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Response Surface Optimization of Fixed Bed Adsorption of Cr⁺⁶ Onto Low-Cost Adsorbent

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Abstract

The paper emphasizes the removal of Chromium from tanning industry effluent using adsorption as a cost effective option. The essential source of contamination identified from variable amounts of liquid discharges was Chromium (Cr⁺⁶). A column study was carried out using Shrimp shell waste (SSW) as an adsorbent in the removal of Cr⁺⁶ ion from synthetic solutions. Operational factors such as the size of adsorbent, bed depth and compared their adsorption capacities thereof. For a given size, the adsorption capacity increased by a reduction in the amount of Chromium. The Cr+6 removal based on adsorbent size was in the order: 150 microns> 300 microns> 600 microns. The experimental data was optimized and modelled using Response Surface method, and a 2³ factorial Central composite design (CCD) was applied, and the data was analyzed for ANOVA. A *P*-Value<0.005 indicated that the probability of the experimental results was significant.

Introduction

Tannery effluents are rampant as the most noteworthy pollutants among every industrial waste generating vast amounts of Chromium. For example, in India alone, around 2000–3000 tons of Cr^{+6} escapes into the water environment every year from tanneries. The permissible Chromium suggested is 2 mg/l, whereas it is extending in the range of 2000 and 5000 mg/l in the wastewaters.¹

The elevated concentrations of Chromium may cause many toxic, mutagenic and carcinogenic health effects. Out of the three oxidation states of Chromium, the Cr⁺³ is the most stable. The Cr⁺³ is essential in trace amounts required by humans, though unstable in a water environment because of its lower solubility in water. The Cr⁺⁶ concentration ranges in 0.5 to 270 mg/L in industrial effluents, which is highly toxic to many living beings, including

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Keywords

Adsorption; ANOVA; Chromium; Column Study; Response Surface Method; SSW. plants and animals.² The discharges of Cr^{+6} have tolerance limits of 0.1 mg/L (into inland surface waters), 0.05 mg/L (into potable water).^{3,4}

Numerous Chromium removal technologies are employed which include reduction,⁵ chemical precipitation, electrochemical precipitation, ion exchange, adsorption, solvent extraction, and bio-sorption,⁶ membrane separation,⁷ reverse osmosis and Nanofiltration,⁸ emulsion per traction technology,⁹ Out of various demerits of these methods, the most important being uneconomical. Adsorption technology is considered because of its cost-effectiveness and regenerative nature. Adsorption can remove variable pollutants such as heavy metals, dyes, phenols etc.^{10, 11}

Response surface method was used by many researchers in the optimization of various process parameters in the adsorption process. Several studies are detrimental towards the use of many low-cost adsorbents including agricultural wastes, fruit wastes, microbes, industrial wastes, sludge and so on.¹²⁻²⁰

In this paper, the efficiency of Shrimp shells powder in the elimination of Chromium the from aqueous media was studied. The removal efficiency of SSW powder is tested for variable particle sizes, bed depths and a comparative study has also been done.²⁰ To optimize and reduce the experimental complexity, time, the response surface methodology was used for process optimization.

Materials and Methods Preparation of Stock Solution

A known quantity of 0.2828 gms of Potassium Dichromate ($K_2Cr_2O_7$) was dissolved in 100ml of de-ionized water to prepare the standard solutions of Cr(VI) of 1000 ppm concentration. Subsequent dilutions were made from the standard solutions for performing the experiments; the initial (50 mg/L) and final concentrations were obtained from UV-Vis spectrophotometer having wavelength range between 520-550 nm.²¹ The pH of the samples was regulated with acid (HCI) and base (NaCI). The oxidation of Cr⁺³ to Cr⁺⁶ is required to be done before the analysis of each sample to reduce Cr⁺⁶ to Cr⁺³.

Preparation of Shrimp Shell Powder

The Shrimp shell waste was obtained from a seafood processing unit; after collection, they were washed, dried and roughly ground to powder. Afterwards, the powder was soaked in HCl overnight, then treated with a base (NaCl) to remove any traces of acid and then rinsed with de-ionized water thoroughly to attain neutral pH. Now washed material was sun-dried and then in an oven at $103\pm2^{\circ}$ C. The so dried powder was named as Shrimp shell waste (SSW) powder was further crushed, and after sieving, the obtained particle sizes were 150 microns, 300 microns and 600 microns. These three powders having variable sizes were stored in air-tight bags for experimental use.

