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Original Research Article

Removal of Cr(VI) using Sapindus trifoliatus through Biosorption: Process Optimization, Modeling and Statistical Analysis

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Abstract

Heavy metal contamination by chemical processing industries is detrimental to aquatic life. In this study, a factorial experimental design technique was used to optimize the chromium removal through biosorption from synthetic solution using Sapindus trifoliatus fruit powder (soapnut) as adsorbent. The process was analyzed and modeled using factorial design 24. The four process parameters considered were pH, metal concentration, soapnut concentration and soapnut particle size at two different levels of pH (4.0 and 8.0), metal concentration (100 and 500 mg/L), Soapnut concentration (5 and 10 g) and soapnut particle size (3 and 12 mm). Experiments were carried out in a bubble column system with working volume of 2L. The efficiency of chromium removal during an exposition time of 72 h was studied. The results were statistically analyzed using the Student's t-test and analysis of variance to define the most important process variables affecting the chromium removal efficiency. It was observed that the most significant factor affecting Cr(VI) was ascribed to metal concentration.
Keywords: Cr(VI), heavy metal, factorial experiment, Sapindus trifoliatus.

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INTRODUCTION

Urbanization and industrialization are major causes of environmental pollution. Water and soil pollution instigated by significant amount of toxic waste and controlled solid waste from the industry. Solid wastes stocking, mining, atmospheric deposition and using of agrochemicals are resulting in the heavy metal pollution in soils. This may pose risk and hazards to humans and the ecosystem. Therefore, in order to maintain good quality of environment and keep them free from contamination, continuous efforts have been made to develop technologies that are easy to use, sustainable and economically feasible. Still the research is under progress to discover the efficient ecofriendly process to reduce the concentration of heavy metals from its contaminations [1].

One such heavy metal, chromium is being released into the environment and the water bodies have become a matter of concern in all the tannery areas [2]. The hexavalent chromium [Cr(VI)] belongs to the family of compounds containing chromium in +6 oxidation state. These compounds are chromium trioxide, various salts of chromate and dichromate, used in textile dyes, tanning, wood preservation, stainless steel, and electroplating industries [3]. Cr(VI) is known to be carcinogenic, even smaller amounts of Cr(VI) in reduced form can enter the cells and damage DNA, causing cancer [4]. Toxicity of Cr(VI) is due to its high oxidative properties as it causes oxidative reactions in bloodstream leading to hemolysis and ultimately kidney failure [5]. In recent times, several species of fruits and leaves have been reported as biological adsorbent for the removal of heavy metals through biosorption at low cost with an eco-friendly way [6].

The present study focuses on the removal of Cr(VI) through biosorption using fruits from a plant called *Sapindus trifoliatus*. *Sapindus trifoliatus* belongs to the *Sapindus* genera, meaning "cleanser" and indicus signifying 'of India'. These trees and bushes found in South Asia, bearing fruits colloquially called as cleanser nuts or soapberries. It contains saponins (regular surfactants) utilized by local Indians and Nepalese. The soapberries keep the hair long and sound, are helpful in the treatment of lice and dandruff and used as an herb for skin issues like dermatitis and psoriasis. It is utilized as cleanser, bio-surfactant, and healing in the current science. It is characterized by 10–12% saponin, 10% sugars, and 25–30% unsaturated fats [7]. This study aims to optimize the process parameters for effective biosorption of Cr(VI) that carried out by a two-level, four-factor, full factorial experimental design.

