Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21047

81 (2017) 118–122
June

Optimization of process parameters for Cr(VI) removal by seed powder of prickly pear (*Opuntia ficus-indica* L.) fruits using Taguchi method

Sabrina Aziri, Smail Meziane*

Laboratory of Applied Chemistry and Chemical Engineering, Faculty of Science, University Mouloud Mammeri of Tizi-Ouzou, BP NO. 17 RP, 15000 Tizi-Ouzou, Algeria, emails: smmeziane@yahoo.fr (S. Meziane), sabrina.aziri@gmail.com (S. Aziri)

Received 5 January 2017; Accepted 17 June 2017

ABSTRACT

Hexavalent chromium is one of the most toxic and carcinogenic heavy metals in aqueous solutions. It is widely used for industrial purposes and released into the environment in large quantities. In this study, Taguchi experimental method was applied to optimize the process parameters for the removal of hexavalent chromium ions from aqueous solutions. Adsorption experiments using seed powder of prickly pear (*Opuntia ficus-indica* L.) fruits as a new low-cost adsorbent were performed in batch reactor. The five selected controllable parameters, each at three levels, were initial pH of solution (pH_0), adsorbent dose (m), initial concentration of metal (C_0), time of contact (t), and temperature (T). The L_{18} orthogonal array experimental design and "the higher-is-better" criterion were selected to determine optimum removal conditions. The data from all experiments were analyzed using signal-to-noise (S/N) ratio and analysis of variance. The obtained results revealed that the initial pH of the solution was the most important parameter contributing to the removal efficiency (82.48%) followed by adsorbent dose (10.21%), and contact time (5.56%). The optimal conditions for chromium(VI) removal were determined at initial pH of 1, adsorbent dose of 6.0 g/L, initial concentration of metal of 30 mg/L, temperature of 55°C, and time of contact of 80 min, and the Cr(VI) removal percentage was 98.24%. A multiple linear regression equation was developed for estimating predicted values.

Keywords: Chromium(VI); Adsorption; Prickly pear seeds; Optimization; Taguchi method

1. Introduction

Chromium (Cr) is one of the heavy metals, which is widely used in various industries, including chrome plating, wood preservation, leather tanning, pulp production, film and photography, petroleum refining, pigments, catalysis, metal finishing, brass, and electrical and electronic equipment [1]. However, these processes discharge large amounts of wastewater containing chromium into the environment, which cause serious pollution to soil, groundwater, and river water. In aqueous solutions, chromium exists mainly as Cr(VI) as anion and Cr(III) as cation, and it is known that Cr(VI) is more toxic due to its carcinogenic, mutagenic, and teratogenic effects [2]. Therefore, controlling Cr(VI) released into streams and rivers is very important for human health as well as environment. Thus, Cr(VI) must be physically or chemically reduced from water and wastewater to an acceptable level. According to the U.S. Environmental Protection Agency (EPA) [3], the maximum permissible limit of Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in drinking water is 0.05 mg/L.

In the last decades, various methods of treating wastewater containing heavy metals have been developed such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery, and electrocoagulation. However, these methods suffer from several setbacks in the form of technological and/or economic constraints [4]. Recent researches have been focused on the development of cost-effective treatment methods. Adsorption is one of the physical–chemical treatment process found to be effective in heavy metal removal

* Corresponding author.

1944-3994/1944-3986

from water and wastewaters. Activated carbon is the adsorbent of choice for the removal of heavy metals. However, due to its high cost and the cost involved in regenerating, a considerable number of low-cost adsorbents have been developed and tested. Recent studies showed that hexavalent chromium can be removed using biosorbents from agricultural wastes such as mangosteen peel [5], potato starch [6], fruiting bodies of the jelly fungus [7], and rice husk ash [8]. However, because of its high toxicity and mobility in ecosystems, hexavalent chromium is considered as a high priority environmental pollutant. Consequently, the search for new low-cost adsorbents with higher removal efficiency is more than necessary.

