REMOVAL OF HEXAVALENT CHROMIUM BY EUCALYPTUS LEAF POWDER: OPTIMIZATION BY TAGUCHI METHOD

Submited on 29/01/2020 – Accepted on 05/05/2020

Abstract

Batch adsorption process of metal pollutants in aqueous phase can be influenced by several parameters such as initial pH of the solution, dose of the adsorbent, concentration of the adsorbate, contact time, temperature, agitation rate and adsorbent characteristics. In this study Taguchi's statistical approach was used to optimize the parameters of Cr(VI) biosorption by eucalyptus leaf powder. The orthogonal array L9 with three levels was applied to determine the optimal conditions for adsorption. The obtained results show that Cr(VI) removal is maximum (96.51%) with the low level of initial pH solution (1.0) and initial metal concentration (50 mg/L) and, with the high level of the adsorbent dose (3.0 g/L) and contact time (70 min). The analysis of variance of the experimental results, carried out for a level of significance of 5%, revealed that the initial pH solution is the most important parameter influencing the adsorption efficiency of chromium (VI) with a percentage contribution of 47.60%.

Keywords: Chromium (VI), eucalyptus leaf powder, adsorption, optimization, Taguchi method.

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INTRODUCTION

After its discovery in 1797–1798, chromium (Cr) and its salts found a wide range of applications in the chemical industry, graphics industry, tanning industry, artistic paints, anticorrosion paints, electroplating, steel alloys, stainless steel welding, and a multitude of other uses [1,2]. For the last 15 years, chromium has been classifed among the 20 most lethal environmental contaminants [3]. Epidemiological studies have shown that occupational and environmental exposure to metals such as chromium was associated with increased risk of various cancers and adverse health effects [4]. Chromium, which is strongly influenced by redox conditions, exists in the aquatic environment in an equilibrium between Cr(VI) and Cr(III). Cr(VI) is highly soluble, carcinogenic and 100 times more toxic than Cr(III) [5], which has been suggested to be essential for the maintenance of normal glucose tolerance in animals and humans.

Hexavalent chromium is an example of transport into the cells followed by metabolic reduction to trivalent chromium that is assumed to induce mutations and ultimately carcinogenesis by a direct reaction with deoxyribonucleic acid (DNA) [6,7].

Hexavalent chromium can also cause severe infections such as, skin and lung cancers, hepatic diseases and bronchial tract infections [8]. According to the recommendation of the World Health Organization [9], the maximum allowable limit for Cr(VI) in drinking water is at the level of 0.05 mg/L and its concentration in industrial wastewaters varies from 0.5 to 270 mg/L.

During the industrial processes, unused chromium salts are usually discharged in the final effluents, which causing a serious threat to the environment. Therefore, it is indispensable to remove Cr(VI) from wastewater before being released into the environment. In order to improve the removal efficiency of Cr(VI) from wastewater, numerous methods have been developed including chemical precipitation and electro-precipitation method, electrocoagulation, membrane filtration, ion exchange and electrochemical ion exchange process, liquid-liquid extraction, electrodialysis, phytoremediation in constructed wetland, infiltration percolation, photocatalysis and adsorption [10].This last is one of the attractive processes because of its high efficiency, flexibility, simplicity of design and operation without secondary toxic slurries [11]. Many investigations have been carried out on the effective removal of heavy metals from solution using natural adsorbents derived from agricultural wastes [12, 13, 14, 15].

However, optimization of parameters involved in this process plays a key role in maximizing the sorption efficiency. Statistical design of experimental methods provide an easier and equally efficient approach to optimize several operational variables [16]. The design of experimental (DOE) methods lead to more information after running fewer experiments. These methods included full factorial method, response surface method, Taguchi method and mixture method. The advantages of Taguchi method over the other methods are that numerous factors can be simultaneously optimized and more quantitative information can be extracted from fewer experimental trials [17]. This method which was widely used in improving the quality of manufactured goods and now being used in various other fields, and particularly for process parameters optimisation in wastewater treatment studies contaminated by organiques [18, 19, 20] and inorganiques [16, 17, 21, 22] polluants.