EXPERIMENTAL

Soapnut fruits (adsorbent) were obtained from a local shop, Hyderabad, India and were grounded to powder using a domestic mixer. The fruit composed of outer skin and seed inside were crushed together and boiled to remove saponin to avoid foam formation during the experiments. The powder was dried at overnight and sieved using standard ASTM sieves to two different average sizes of 3 and 12mm. A synthetic solution, 1000 ppm of potassium dichromate ($K_2Cr_2O_7$) was prepared. Further, it was made up to required concentrations and used as adsorbate. The reagent, 0.25% w/v of 1, 5-diphenylcarbazide in 50% acetone was prepared and used for the determination of chromium using spectrophotometer (ELICO SL 159) adapting to the procedure specified by Gilcreas *et al.* [8]. Double distilled deionized water was used to prepare the solutions. For biosorption studies, bubble column experiments were carried out in 2.5L sterilized plastic bottles containing 2L of aqueous Cr(VI) solution (100 and 500 ppm). The columns were fixed on a wooden plank in inverted position. Air was supplied (1L per min) from compressed zone at the bottom of column using air pump (SEBO SB-648A). The solution pH was measured and adjusted to the desired point by the calibrated pH meter (ELICO LI 127) using 0.5 N HCl and 0.1 N NaOH solutions. Adsorbent, 5 and 10g were taken to the respective column. Biosorption studies were carried out for 72 h. After 72 h, the adsorbents were separated by filtration. The filtrate was analyzed for non-adsorbed Cr(VI) content present in the solution.

Further, the percentage removal of Cr(VI), denoted as R, was deduced by using the equation (1).

$$\boldsymbol{R}\ (\%) = \left(\frac{C_i - C_t}{C_i}\right) \times \mathbf{100} \ \ldots\ldots\ldots\ldots\ldots\ldots \ \mathbf{(1)}$$

C_i and C_t denote Cr(VI) concentration determined at initial time, and at a given time t, respectively. The adsorption capacity of soapnut can be determined from equation (2).

$$q_e = \left(\frac{C_i - C_e}{W}\right) \times V \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Where, V is volume (L) of the solution taken, C_i is initial concentration (mg/L) of the Cr(VI), C_e is equilibrium concentration (mg/L) of Cr(VI), and W is weight (g) of the adsorbent taken.

Design of experiments-full factorial method

For optimization of the effective biosorption, the factorial experimental design was employed [9]. The design determines the effect of each factor as it varies with change in the level of other factors and the effect of each factor on the response [9]. Interaction effects of various factors can only be attained by using the design of experiments method. Factorial designs are promising way in examining variations [10]. Hence, independent studies are combined into one where a common experimental design with all input factors is set at two levels each. These levels are called 'high' and 'low' or '+1' and '−1' respectively. If there are k factors each at two levels, a full factorial design has 2^k runs [11]. In the present study, four factor two-level full factorial designs were used for the modeling of the adsorption process. All experiments were carried out with duplicate.

RESULTS AND DISCUSSION

Design of Experiment

Table 1 shows the factorial design in a standard order matrix. The levels and ranges of the selected process parameters (A: pH, B: Initial concentration of Cr(VI), C: Adsorbent dose, and D: Adsorbent particle size) which have much influence in chromium removal are given. Table 2 gives information on percentages of Cr(VI) removal by soapnut for a 2^2 factorial design with 2 replicates. The effect of a factor is defined as the change in response produced by a change in the level of the factor as described in equation 1. It was observed that the initial Cr(VI) concentration plays a vital role in soapnut's adsorption activity, and other parameters like pH and adsorbent dose also affect the adsorption process significantly.

Table-1: Experimental levels and ranges of variables

Variable	Symbol	Range	
		+1	-1
pH	A	3	8
Cr ion concentration (mg/L)	B	100	500
Adsorbent dose (g)	C	5	10
Adsorbent size (mm)	D	3	12

Modeling of Process and Statistical Analysis

Table 2 gives the factorial design for four variables and respective Cr(VI) removal efficiencies. The interacting factors affecting the removal of Cr(VI) were determined by performing the analysis of variance (ANOVA). The sum of squares (SS) value of each factor quantifies its importance in the process. As the value of SS increases; the significance of the corresponding factor in the process also increases (Table 3). The interaction effect of each parameter had the P value <0.05. Therefore, it can be considered as significant **[**12**]**. From Table 3, the interaction between different factors can be determined. Significantly, the factors, A and B are having the major effect on chromium removal. The adsorption process can be modeled in terms of coded form and the same as given in Eq.(3).

$$R\ (\%) = X_0+X_1\ A+X_2\ B+X_3C+X_4D+X_5AB+X_6\ AC+X_7AD+X_8BC+X_9BD+X_{10}CD \ldots\ldots\ldots (3)$$

Here, R (%) is the percentage removal of Cr(VI), X_0 is the global mean, X_1, X_2, … X_{10} represent the other regression coefficients. A, B, C, and D stands for pH, initial concentration of Cr(VI), the dosage of adsorbent, and adsorbent particle size, respectively.

