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Adsorption study of chromium(VI) by dried biomass of tea leaves

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Chromium contamination has increased in the last few years in industrial effluents. Environmental Protection Act has set an enforceable Criteria Maximum Concentration (CMC) level of total chromium in freshwater as 16 µg/L. The aim of this study was to investigate the Cr^{VI} adsorption on used and dried tea leaves (*Camellia sinensis*). The parameters used to study the adsorption behaviour of chromium on tea leaves were pH of the reaction mixture, initial chromium concentration, dried biomass of tea leaves and agitation speed. The batch kinetic studies showed that adsorption had increased with increase in dried biomass and decrease in pH. No significant variation in the removal efficiency was seen with the increase in agitation speed. Response Surface Methodology was used as a tool of varying multiple experimental parameters simultaneously to get the output. Maximum removal efficiency (84.57%) was obtained after 24 h at pH 5.7; initial chromium concentration of 19.9 mg/L, agitation of 4.2 rpm and dried biomass of 1.5 g. Successful adsorption by tea leaves had been further confirmed by Scanning Electron Microscope, which showed the appearance of smoother surface after adsorption.

Keywords: *Camellia sinensis*, wastewater, chromium, response surface methodology, scanning electron microscope.

1. Introduction

Chromium is one of the most widely used industrial metals. Due to its wide applications, contamination of chromium has increased in the last years in industrial effluents[1]. US Environmental Protection Act has set an enforceable Criteria Maximum Concentration (CMC) level of total chromium in freshwater as 16 µg/L[2]. Chromium exists in several oxidation states, but the most stable and common forms are Cr^0, the trivalent Cr^{III}, and the hexavalent Cr^{VI}. Cr^{VI} is considered the most toxic forms of chromium. It has been reported to cause severe eye irritations, skin ulcers, liver disorder, renal failure, intravascular haemolysis, reproductive and development effects and cardiovascular effects leading to death[3,4]. Cr^{III} is less toxic as it is relatively insoluble in water, presents lower mobility, and is mainly bound to organic matter in soil and aquatic environments. Chemical methods of chromium removal are quite effective in removing it from industrial effluent but are expensive and often cause disposal problem of toxic sludge generated. Biodegradation by microorganisms are cost-effective but thick biofilm may cause diffusion barrier for the chromium. Physical methods such as adsorption offers significant advantages like cost-effective, availability, simple design, ease of operations and efficiency in comparison with other methods[5–9].

The objectives of this study were to investigate the potential of dried mass of used tea leaves (*Camellia sinensis*) as an adsorbent to remove chromium from aqueous solution. *Camellia sinensis* is a species of plant which is used to produce tea. India is a land of tea lovers. India produces approximately 715,000 tonnes of tea every year, thereby making it leading producer of tea after China. But in most cases the tea leaves are disposed off after one time use, thereby generating huge tea leaf wastes. These tea leaves can adsorb a number of heavy metal ions[10]. The parameters used to study the adsorption behaviour of chromium on tea leaves were pH of the reaction mixture, initial chromium concentration, dried biomass of tea leaves and agitation speed.

Conventional methods of adsorption studies consist of only one variable at a time while maintaining others constant. These techniques require many experimental runs making it more time consuming. They also eliminate the interaction effects of other parameters, thereby leading to false optimal conditions. Design of Experts (DOE) is a structured method of varying multiple experimental parameters simultaneously to get effects in the output. It can identify the factors that can cause change in response. It is also used to study a large number of variables in a small number of experimental runs[11]. Response Surface Methodology is one of these tools which can determine the optimal operating conditions of a system[12,13].

2. Experimental

2.1. Preparation of adsorbent:

Waste tea leaves were obtained from a nearby stall and were boiled further for at least ten to fifteen times until a colorless filtrate was obtained. The decolorized leaves were continued to dry in an oven at around 105ºC until constant weight was obtained. After drying, dried leaves were ground to fine powders or dust in a grinder. Dusts were collected by passing through a sieve of 0.05 cm diameter. Selected dried leaves powder were kept in an air tight container at room temperature for adsorption studies.