Batch adsorption studies have shown that metal removal is dependent upon numerous process parameters including initial pH, temperature, time of contact, biosorbent dose, degree of agitation, and the parameters related to the state of the adsorbate and adsorbent. Their optimization through experimental design to improve removal efficiency is an effective way to minimize the number of experiments, and thus to reduce the time and costs. The Taguchi design method is a powerful tool in experiment design for optimizing the process parameters. In this method, the parameters are arranged into an orthogonal array [9]. An orthogonal array is a fractional factorial design, which assures a balanced comparison of levels of any parameter. This statistical method was widely applied in manufacturing processes optimization, and now being used in various other fields, particularly for process parameters optimization in wastewater treatment studies contaminated by heavy metals. More recently, Taguchi orthogonal array design was applied for process parameters optimization studies of heavy metal removal from aqueous solutions including Cd(II), Cu(II), and Ni(II) ions. A Taguchi L_{16} orthogonal array was used by Zolgharnein et al. [10] for multivariate optimization of Cd(II) removal by *Carpinus betulus* tree leaves from an aqueous solution in a batch system. The controllable parameters such as temperature, amount of sorbent, initial concentration of Cd(II), pH value, and particle size have been optimized. The contribution percentages of the initial pH value and the adsorbent dose were the greatest for the removal percentage of Cd(II) by this adsorbent. Özdemir et al. [11] used the Taguchi L_{32} orthogonal array design to optimize Cu(II) biosorption by *Spaghnum* moss. The authors studied five parameters such as agitation time, initial concentration of metal, temperature, biosorbent dosage, and pH of solution, each at two levels. In both of these studies, biosorbent dosage was found to be the most effective parameter. On the other hand, the optimization of Ni(II) from wastewater by calcined oyster shell powders (OSP) was studied by Yen and Li [12]. The L_{18} orthogonal array experimental design was selected to optimize five parameters, including pH of the solution, OSP calcined temperature, Ni(II) concentration, OSP dose, and contact time. Among these parameters, pH of the solution was found to be the most effective parameter followed by the calcined temperature of OSP, and the least was the contact time. Similar finding was found by Yen [13] with the same biosorbent for Taguchi optimization of Cd(II) removal from aqueous solutions. Pundir et al. [4] have applied this method to optimize the process parameters for the removal of copper and nickel by growing *Aspergillus* sp. For the purpose, an L_9 orthogonal array design was adopted to investigate the effect of four parameters each at three levels. The authors found that concentration of copper/nickel was a more important factor than inoculum concentration, pH, and temperature. However, no study has been reported on the use of the fractional factorial design based on Taguchi's orthogonal array regarding the batch optimization of chromium(VI) ions removal from aqueous solutions.

In this work, the solid waste remaining after cold press oil extraction from crushed seeds of prickly pear (*Opuntia ficus-indica* L.) fruits was used as a new low-cost adsorbent for the removal of Cr(VI) ions from aqueous solutions. The purpose of the study was to optimize the adsorption process parameters using a statistical approach based on Taguchi array design to improve removal efficiency for future industrial use. S/N ratio and analysis of variance (ANOVA) were used to determine optimal adsorption conditions. Confirmation experiments were also conducted at the optimized conditions.

2. Materials and methods

2.1. Adsorbent and adsorbate

In this study, the solid residue of the cold press oil extraction from the seeds of prickly pear (*Opuntia ficus-indica* L.) fruits was used as an adsorbent for Cr(VI) removal from aqueous solutions. The adsorbent, named prickly pear seed oil cake (PPSOC), was collected from a local unit to produce vegetable oils. The PPSOC was dried in an oven at 80°C for 24 h and grounded in a mortar. The obtained powder (PPSOCP) was first washed several times with boiling water, and then rinsed with distilled water in order to remove any impurities (dust, soluble and colored compounds, etc.). After drying in an oven at 80°C until a constant weight was achieved, the PPSOCP was sieved to get particles of 0.165 ± 0.006 mm size and then stored in a sealed glass bottle until use.

A stock solution of Cr(VI) was prepared (1,000 mg/L) by dissolving 2.828 g of potassium dichromate of analytical grade (Labosi, France) in 1 L of distilled water. The working solutions of desired concentrations were prepared as needed by diluting the stock Cr(VI) solution.