Including the respective regression coefficients in Eq.(3) the biosorption process can be modeled as follows.

$$R\ (\%) = 68.09–12.31A–20.46B+1.80C–4.31D –3.67AB–0.04AC+5.65AD+0.52BC–4.18BD–1.38\ CD$$

Interaction Effects

The main effect plot gives differences between level means for one or more factors. The response mean for each factor level is connected by a line. The removal of chromium by soapnut was affected by four main factors measured at two levels high and low [13]. The main effect plots of these four factors are depicted in Fig.1. A horizontal line (parallel to the x-axis), indicates no main effect; each level of the factor affects the response in the same way. It was observed that the response mean was obtained same across all the factor levels. Whereas, when the line is not horizontal, then there is a main effect and different levels of the factor affect the response differently. A steeper the slope of a line gives a greater magnitude of the main effect. In Fig.1, pH and metal concentration have steeper slopes compared to other factors such as soapnut dose, and soapnut particle size. Hence, they do affect response differently at two different levels.

Table-2: Factorial design for four variables and respective Cr(VI) removal efficiencies

Run No	pH	Cr Concentration (mg/L)	Adsorbent dose (g)	Adsorbent particle size (mm)	Removal of Cr(VI) (%)
1	-1	-1	-1	-1	97.10 ± 0.5
2	1	-1	-1	-1	71.56 ± 0.5
3	-1	1	-1	-1	84.34 ± 0.5
4	1	1	-1	-1	23.88 ± 0.5
5	-1	-1	1	-1	96.92 ± 0.5
6	1	-1	1	-1	89.13 ± 0.5
7	-1	1	1	-1	83.04 ± 0.5
8	1	1	1	-1	33.22 ± 0.5
9	-1	-1	-1	1	97.47 ± 0.5
10	1	-1	-1	1	78.80 ± 0.5
11	-1	1	-1	1	35.29 ± 0.5
12	1	1	-1	1	41.87 ± 0.5
13	-1	-1	1	1	97.28 ± 0.5
14	1	-1	1	1	80.16 ± 0.5
15	-1	1	1	1	51.73 ± 0.5
16	1	1	1	1	27.68 ± 0.5

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Interaction plot is used to visualize possible interaction effects between the considered parameters when the effect of one parameter depends on the level of the other parameter. Fig.2 shows the interaction plot for Removal of Cr(VI) in terms of fitted means. Parallel lines in an interaction plot indicated that there no interaction. Greater the difference in slope between the lines explains there is a higher degree of interaction [14]. From Fig.2, it has been found out that the pH has significant interaction with Cr levels and also with adsorbent particle size. The analysis for the interaction clearly indicates that Cr level is associated with adsorbent size and has minimal interaction with adsorbent dose. Thus, it revealed that the dosage of adsorbent and its particle size have little or no interaction effects on Cr removal.

The Normal plots

The normality of given data can be checked by plotting a normal probability plot of the residuals. The normal probability plot of the residuals is shown in Fig.3. If data points on the plot fall nearly close to the straight line, then the data can be said as normally distributed. As seen in Fig.3, The data points are apparently close to the straight line that indicates the experimental values belong to a normally distributed population. The Pareto chart of the effects is used to determine the magnitude and the importance of an effect. The Pareto chart of standardized effects has been given in Fig.4.

At this juncture, the Pareto chart displays the absolute value of the effects with an extended reference line on the chart. Any effect that extends beyond this reference line is potentially important. Here, A and B are shown to be important factors, as they extended beyond the reference line which having a magnitude of 2.571. It explicated that the absolute value of B is 5.8 and A is 3.5 approx.