The present study aims to investigate the possible use of eucalyptus leaves, an agricultural waste material, for the removal of hexavalent chromium ions from aqueous solution.Taguchi's statistical approach was applied to optimize the adsorption process.

2. MATERIAL AND METHODS

2.1. Adsorbent and Adsorbate

In this study, the eucalyptus leaves (EL) were used as a biosorbent for Cr(VI) removal from aqueous solution. The EL were dried in an oven at 80°C for 24h and grounded in a mortar. The obtained powder was first washed several times with hot water, and then rinsed with distilled water. After drying in an oven (Memmert, Germany) at 80°C until a constant weight was achieved, the eucalyptus leaf powder (ELP) was stored in hermetic bottle until use.

An aqueous stock solution (1000 mg/L) of Cr(VI) ions was prepared by dissolving potassium dichromate salt $K_2Cr_2O_7$ in distillated water. The stock solution of Cr(VI) was diluted with distilled water to obtain the required initial concentration Cr(VI) solutions.

2.2. Batch Adsorption Studies

Adsorption experiments were carried out by introducing a given quantity of ELP in a cylindrical reactor containing 50 mL of hexavalent chromium solution. The reactor was placed in a temperature-controlled water bath. The mixture was agitated using a mechanical stirrer at a constant stirring speed (250 rpm) and temperature (25°C) and filtrated using Whatman filter paper (N°3), after a fixed agitation time. The residual concentration of Cr (VI) was determined spectrophotometrically at 540 nm using a double beam UV–visible spectrophotometer (SHIMADZU UV-1601PC) after complexation with 1.5 diphenylcarbazide in an acidic medium [23].

The percentage of chromium removal, R (%), was determined as follows:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

Where C_0 and C_e represent the initial and final chromium (VI) concentrations (mg/L), respectively.

2.3 Taguchi method

The Taguchi method uses a statistical measure of performance called signal-to-noise (S/N) ratio.Usually, three types of S/N ratio analysis are applicable, namely: larger-the-better, nominal-the-best, and smaller-the-better types [24]. As the goal of this study was to remove Cr(VI) from wastewater by ELP, the larger-the-better quality characteristic was selected. The related S/N ratio is given by the following equation:

$$S/_N = -10 \times \log\left(\frac{1}{r}\sum_{i=1}^{r}\frac{1}{R_i^2}\right) \qquad (2)$$

where r is the number of repetitions under the same experimental conditions, and R_i is the result of each repeated measurement, which is the Cr(VI) removal percentage.

In this study, each run was repeated three times. With the four three-level parameters, L9 orthogonal array design was chosen to perform the experiments. The four selected factors including initial pH of solution, initial concentration of Cr(VI), dose of adsorbent and time of contact. These parameters and their levels are given in Table 1.

***Table 1**.Parameters and their levels.*

Parameters	Symbols	Levels		
		1	2	3
Initial pH of solution	pH_0	1.0	2.0	3.0
Dose of adsorbent (g/L)	D	0.2	1.6	3.0
Initial concentration of Cr(VI)(mg/L)	C_0	50	100	150
Time of contact (min)	t	10	40	70

The analysis of variance is used to determine which factors have a significant effect at a given risk level on the quality characteristic. It also serves to determine the percentage contribution of each factor on the adsorption process [25].

3. RESULTS AND DISCUSSION

3.1. Global analysis of the obtained results

The experimental results of the adsorption yield of Cr (VI) on the powder of eucalyptus leaves and the calculated values of the (S/N) ratio are presented in Table 2. The results show a large variation in the average yield (R_m) of adsorption. Under the experimental conditions, average yield varied from 5.85 to 77.92% and the corresponding change in S/N ratio is 15.32 à 37.83.