2.2. Batch adsorption experiments

Batch adsorption experiments were carried out by shaking a mixture of a given amount of seed powder and 50 mL of chromium solution in a 400 mL cylindrical reactor. The reactor was placed in a temperature-controlled water bath equipped with mechanical stirrer. The stirring rate was kept constant at 250 rpm for all the adsorption experiments. The initial pH of the chromium solutions was monitored by adding 0.1 M HCl and 0.1 M NaOH solution as required, and was measured by a Hanna HI 221 pH meter (Japan). After the fixed contact time, the powder was removed by filtration using filter paper (Whatman No. 3). The concentrations of Cr(VI) in the filtrate were determined at 540 nm according to the spectrophotometric standard method using 1,5-diphenylcarbazide reagent [14]. The percentage removal of Cr(VI) ions, denoted y, was computed using the following equation:

$$y\,(\%) = \left(\frac{C_0 - C_f}{C_0}\right) \times 100 \tag{1}$$

where C_0 and C_f are the initial and final Cr(VI) concentrations, respectively.

2.3. Taguchi method

Using the Taguchi experimental design method, an orthogonal array of L_{18} type with five parameters, each at three levels, was selected for this study [12]. L means Latin square and 18 denotes the experiment number of the matrix. The five chosen parameters for this adsorption study were initial pH of solution (pH_0), adsorbent dose (m) in g/L, initial concentration of metal (C_0) in mg/L, time of contact (t) in min and temperature (T) in °C. The levels of these parameters (in coded and actual values) and the L_{18} orthogonal array with 5 columns and 18 rows used are shown in Table 1. Each row of the design represents an experiment, which was repeated under the same conditions three times.

The Taguchi orthogonal array design uses a generic S/N ratio as a quantitative measure for process optimization more economically. Usually, three categories of S/N ratio analysis are applicable, namely: lower is better (LB), nominal is best (NB), and higher is better (HB). In order to maximize the Cr(VI) adsorption yield, the HB characteristics is adopted, in which the S/N ratio (denoted η and expressed in a decibel scale, dB) is evaluated by the following equation [15,16]:

$$\eta = -10 \times \log\left(\frac{1}{r}\sum_{i=1}^{r}\frac{1}{y_i^2}\right) \tag{2}$$

where r is the replication number of the experiment. The overall mean value of S/N ratio is expressed as:

$$\eta_m = \frac{1}{n}\sum_{i=1}^{n}\left(\eta_i\right) \tag{3}$$

where n is the number of experiments in the orthogonal array and η_i is the mean S/N ratio for the ith experiment. Furthermore, signal to noise ratio and ANOVA were performed to evaluate the effects of selected parameters and to optimize removal process efficiency. Finally, confirmation experiments were conducted at optimum values of the process parameters.

3. Results and discussion

3.1. Effect of controllable parameters on Cr(VI) removal

The results of the Cr(VI) adsorption and S/N ratio values for the 18 sets of experiments are shown in Table 1. According to these data, experiment no. 3 gave the highest mean yield (87.69%) of Cr(VI) removal and had the largest S/N ratio (38.86). Experiment no. 16 showed the lowest yield of Cr(VI) removal, at 20.78%.

Table 2 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), absorbent dose at level 3 (6.0 g/L), initial metal concentration at level 1 (30 mg/L), temperature at level 3 (55°C), and contact time at level 3 (80 min). Thus, the optimal combination of process parameter levels for maximum removal of Cr(VI) is $pH_0 1$ $m3$ $C_0 1$ $T3$ $t3$. Table 2 shows also the difference between level 3 (L3) and level 1 (L1) of mean S/N ratio values for each parameter. The effect of a parameter is defined as the absolute difference between the average S/N ratios of two levels. The parameter with highest absolute difference value indicates higher significance on the response characteristic.