2.2. Batch adsorption studies:

A stock solution was prepared which contains 1000 mg/L (ppm) of chromium(VI) using analytical grade potassium dichromate ($K_2Cr_2O_7$) in distilled water. The adsorption process was carried out in 250 ml flasks with dried tea leaves as adsorbent and 12.5 mg/L of Cr^{VI} solution as adsorbate. The batch adsorption studies were carried out by varying the experimental parameters namely agitation speed, dried biomass and pH. We varied one of the parameter at a time keeping the other three constant to obtain the kinetics data as shown in Table 1. The resulting mixture was then agitated in a shaker with varying speed as given in the table. This was followed by centrifugation and filtration by Whatmann Filter Paper No. 1. The filtrate containing the residual chromium was then measured by 1,5-diphenylcarbazide (1,5-DPC) and determined using a visible spectrophotometer at 540 nm.

The tables (Tables 1–3) show the different set of reactions we used:

Removal efficiency:

The percentage chromium removal efficiency (%) was calculated as follows:

Table 1. Variation in dried biomass

pH	Agitation speed (rpm)	Dried biomass (g)
7	50	1
7	50	2

Table 2. Variation in agitation speed

pH	Dried biomass (g)	Agitation speed (rpm)
7	1.5	0
7	1.5	50
7	1.5	100

Table 3. Variation in pH

Dried biomass (g)	Agitation speed (rpm)	pH
1.5	50	5
1.5	50	7
1.5	50	9

Removal efficiency = $((C_i - C_f)/C_i) \times (100)$

where C_i and C_f were the initial and final chromium concentration in the solution in mg/ml.

2.3. Optimization of process parameters for removal of chromium using Response Surface Methodology (RSM) by "Design-Expert Version 11" software:

The process parameters, like initial concentration of chromium (ppm), pH, dried biomass of tea leaves (g) and agitation speed (rpm) were taken as input variables in Response Surface Methodology. A set of thirty experiments with varied values of process parameters were suggested by the Design Expert 11 software. The output i.e. the response was chosen to be the chromium removal efficiency (%), which was found out experimentally. This response was studied and analysed by the software. All experiments were carried out for 24 h at 30ºC.

2.4. SEM analysis:

The SEM analyses of the dried tea leaves biomass (adsorbent) were carried out before and after adsorption of chromium(VI).

3. Results and discussion

3.1. Batch kinetic study of adsorption of chromium(VI) by dried tea leaves:

3.1.1. Effect of pH in chromium(VI) removal by dried tea leaves:

Chromium(VI) was removed from the solution by the dried tea leaves. As shown in the Fig. 1, best removal was obtained at pH 5 with the initial chromium concentration of 12.5

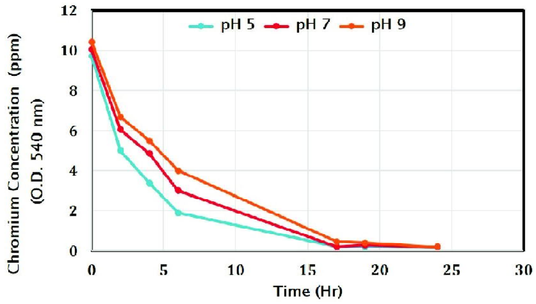


Fig. 1. Removal of chromium(VI) by dried tea leaves at different pH.

mg/L by 1.5 g of dried biomass. From the above results, it can be stated that the order of removal of chromium is pH 5 > pH 7 > pH 9. It is known that the functional group present in the tea biomass are hydroxyl group (OH) of alcohol and phenol, carbonyl group (C=O), aliphatic amines (NH_2), carboxyl group (C(=O)OH) along with some alkanes, alkenes, esters and ethers[14]. The decrease in pH results in the formation of the protonated forms of the functional groups present in the biomass. Thus the amine ($-NH_2$) groups get converted to (NH_3^+) and acquire positive charges. Chromium(VI) being present in the anionic part of the salt as chromate ($Cr_2O_7^{2-}$) interacts with the positively charged groups present on the biomass and binds the adsorbent. On the other hand, at higher pH values, the acid groups such as (COOH) on the adsorbent surface ionize to produce negatively charged ions (COO^-) which decreases the adsorption capacity.

