.25-1.75 gm in 50ml solution), agitation time (0 -120min), pH (2-10) and adsorbent size (63μm, 89μm and 125μm). The solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

Metal analysis

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer.

To estimate the percentage removal of copper from aqueous solution, the following equation was used.

$$\text{Removal of Cu (II)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w} \qquad (2)$$

Where q_e (mg/g) is the amount of copper adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium metal ion concentration (mg/l), v is the volume of aqueous solution (ml) and w is the adsorbent weight (g).

Experimental design and procedure

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [16]. A standard RSM design called Box-Behnken Design (BBD) was applied in this work to study the variables for adsorption of copper from aqueous solution using in a batch process. BBD for three variables (initial Cu (II) concentration, pH and biomass dosage), each with two levels (the minimum and maximum), was used as experimental design model. The model has advantage that it permits the use of relatively few combinations of variables for determining the complex response function [27]. A total of 15 experiments are needed to be conducted to determine 10 coefficients of second order polynomial equation [28, 29]. In the experimental design model, initial Cu (II) concentration (20-60 mg/l), pH (5-7) and biomass dosage (25-35 g/l) were taken as input variables. Percentage removal of Cu (II) was taken as the response of the system. Three factors were studied and their low and high levels are given in Table 2. The experimental design matrix derived from BBD is given in Table 3.

Basically this optimization process involves three major steps, which are, performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model.

$$Y = f(X_{1,} X_{2,} X_{3,} X_{4,} .....X_n) \qquad (3)$$

Where Y is the response of the system and X_i is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surfaces.

The optimization of Cu (II) uptake was carried out by three chosen independent process variables using Box-Behnken design with 12 unique runs including 3-replicates at center points. The quadratic equation model for predicting the optimal point was expressed according to Eq (4).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^{\,2} + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta x_i x_j + \varepsilon \qquad (4)$$

Percentage adsorption was studied with a standard RSM design called Box-Behnken Design (BBD). Fifteen experiments were conducted in duplicate according to the scheme mentioned in Table 3. *Matlab* program was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability in dependent variables was explained by the multiple coefficient of determination, R^2 and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range [16].

Results and Discussions

Results of BBD experiments

The results of the each experiments performed as per the software are given in Table 3. Empirical relationships between the response and the independent variables have been expressed by the following quadratic model.

$$Y = 91.6167 - 3.0075X_1 + 9.6213X_2 - 1.4662X_3 - 1.6096X_1^2 - 12.0821X_2^2 - 4.2071X_3^2 - 0.0850X_1X_2 + 1.49X_1X_3 - 0.0025X_2X_3 \quad (5)$$

Where Y is the percentage removal of Cu (II).

Regression coefficient of full polynomial model is given in Table 4. Analysis of variance has been calculated to analyze the accessibility of the model. The analysis of variance for the response has been predicted in Table 5. To evaluate the goodness of the model, the coefficient of variation (the ratio of the standard error of estimate to the mean value expressed as a percentage) and F-value tests has also been performed. The F distribution is a probability distribution used to compare variances by examining their ratio. If they are equal then F value would equal to one. The F value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the F value and the more likely that the mean square contributed by the model is significantly larger than error mean square. As a general rule, if P-value is less than 0.05, model parameter is significant (refer to Table 4). On the basis of analysis of variance, the conclusion is that the selected model adequately represents the data for Cu (II) removal from aqueous solution by Custard apple peel powder. The experimental values and the predicted values are in perfect match with R^2 value of 0.991 (refer to Fig 1). This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. The optimum values of initial concentration of Cu (II), pH and adsorbent dosage from Box-Behnken design were found to be 17.6572 mg/l, 6.40213 and 28.139 g/l respectively. The maximum predicted adsorption of Cu (II) was found to be 99.3912%.

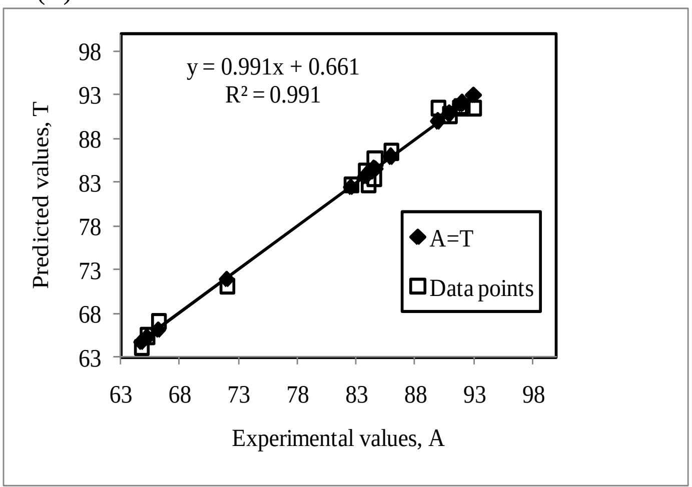

Fig 1. Parity plot showing the distribution of experimental vs predicted values of percentage removal of Cu (II).