Table-3: Analysis of Variance and Estimated regression coefficients of significant factors

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Effect	Coefficient	SE coefficient	95% CI	T-Value
A	1	2422.8	2422.8	13.22	0.015	-24.61	-12.31	3.38	(-21.00,-3.61)	-3.64
B	1	6698.6	66698.6	36.56	0.002	-40.92	-20.46	3.38	(-29.16,-11.7)	-6.05
C	1	52.1	52.05	0.28	0.617	3.61	1.80	3.38	(-6.89,10.50)	0.53
D	1	296.8	296.76	1.62	0.259	-8.61	-4.31	3.38	(-13.01,4.39)	-1.27
AB	1	215.0	214.98	1.17	0.328	-7.33	-3.67	3.38	(-12.36, 5.03)	-1.08
AC	1	0.0	0.03	0.00	0.990	-0.09	-0.04	3.38	(-8.74, 8.66)	-0.01
AD	1	510.0	510.47	2.79	0.156	11.30	5.65	3.38	(-3.05, 14.35)	1.67
BC	1	4.3	4.28	0.02	0.885	-1.03	-0.52	3.38	(-9.22, 8.18)	-0.15
BD	1	279.8	279.78	1.53	0.271	-8.36	-4.18	3.38	(-12.88, 4.52)	-1.24
CD	1	30.0	30.29	0.17	0.701	-2.75	-1.38	3.38	(-10.07, 7.32)	-0.41
Error	5	916.1	183.22							
Total	15	11426.1								

S	R-sq	R-sq (adj)	R-sq (pred)
13.5358	91.98%	75.95%	17.90%

A contour plot (Fig.5) is a graphical representation of a 3-dimensional surface by plotting constant z-slices, called contours, on a 2-D format. It can be used to explore the potential relationship between three variables. As cited in Fig.5, the contour plot shows the influences of Cr(VI) concentration (y), pH (x) on the removal of Cr. The darker regions indicate higher removal. The contour levels reveal a peak centered at the –1 level of both factors. The percentage removal of Cr in this peak region is greater than 90. Similarly, adsorbent dose (y) versus Cr(VI) level (x), a low level of metal concentration at both –1 and +1 levels of adsorbent dose gives >90% removal of Cr(VI). In the plot of adsorbent size versus pH, the peak region shows 80–90% removal for lower levels of both the factors.