***Table 2.** Experimental results and S/N ratio values for Cr(VI) removal*

Essay	Controllable factors in coded values				Removal(%)				S/N ratio
	pH_0	D	C_0	t	R_1	R_2	R_3	R_{moy}	
1	1	1	1	1	14.53	13.75	14.15	14.14	23.00
2	1	2	2	2	57.30	58.09	57.52	64.79	35.21
3	1	3	3	3	77.87	78.66	77.22	77.92	37.83
4	2	1	2	3	21.37	21.89	21.36	21.54	26.66
5	2	2	3	1	14.29	14.35	13.93	14.19	23.04
6	2	3	1	2	55.99	54.44	54.86	55.10	34.82
7	3	1	3	2	5.56	6.04	5.94	5.85	15.32
8	3	2	1	3	16.89	16.71	16.78	16.79	24.50
9	3	3	2	1	9.46	9.06	10.63	9.72	19.69

3.2. Effect of parameters on Cr(VI) removal

Table 3 shows the mean S/N ratio values for each level of the controllable parameters. As can be seen in this table and according to the higher mean (S/N) ratio base, the optimal conditions for Cr(VI) removal are initial pH solution at level 1 (1.0), adsorbent dose at level 3 (3.0 g/L), initial metal concentration at level 1 (50 mg/L) and contact time at level 3 (70 min). Thus, the optimal combination of process parameter levels for maximum removal of Cr(VI) is $pH_{01}D_3C_{01}$ t_3. The representation of the main effects of each individual parameter at different levels is given by Figure 1.

Table 3. *Mean S/N ratios and main effects of design parameters*

Parameters	Mean (S/N) ratios			L3-L1
	L1	L2	L3	
pH_0	32.02	28.17	19.84	-12.18
D	21.66	27.58	30.78	9.12
C_0	27.44	27.19	25.40	- 2.04
t	21.91	28.45	29.67	7.76

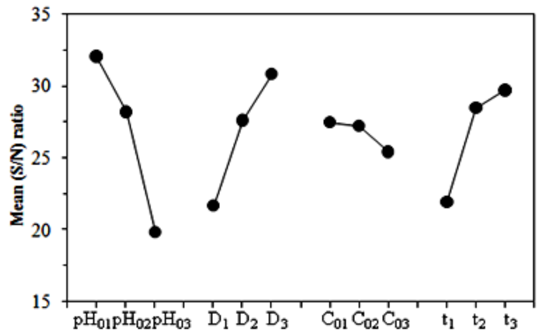

Figure 1*: Main effects of parameters which each parameter is at a given level*

3.3. Analysis of variance

Analysis of variance (ANOVA) is a statistical method that uses the Fischer test (F-ratio) to determine the impact of each parameter on the adsorption process and its contribution to the total variance of all design parameters [26].

The analysis of variance of the experimental results of the adsorption of chromium (VI) by EL powder is given in Table 4. This analysis was performed with a 95% confidence level. A parameter is considered significant on the response if the value of its F-ratio is higher than the critical value given by the Fisher table.

If the degree of freedom of the error is equal to zero, the calculation of F-ratio is not possible. To estimate the variance of the error, in this case, the sum of the squares of the error is replaced by the pooling of the sum (s) of the lowest square (s) of the parameter (s) [27]. This case is specific to orthogonal tables whose degree of freedom (df) is equal to the sum of the degrees of freedom of the design parameters.

According to the obtained results, the initial pH of the solution, with an F-ratio value of 31.19, well higher than the critical value (19.00) given by the Fisher table, is considered to be the most influential parameter on the adsorption efficiency of chromium (VI). This parameter is also the one with the highest percentage of contribution (ρ_F). This clearly indicates that the adsorption of chromium (VI) on the studied biosorbent is significantly influenced by the initial pH of the solution unlike the other selected parameters, as it determines the ionic species present in solution and the surface charge of the adsorbent [28,29]. These results are consistent with those of previous studies on the removal of heavy metals in the aqueous phase by different biosorbents [24, 30].