Effect of pH and initial concentration of Cu (II) on removal of Cu (II) by Custard apple peel powder

The percentage adsorption of Cu (II) with Custard apple peel powder was studied by pre-selected range of pH and initial concentration of Cu (II). The results have been depicted in Fig 2. The results indicated that the maximum adsorption has been occurred in the acidic range and at low initial concentration of Cu (II).

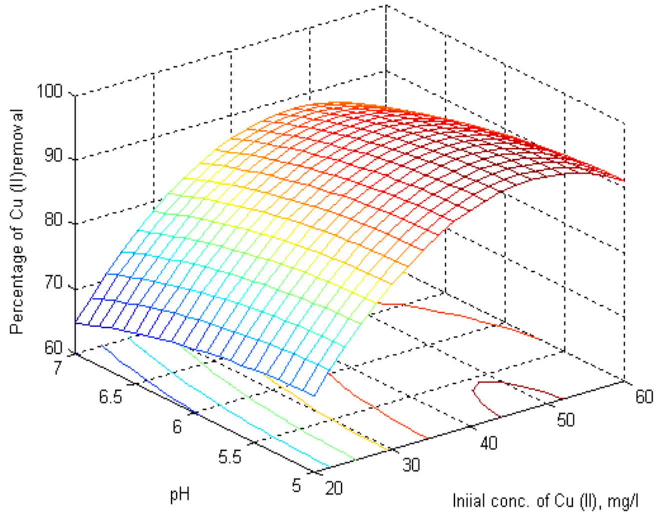

Fig 2. Response surface of 3D plot indicating the effect of interaction between initial concentration and pH on removal of Cu (II) while holding the biomass loading at 28.139 g/l

Effect of pH and adsorbent dosage on removal of Cu (II) by Custard apple peel powder

pH and adsorbent dosage are most important process parameters for assessing the removal capacity of an adsorbent. Adsorption experiments were carried out as per the selected model with selected range of pH and adsorbent dosage. The maximum adsorption of Cu (II) metal ions was 99.3912 % for Custard apple peel powder at pH 6.40213 and adsorbent dosage 28.139g/l (Fig 3). Thus with Custard apple peel powder, adsorption takes place mainly in acidic medium.

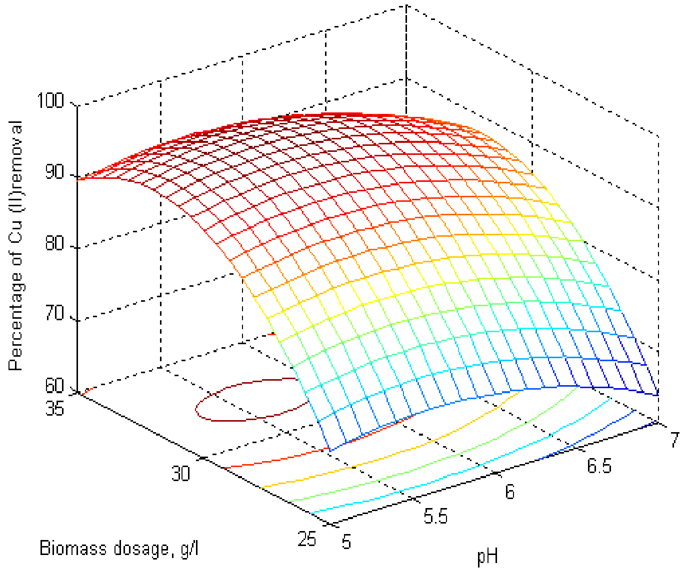

Fig 3. Response surface of 3D plot indicating the effect of interaction between Biomass loading and pH on removal of Cu (II) while holding initial concentration at 17.6572 mg/l

Effect of adsorbent dosage and initial concentration of Cu (II) on removal of Cu (II) by Custard apple peel powder

The combined effect of adsorbent dosage and initial concentration Cu (II) has been presented in Fig 4. The results show that the maximum adsorption was recorded at the 28.139 g/l adsorbent dosage and lower initial concentration of Cu (II).

Table 1. Some applications of Box-Behnken Design in separation technology

S.No.	Metal	Adsorbent	Objective of the study	References
1.	Cr(VI)	Mixed culture of Pseudomonas aeruginosa & Bacillus subtillis	To evaluate the effects and interactions of the process variables, biomass concentration, pH, temperature and contact time.	[17]
2.	Zn(II)	Magnetic nanoparticle	To optimize three variables pH of solution, amount of extract and amount of nanoparticles for extraction of zinc samples	[18]
3.	Cadmium(II)	Cynobacterium Synechocystis pevalekii	To study the optimize pH, biomass & metal concentration for cadmium removal.	[19]
4.	Cadmium(II)	Carbon aerogel	To study the optimize pH, adsorbent dosage and temperature for cadmium removal.	[20]
5.	Cr(VI) Ni(II) Zn(II)	Bacillus brevis Sp.	To evaluate the interactive effects of three most important parameters pH, temperature and metal ion concentration.	[21]
6.	Pb(II) Cd(II) Cu(II)	Trichoderma viride	To Optomize the various environmental conditions for biosorption of Pb(II), Cd(II)& Cu(II) by investigating as a function of initial metal ion concentration, temperature, biosorbent loading and pH.	[22]
7.	Cu(II)	Ascophyllum nodosum	To evaluate the effects of temperature, pH & initial concentration in the Cu(II) sorption process on the adsorption	[23]
8.	Pb(II)	Carbon aerogel	To study the influence the three parameters, adsorbent concentration, pH & temperature on the percentage removal of Pb(II).	[24]
9.	Pb(II)	Pistacia Vera L	To study the influence the three parameters, initial concentration, pH & contact time for the maximum removal of Pb(II)from aqueous solution.	[25]