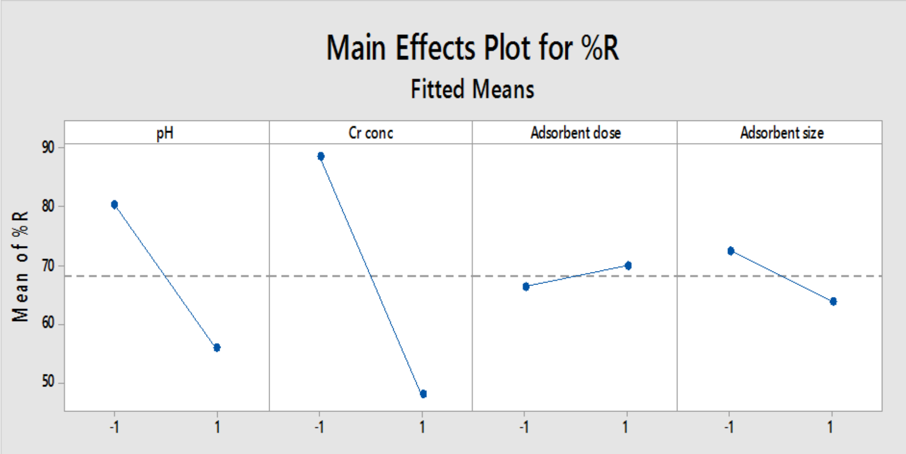

Fig-1: Main Effects plot for % Removal of Cr(VI) with fitted means

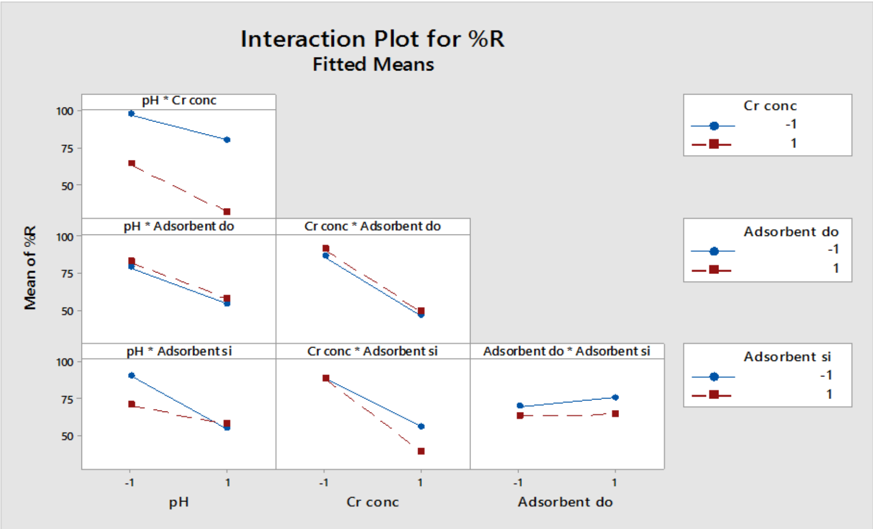

Fig-2: Interaction plot for Removal of Cr(VI) with fitted means

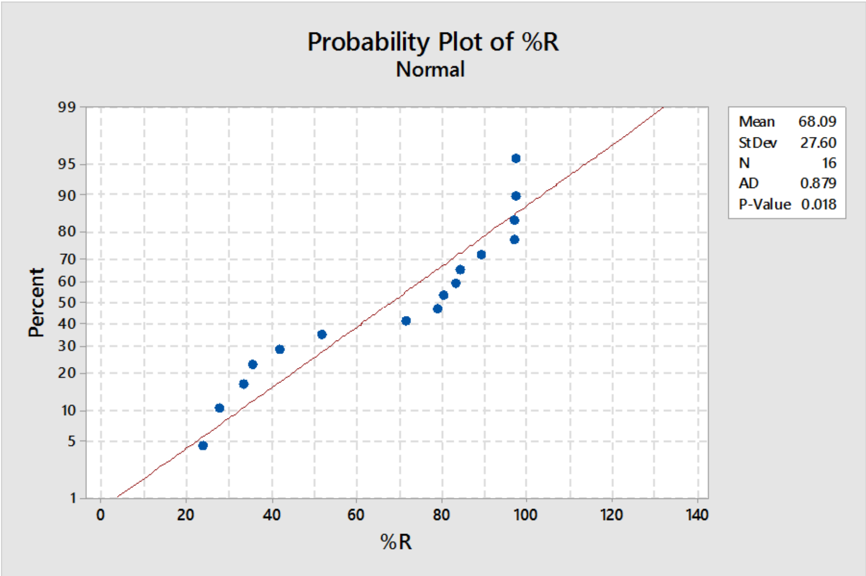

Fig-3: Normal probability plot

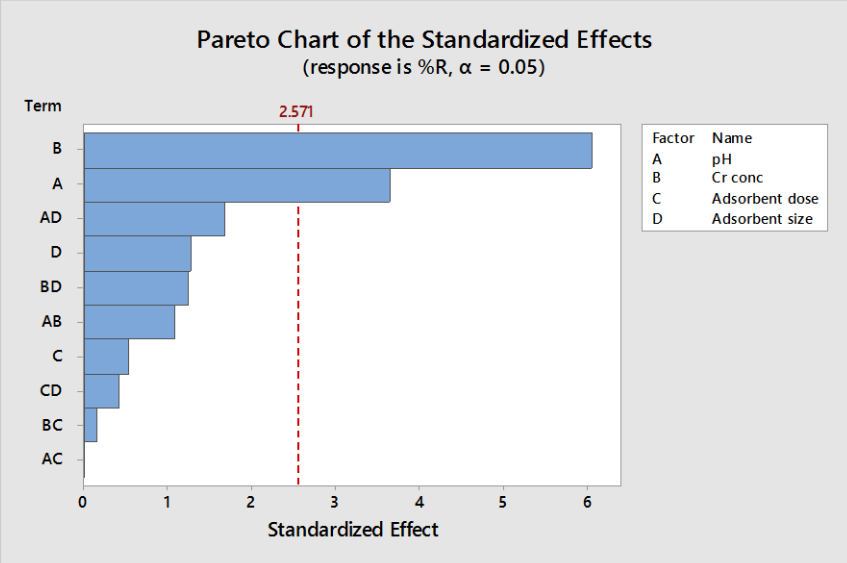

Fig-4: Pareto chart of standardized effects

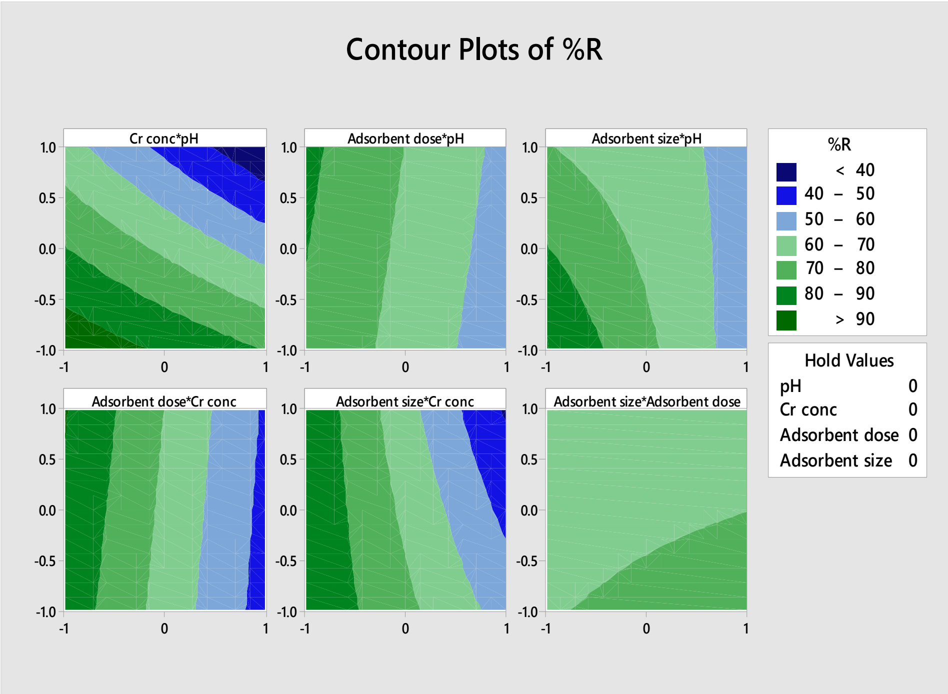

Fig-5: Contour plots for % Removal of Cr(VI)

CONCLUSION

The optimization of biosorption process using *Sapindus trifoliatus* (soapnut) fruit as adsorbent was carried out with due importance for removing Cr(VI). The optimization was attempted through two-level, four-factors, and full factorial experimental design. The four factors were considered namely, pH, initial concentration of Cr(VI), adsorbent dose, and adsorbent particle size. The experiment result revealed that a low pH level, low metal concentration with moderate adsorbent dose, and less adsorbent size are favorable for removing maximum chromium. The significant factors were found to be metal concentration and pH. A lower pH contributes to higher chromium-free ion generation by cleavage of chromium salt. Adsorption of chromium onto the adsorbent surface is significantly affected by adsorbent particle size as more number of adsorbing sites is present on smaller sized particles of soapnut. The interactions between pH, chromium and adsorbent particle size also contributed significantly to a maximum chromium removal. From the study, it is apparent that the process with the bubble column using soapnut as the adsorbent is an effective alternative for large-scale remediation of heavy metal contamination.

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