Table 1
Experimental results and S/N ratio values for Cr(VI) removal

Essay	Control parameters										Removal (%)				η
	In coded values					In actual values					y_1	y_2	y_3	y_m	
	pH_0	m	C_0	T	t	pH_0	m	C_0	T	t					
1	1	1	1	1	1	1	2	30	25	20	41.38	44.63	42.44	42.81	36.62
2	1	2	2	2	2	1	4	75	40	50	64.23	66.11	65.05	65.13	36.27
3	1	3	3	3	3	1	6	120	55	80	87.29	87.67	88.10	87.69	38.86
4	2	1	1	2	2	2	2	30	40	50	41.23	39.02	42.73	41.00	32.24
5	2	2	2	3	3	2	4	75	55	80	59.70	59.47	58.75	59.31	35.46
6	2	3	3	1	1	2	6	120	25	20	57.12	55.42	55.64	56.06	34.97
7	3	1	2	1	3	3	2	75	25	80	15.47	19.94	16.66	17.36	24.65
8	3	2	3	2	1	3	4	120	40	20	14.93	15.95	15.44	15.44	23.76
9	3	3	1	3	2	3	6	30	55	50	24.59	26.44	23.48	24.84	27.87
10	1	1	3	3	2	1	2	120	55	50	53.32	49.25	51.67	51.41	34.21
11	1	2	1	1	3	1	4	30	25	80	80.21	80.03	80.43	80.22	38.09
12	1	3	2	2	1	1	6	75	40	20	65.11	65.78	65.22	65.37	36.31
13	2	1	2	3	1	2	2	75	55	20	33.49	34.01	33.37	33.62	30.53
14	2	2	3	1	2	2	4	120	25	50	49.85	51.84	50.57	50.75	34.11
15	2	3	1	2	3	2	6	30	40	80	78.82	78.88	78.66	78.79	37.93
16	3	1	3	2	3	3	2	120	40	80	20.54	21.41	20.41	20.78	26.35
17	3	2	1	3	1	3	4	30	55	20	21.24	20.92	22.04	21.40	26.60
18	3	3	2	1	2	3	6	75	25	50	21.65	23.47	22.01	22.38	26.98

Under the experimental conditions of the study, it was found that the initial pH of the solution had the most significant effect on the adsorption process as it had the largest absolute difference (10.2) followed by adsorbent dose (3.72) and time of contact (2.76). However, the effects of initial Cr(VI) concentration and temperature were found to be insignificant as the absolute differences (0.52 and 0.35, respectively) were relatively small comparing to those of other parameters. The positive difference for adsorbent dose, time of contact, and temperature indicates an effect to increase Cr(VI) removal, while the negative difference for initial pH of the solution and initial Cr(VI) concentration reveals the opposite effect. The representation of the effects of individual controllable parameters at different levels is given by Fig. 1.

3.2. Analysis of variance

ANOVA is a statistical method for determining the significance of the process parameters affecting the quality characteristic [17]. A parameter is considered to be significant if its influence is large compared with the experimental error, as estimated by the ANOVA. The relevant parameters used in ANOVA are sum of squares (SS), variance (V), F-ratio (F), and percentage contribution (ρ_p). Table 3 shows the results of the ANOVA, which performed at a level of confidence of 95%. Greater F-ratio value and percentage contribution (ρ_p) for a parameter determine higher impact of the parameter on the percentage of Cr(VI) removal. According to these results, the parameters affecting the adsorption process are, in decreasing order of importance, initial pH of the mixture, adsorbent dose, and contact time. However, initial pH of the solution, with F-ratio value of 258.717 and percentage contribution equal to 82.48%, was determined to be the most significant parameter affecting the Cr(VI) removal from aqueous solution by PPSOCP. The remaining parameters, that is, initial concentration of metal and temperature were found to be not significant since their F-ratios are lower than the critical value of 4.7374.