For the other parameters, i.e., the adsorbent dose and the contact time, they are significant for a 90% confidence level since the calculated values of F-ratio (17.23 and 14.01, respectively) were higher than the critical value given by the Fisher table (9.00). The ranking of the parameters in descending order of their percentage contribution on the adsorption process is pH_0>D>t. The contribution of each factor on Cr(VI) biosorption by the powder of eucalyptus leaves is given in Figure 2.

Table 4*. Analysis of variance for chromium(VI) removal using ELP.*

Factors	df	SS_F	V	F-ratio	SS_F'	ρ_F (%)
pH_0	2	232.510	116.25	31.19*	225.106	47.60
D	2	128.406	64.203	17.23**	120.952	25.58
C_0	2	7.454	3.727			
t	2	104.399	52.199	14.01**	96.945	20.51
Error	0					
Pooled error	2	7.454	3.727			6.31
Total	8	472.768				100

$F(0.05,2,2) = 19.00$; * Significant at 95% , $F(0.1,2,2)= 9.00$; ** Significant at 90%

SS_F: sum of squares of factors; V: variance; SS_F':sum of squares corrected

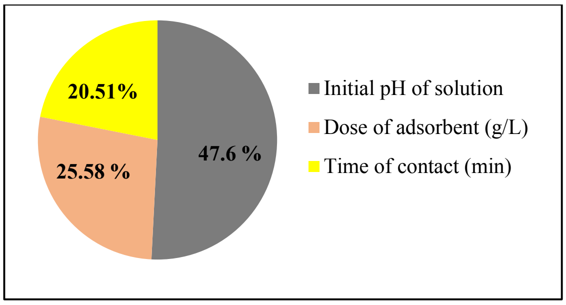

Figure 2*: Relative contribution of each factor (%) on Cr(VI) biosorption*

3.4. Confirmation experiments

The final step of Taguchi method is performing confirmation experiments to evaluate quality characteristics.The predicted $(S/N)_{opt}$ ratio using the optimal level of the process parameters, can be calculated as given:

$$(S/N)_{opt} = (S/N)_m + \sum_{i=1}^{k} \left(\left(\overline{S/N}\right)_i - (S/N)_m \right) \quad (3)$$

where $\overline{(S/N)}$ is the mean value of S/N ratio at the optimum level of the parameter, $(S/N)_m$ is the average value of the S/N ratios and k is the repetition of each optimum level of the parameter.

Five confirmation experiments were conducted using the optimal combination of process parameters. Predicted and experimental values of the S/N ratio and elimination efficiency are reported in Table 5. The results show that there is a good agreement between the values predicted by the model and the values determined experimentally.

Table 5.*Results of confirmation experiments for Cr(VI) removal*

	Optimal removal parameters	
	Predict	Experiment
Level	$pH_{01}D_3t_3$	$pH_{01}D_3C_{01}t_3$
% Removal	90.27	96.51
S/N Ratio	39.11	39.69

4. CONCLUSION

In this study, Taguchi L_9 (3^4) orthogonal array experimental design was applied to determine the optimum operating conditions for the adsorption of hexavalent chromium on eucalyptus leaf powder.

The results indicated that the Taguchi method gives a suitable approach for optimization of removal percentage of Cr (VI) under experimental conditions studied. The maximum percentage of Cr(VI) removal (96.51%) was at $pH_0 = 1$, initial Cr(VI) concentration = 50 mg/L, adsorbent dose of 3.0 g/L and time of contact = 70 min. The influence of the parameters in descending order is $pH_0 > D > t$. The initial solution pH has the greatest contribution (47.60%) in the removal of Cr(VI) by ELP.

5. REFERENCES

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