Continuous Fixed Bed Column Studies

A column with 2.5 cm internal diameter and having bed height 50 cm was set-up in a laboratory for conducting continuous fixed-bed column studies. A known quantity of freshly ground SSW powder was filled in the column bed for each set of experiments with varying bed depths and adsorbent sizes, respectively. The metal solution of known initial concentration (C_i) selected based on industrial range²² was continuously pumped using a peristaltic pump with a flow rate of (V = 5 mL /min, for all the experimental sets. The metal adsorption capacity can be estimated by the equation given below:

 Cr^{+6} adsorption Capacity (mg/g) = $(C_i - C_p)^*V/M$

Where, C_{e} and M being the equilibrium concentration of the Cr^{+6} ion and weight of the adsorbent used in the column.

Central Composite Design (CCD)

The extensively employed model for fitting is CCD in Response Surface Methodology. In this method, only a minimum number of experiments are required for experimental modelling. Usually, the Central Composite Design (CCD) involves a 2ⁿ factorial and n^c centre runs (six replicates). The response surface models using ANOVA (Analysis of Variance) have arrived from the respective experimental responses and the corresponding optimized factors. Also, the statistical parameters were estimated using response surface methods. Essentially, the process optimization comprises of three chief steps, to carry out the design of experiments (DOE), using a mathematical model for coefficient calculation and response prediction and to examine the appropriateness of the model.

Time (Hrs)	Cr* ⁶ Conc. (mg/L) = 50 mg/L								
(1115)	BD=20 cm			BD= 40 cm			BD= 60 cm		
	Α	В	С	Α	В	С	Α	В	С
0.5	16.42	18.53	22.98	14.77	27.34	30.99	20.98	23.75	34.32
1	9.67	8.43	17.65	8.02	14.78	18.43	14.23	17	21.76
1.5	7.49	6.45	13.09	5.87	10.54	14.19	12.05	14.82	17.52
2	6.24	5.87	8.54	4.59	6.54	9.76	10.8	15.88	13.09
2.5	5.56	7.9	7.65	3.91	5.32	8.97	8.12	12.65	12.3
3	4.65	16.96	7.34	3.33	7.54	13.87	3.87	8.55	7.45
3.5	3.98	26.09	10.67	2.99	12.76	22.76	2.23	5.13	10.43
4	3.56	34.45	16.86	18	20.66	27.45	9.65	14.78	16.75
4.5	5.56	42.68	22.87	24.01	27.44	34.87	13.87	21.66	22.9
5	12.76	43.21	29.33	30.47	32.89	38.76	18.55	27.31	28.09
5.5	19.64	44.9	35.89	37.03	38.54	41.66	27.43	32.65	32.67
6	28.64	45.96	39.65	40.79	42.3	43.78	34.87	39.76	38.15
6.5	37.96	44.67	43.02	44.16	43.99	44.74	39.77	40.32	40.43
7	45.89	43.86	42.66	43.8	44.67	45.43	41.22	41.17	41.21
7.5	47.65	43.33	41.76	42.9	45.31	46.55	43.86	42.33	42.77
8	47.08	43.05	41.34	42.48	46.76	47.44	44.12	43.44	43.9

Table.1 Adsorbate Concentration w.r.t Bed Depth at various time intervals

Results and Discussion

Influence of Size on Adsorption Capacity

Replicates of column experiments with the three selected adsorbent sizes 150, 300 and 600 microns were conducted with an initial Cr⁺⁶ concentration of 50 ppm. A total of nine experimental sets were constructed in the study with varying factors, as discussed earlier. Table.1 Shows the concentration of Cr⁺⁶ with time from 0.5 to 8.0 hrs in column adsorption. It was noticed that the metal ion removal increased till a specific time increment and later on, it gradually decreased as it reached saturation of the adsorbent material. A fresh adsorbent was used for each experimental set-up, and the adsorption capacity was observed for the factors mentioned above with three levels. The mean of the replicates calculated for all the three adsorbent sizes and the values are given in Table.1. The column breakthrough analysis gives an idea on the saturation time of an adsorbent and the extent of adsorption, which can therefore be compared with other adsorbents for their suitability analysis. The breakthrough curves for the selected adsorbent size were plotted for 20 cm, 40 cm and 60 cm bed depths as shown in Fig.1 a), b) & c). It is evident that the smallest sized adsorbent, i.e. 150 µm reached the breakthrough (equilibrium) concentration first than others. The highest performance (removal) was 2.23 ppm, 5.13 ppm and 7.45 ppm shown in the order 150 µm > 300 μ m > 600 μ m size, respectively. The above particulars illustrate, smaller the adsorbent size, greater the adsorption capacity and though the surface area of the smaller particles is less but more number of such particles occupy the column might be the reason.