Table 2
Mean S/N ratios and main effects of design parameters

Parameters	Mean S/N ratios			L3 – L1
	L1	L2	L3	
pH_0	36.06	34.21	26.03	–10.20
m	30.10	32.38	33.82	3.72
C_0	32.56	31.70	32.04	–0.52
T	31.90	32.14	32.26	0.35
t	30.80	31.95	33.55	2.76

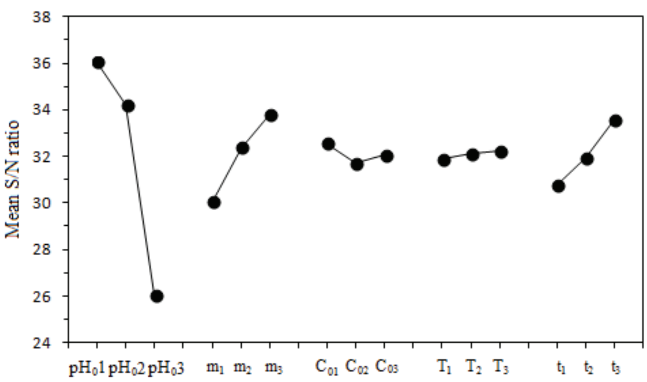

Fig. 1. Effect of each process parameter on the S/N ratio.

3.3. Confirmation experiments

Once the optimal level of design parameters has been determined, the final step of Taguchi method is to predict and verify the quality characteristic using the optimal parametric combination. The predicted S/N ratio (η_{opt}) using the optimal level of the design parameters can be calculated as given by Eq. (4):

$$\eta_{opt} = \eta_m + \sum_{i=1}^{k}\left(\bar{\eta}_i - \eta_m\right) \quad (4)$$

where $\bar{\eta}_i$ is the mean value of S/N ratio at the optimum level of the parameter and k is the repetition of each optimum level of the parameter. For that purpose, five confirmation experiments were performed using the optimal combination of process parameters. The average value of the characteristic is obtained and compared with the predicted value. Table 4 shows good agreement between the predicted and actual values of percentage removal of Cr(VI).

3.4. Multiple linear regression model

A multiple linear regression equation was developed to correlate Cr(VI) removal with the five controllable parameters. The regression equation developed is given by Eq. (5) with the determination coefficient (R^2) being equal to 0.9574.

Table 3
Analysis of variance for chromium(VI) removal

Source	df	SS	V	F-ratio	ρ_p (%)
pH_0	2	341.347	170.674	258.72*	82.48
m	2	42.262	21.131	32.03*	10.21
C_0	2	2.232	1.116	1.69	0.54
T	2	0.393	0.196	0.30	0.10
t	2	22.999	11.500	17.43*	5.56
Error	7	4.618	0.660		1.11
Total	17	413.851			100

Tabulated F-ratio at 95% confidence level: F (0.05,2,7) = 4.74.
*Significant at 95% confidence level.

Table 4
Results of confirmation experiments for Cr(VI) removal

	Optimal removal parameters	
	Predict	Experiment
Level	$pH_0$1 m3 $C_0$1 T3 t3	$pH_0$1 m3 $C_0$1 T3 t3
% Removal	98.24	98.68
S/N Ratio	39.85	39.88

$$\text{Cr(VI) removal (\%)} = 53.91 - 22.54\ \text{pH}_0 + 106.76\ m - 0.013\ C_0 + 0.048\ T + 0.304\ t \quad (5)$$

The closer the determination coefficient (R^2) value to unity, the stronger the model is and the better it predicts Cr(VI) removal. Thus, the developed model can be used for estimating Cr(VI) adsorption efficiency in the design stage of removal by prickly pear seeds.

4. Conclusion

Taguchi L_{18} orthogonal array design of experiments has been used to investigate the effects of five control factors on the Cr(VI) removal from aqueous solutions by seed powder of prickly pear fruits. Based on S/N ratio, the optimum removal conditions were initial pH of 1, adsorbent dose of 6.0 g/L, time of contact of 80 min, initial concentration of metal of 30 mg/L, and temperature of 55°C. A removal of 98.24% was obtained at these optimum conditions. The ANOVA showed that initial pH of the solution, adsorbent dose, and contact time were the parameters affecting the adsorption efficiency, where initial pH was the most prominent. The percentage contribution of each controllable parameter in descending order was found to be as: pH_0 (82.48%), m (10.21%), t (5.56%), C_0 (0.54%), and T (0.10%). This study showed that the Taguchi method was suitable to optimize the Cr(VI) removal experiments and the seed powder of prickly pear fruits exhibited high adsorption capacities.