Table 2. Coded and actual values of variables of the experimental design

Factor		**Coded levels of variables**		
		-1.00	**0**	**1.00**
Initial concentration (mg/l)	X_1	20	40	60
pH	X_2	5	6	7
Biomass loading (g/l)	X_3	25	30	35

Table 3. Experimental design and results for the copper removal

Run	**Coded Values**			**Actual values**			**Cu(II) removal**		**Relative error**	**Percentage relative error**
	X1	**X2**	**X3**	**x_1**	**x_2**	**x_3**	**observed**	**Predicted**		
1	-1	-1	0	20	5	30	71.95	71.22	0.7238	1.006
2	-1	1	0	20	7	30	90.85	90.639	0.2112	0.2324
3	1	-1	0	60	5	30	65.17	65.3813	-0.2113	-0.3242
4	1	1	0	60	7	30	83.73	84.4538	-0.7238	-0.8645
5	-1	0	-1	20	6	25	92.05	91.764	0.2862	0.3109
6	-1	0	1	20	6	35	84.63	85.851	-1.2212	-1.4428
7	1	0	-1	60	6	25	83.99	82.769	1.2212	1.4539
8	1	0	1	60	6	35	82.53	82.816	-0.2863	-0.3469
9	0	-1	-1	40	5	25	66.16	67.17	-1.010	-1.5266
10	0	-1	1	40	5	35	64.74	64.2425	0.4975	0.7685
11	0	1	-1	40	7	25	85.92	86.418	-0.4975	-0.579
12	0	1	1	40	7	35	84.49	83.48	1.0100	1.189
13	0	0	0	40	6	30	89.94	91.6167	-1.6767	-1.864
14	0	0	0	40	6	30	92.99	91.6167	1.3732	1.4768
15	0	0	0	40	6	30	91.92	91.6167	0.3033	0.3299

Table 4. Regression coefficient of full polynomial model. (*significant, if P<0.05)

Coefficient	**Parameter estimate**	**P-Value**
β0	91.6167	0.000*
β1	-3.0075	0.0025*
β2	9.6213	0.0000*
β3	-1.4662	0.0417
β11	-1.6096	0.9155
β22	-12.0821	0.1079
β33	-4.2071	0.9975
β12	-0.0850	0.0981
β13	1.49	0.000*
β23	-0.0025	0.0032*

Table 5. ANOVA test results

Source of variation	**Degrees of Freedom**	**Sum of squares**	**Mean square**	**F-Value**	**P-Value**
Regression	9	1418.654	157.6282	67.8955	0.000
Residual	5	11.6081	2.3216		
Total	14	1430.2621			

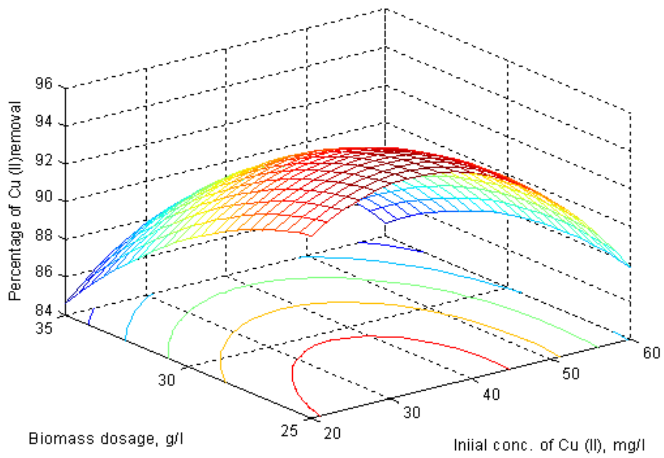

Fig 4. Response surface of 3D plot indicating the effect of interaction between Biomass loading and initial concentration of Cu (II) on removal of Cu (II) while holding the pH at 6.40213.

Conclusions

A detailed batch experimental study was carried out for the removal of Cu (II) from waste water by using Custard apple peel powder. The objective of the present study was to find out the optimum process conditions, using response surface methodology for the removal of Cu (II) from waste water by Custard apple peel powder as adsorbent. Response surface methodology using Box-Behnken design proved very effective and time saving model for studying the influence of process parameters on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. The Experimental values and the predicted values are in perfect match with R^2 value of 0.991. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. The optimal adsorption of Cu (II) was obtained as initial concentration of Cu (II), pH and adsorbent dosage and these were found to be 17.6572 mg/l, 6.40213 and 28.139 g/l respectively, resulting in 99.3912% of maximum predicted adsorption of Cu (II). Eigen values of the model are -12.0823, -4.40558 and -1.41092.

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