Where, A-150 µm, B-300 µm, C-600 µm, BD-Bed Depth

Fig. 1 The breakthrough curves for Time versus Equilibrium concentration for various sizes a), b),c) and for Bed depth d), e) & f)

Influence of Bed Depth on Adsorption Capacity Table.1 shows the influence of bed depth on the

outlet Chromium concentration in the adsorption. The maximum adsorption was found to be at 60 cm. The maximum adsorption capacity was 231.65 ppm, at 150 μ m, respectively. This adsorption indicates that as the depth of the adsorption bed increases the removal also increases. The reason behind this

might be because of an extra dose of adsorbent in the glass column. More the depth of the adsorbent, the metal water passes through the additional layers of adsorbent and increases the travel time along with adsorption. The breakthrough curves can be seen in Fig.1 d), e) & f) show that in all the three cases, the adsorption capacity increased with bed depth.

			Factor 1	Factor 2	Response 1
 Std	Group	Run	a: Size µm	B: Bed Depth cm	Adsorption Capacity mg/g
9	1	1	150	40	126.45
8	1	2	150	40	125.34
2	2	3	150	60	231.65
1	2	4	150	20	105.43
19	3	5	375	40	87.44
18	3	6	375	40	85.44
17	3	7	375	40	86.31
13	4	8	375	60	98.45
12	4	9	375	20	67.44
16	5	10	375	40	75.76
14	5	11	375	40	77.32
15	5	12	375	40	76.45
7	6	13	375	40	75.34
5	6	14	375	40	77.32
6	6	15	375	40	75.34
10	7	16	600	40	56.45
11	7	17	600	40	57.34
4	8	18	600	60	65.34
 3	8	19	600	20	51.22

Table 2: CCD f	or Cr ⁺⁶ foi	factors size	and bed	depth
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Table 3: Response in CCD design values for Cr⁺⁶ adsorption

Soι	urce -	Term df	Error df	F-value	p-value	
Who a-S a ² B ² Sub B-B aB	ole-plot ize oplot 2 ied Depth	3 1 1 2 1 1	3.99 4.07 3.94 4.02 8.79 8.79 8.79	19.69 50.68 4.02 2.16 69.02 84.07 53.97	0.0075 0.0019 0.1165 0.2157 < 0.0001 < 0.0001 < 0.0001	significant



Fig.2: Response surface plot for Cr⁺⁶

Table 4: Fit Statistics for Cr⁺⁶ adsorption

Std. Dev.	13.70	R ²	0.9671
Mean	89.57	Adjusted	0.9461
C.V. %	15.29	R ²	

Optimization using Response Surface

CCD in Response surface method full factorial is used to optimize the experiments, and Table.2 shows the details of runs conducted in the test. The maximum adsorption capacity was obtained in the 3rd run at 231.65 mg/g for adsorbent size 150 μ m and a bed depth of 60 cm. It is evident from the 3D response surface plot in Fig. 2 that the optimum parameters for effective adsorption are 150 μ m and 60 cm and the design values are almost on par with the experimental values. The P-value and F-value in ANOVA are also shown in Table.3 where P<0.0.5 specify model is significant. The fit statistics from Table.4 shows that R² = 0.96, which is a good fit for the selected model.

Conclusion

Chromium ion was eliminated from aqueous media fixed in a continuous column using various particle sizes of SSW powder. The chosen adsorbent can be considered as a reusable waste material for industrial effluent treatment in terms of economic sense. The adsorption capacity is less for low concentrations of Cr⁺⁶, however, it increased with time for the lower initial concentration. Fresh SSW powder with 150 micron size used in column adsorption for 8 hours can bring down Chromium concentration from 50 ppm to 3 ppm. The adsorption capacity of Cr⁺⁶ using SSW adsorbent were as follows: 150 microns> 300 microns> 600 microns. The response surface optimization model was successful in the study using SSW as adsorbent material. ANOVA in the response surface modelling results indicated a good fit for the adsorption. The adsorbent regeneration is irrelevant in the case of low-cost adsorbents as vast amounts of sea waste is being generated and dumped daily. The SSW as an adsorbent addresses a two-fold advantage in terms of reuse of waste as well as the waste disposal aspect mainly in developing countries.

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Conflict of Interest

The authors do not have any conflict of interest.

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