References

[1] S. Srivastava, S.B. Agrawal, M.K. Mondal, Characterization, isotherm and kinetic study of *Phaseolus vulgaris* husk as an innovative adsorbent for Cr(VI) removal, Korean J. Chem. Eng., 33 (2016) 567–575.

[2] M.S. Vale, R.F. Nascimento, R.C. Leitao, S.T. Santaella, Cr and Zn biosorption by *Aspergillus niger*, Environ. Earth Sci., 75 (2016) 462.

[3] EPA (Environmental Protection Agency), Environmental Pollution Control Alternatives, EPA/625/5–90/025, EPA/625/4–89/023, Cincinnati, USA, 1990.

[4] R. Pundir, G.H.V.C. Chary, M.G. Dastidar, Application of Taguchi method for optimizing the process parameters for the removal of copper and nickel by growing *Aspergillus* sp, Water Resour. Ind., (2016). http://dx.doi.org/10.1016/j. wri.2016.05.001i.

[5] K. Huang, Y. Xiu, H. Zhu, Selective removal of Cr(VI) from aqueous solution by adsorption on mangosteen peel, Environ. Sci. Pollut. Res., 20 (2013) 5930–5938.

[6] S.S. Pillai, M.D. Mullassery, N.B. Fernandez, N. Girija, P. Geetha, M. Koshy, Biosorption of Cr(VI) from aqueous solution by chemically modified potato starch: equilibrium and kinetic studies, Ecotoxicol. Environ. Saf., 92 (2013) 199–205.

[7] S. Zheng, H. Huang, R. Zhang, L. Cao, Removal of Cr(VI) from aqueous solutions by fruiting bodies of the jelly fungus (*Auricularia polytricha*), Appl. Microbiol. Biotechnol., 98 (2014) 8729–8736.

[8] S. Sarkar, S.K. Das, Removal of Cr(VI) and Cu(II) ions from aqueous solution by rice husk ash—column studies, Desal. Wat. Treat., 57 (2016) 20340–20349.

[9] M.S. Phadke, Quality Engineering Using Robust Design, Prentice Hall, Englewood Cliffs, New Jersey, 1989.

[10] J. Zolgharnein, N. Asanjarani, T. Shariatmanesh, Taguchi L_{16} orthogonal array optimization for Cd (II) removal using *Carpinus betulus* tree leaves: adsorption characterization, Int. Biodeterior. Biodegrad., 85 (2013) 66–77.

[11] U. Özdemir, B. Ozbay, I. Ozbay, S. Veli, Application of Taguchi L_{32} orthogonal array design to optimize copper biosorption by using *Spaghnum* moss, Ecotoxicol. Environ. Saf., 107 (2014) 229–235.

[12] H.Y. Yen, J.Y. Li, Process optimization for Ni(II) removal from wastewater by calcined oyster shell powders using Taguchi method, J. Environ. Manage., 161 (2015) 344–349.

[13] H.Y. Yen, Taguchi optimization for Cd(II) removal from aqueous solutions using oyster shell powders, Desal. Wat. Treat., 57 (2016) 20430–20438.

[14] L.S. Clesceri, A.E. Greenberg, Standard Methods of the Examination of Water and Wastewater, 20th ed., American Public Environment Federation, Washington, 1998.

[15] P. Ross, G. Taguchi, Techniques for Quality Engineering, McGraw-Hill International Editions, Singapore, 1996.

[16] O. Tan, A.S. Zaimoglu, S. Hinislioglu, S. Altun, Taguchi approach for optimization of the bleeding on cement-based grouts, Tunnelling Underground Space Technol., 20 (2005) 167–173.

[17] W.H. Yang, Y.S. Tarng, Design optimization of cutting parameters for turning operations based on Taguchi method, J. Mater. Process. Technol., 84 (1998) 122–129.