3.1.2. Effect of dried tea leaves biomass (adsorbent mass) in chromium(VI) removal:

The result for kinetic study for removal of chromium(VI) was given in Fig. 2. It had been seen that with the increase in biomass of adsorbent form 1 g to 2 g there was an increase in chromium removal. An increase in biomass results in more

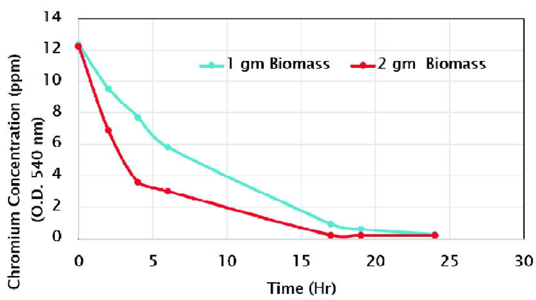


Fig. 2. Removal of chromium(VI) by dried tea leaves with different adsorbent mass.

available surface area for adsorption which in turn, leads to better removal of chromium(VI) from the solution.

3.1.3. Effect of agitation speed (rpm) in chromium(VI) removal by dried tea leaves:

As shown in Fig. 3, there was no significant variation in the removal efficiency with the change in agitation speed.

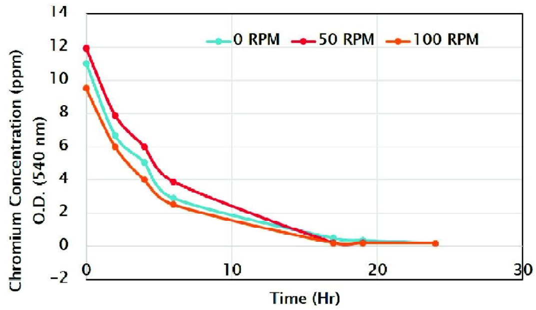


Fig. 3. Removal of chromium(VI) by dried tea leaves with different agitation speed.

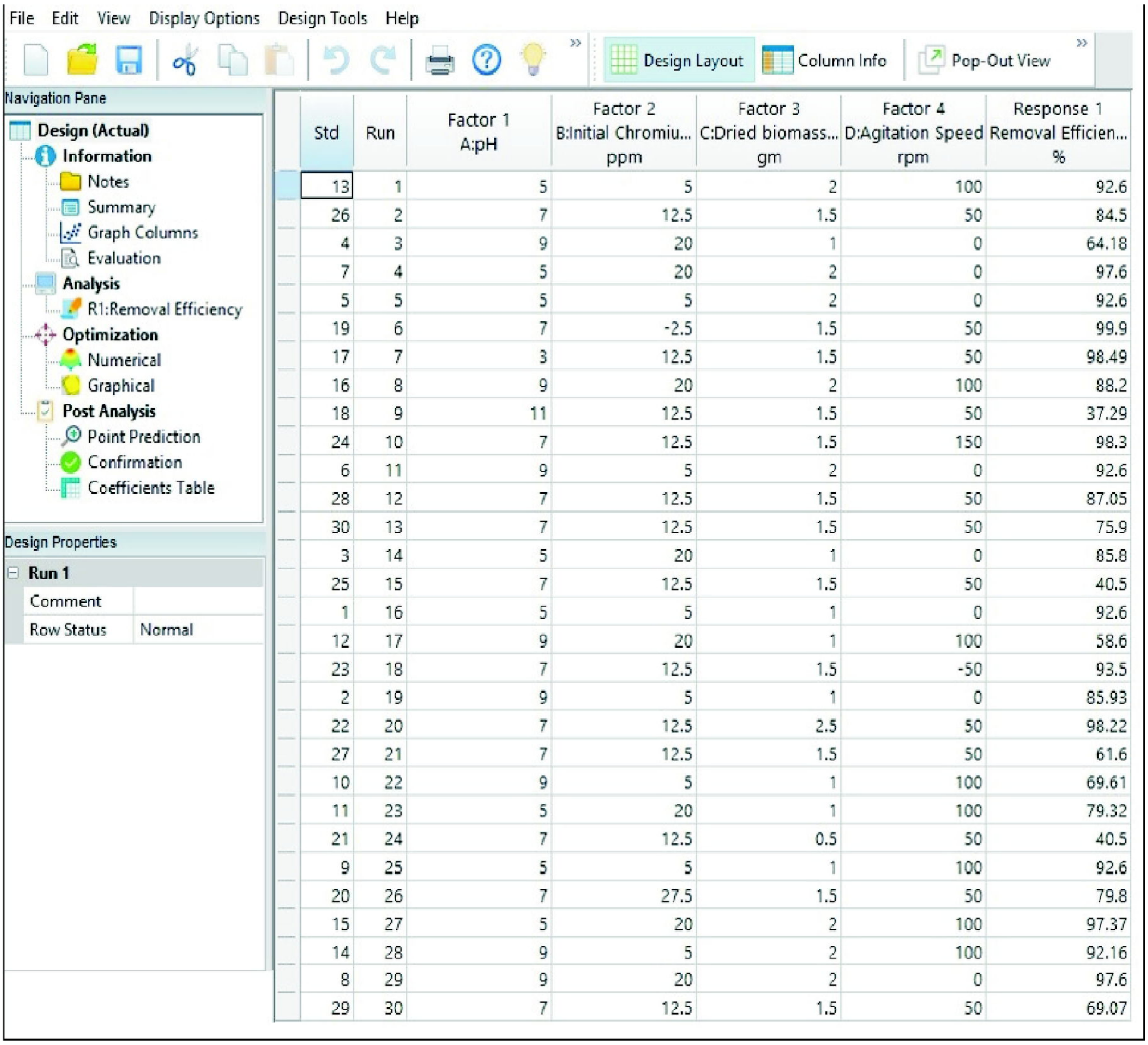
3.2. Optimization of process parameters for chromium(VI) adsorption using Response Surface Methodology:

Response Surface Methodology (RSM) was used to study the effect of different experimental conditions on chromium(VI) adsorption and getting an optimal condition for best chromium(VI) removal by dried tea leaves. The software analysed the response data and suggested the Linear model to be the best fit model. The model F-value of 5.07 implies the model is significant. There is only a 0.39% chance that a F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A (pH) and C (Dried biomass of adsorbent) are significant model terms. The Predicted R^2 of 0.2524 is in reasonable agreement with the Adjusted R^2 of 0.3595; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 7.657 in this model indicates an adequate signal. Hence, the present model provides statistically significant association between the removal efficiency and the input variables.

3.2.1. Effect of pH and initial chromium concentration on chromium removal efficiency:

Fig. 5 explains that as the pH is decreased, the adsorption efficiency increased. This is because decrease in pH results in the formation of the protonated forms of the func-



Std	Run	Factor 1 A:pH	Factor 2 B:Initial Chromiu... ppm	Factor 3 C:Dried biomass... gm	Factor 4 D:Agitation Speed rpm	Response 1 Removal Efficien... %
13	1	5	5	2	100	92.6
26	2	7	12.5	1.5	50	84.5
4	3	9	20	1	0	64.18
7	4	5	20	2	0	97.6
5	5	5	5	2	0	92.6
19	6	7	-2.5	1.5	50	99.9
17	7	3	12.5	1.5	50	98.49
16	8	9	20	2	100	88.2
18	9	11	12.5	1.5	50	37.29
24	10	7	12.5	1.5	150	98.3
6	11	9	5	2	0	92.6
28	12	7	12.5	1.5	50	87.05
30	13	7	12.5	1.5	50	75.9
3	14	5	20	1	0	85.8
25	15	7	12.5	1.5	50	40.5
1	16	5	5	1	0	92.6
12	17	9	20	1	100	58.6
23	18	7	12.5	1.5	-50	93.5
2	19	9	5	1	0	85.93
22	20	7	12.5	2.5	50	98.22
27	21	7	12.5	1.5	50	61.6
10	22	9	5	1	100	69.61
11	23	5	20	1	100	79.32
21	24	7	12.5	0.5	50	40.5
9	25	5	5	1	100	92.6
20	26	7	27.5	1.5	50	79.8
15	27	5	20	2	100	97.37
14	28	9	5	2	100	92.16
8	29	9	20	2	0	97.6
29	30	7	12.5	1.5	50	69.07

Fig. 4. Screen shot of experimental design by the software and the response.

tional groups present on the biomass which now interact strongly with more anionic part of the chromate salt ($Cr_2O_7^{2-}$). On the other hand, increase in initial chromium concentration did not have noticeable effect on removal efficiency. This may be due to the fact that increase of chromium concentration from 5 ppm to 20 ppm was not able to saturate the adsorption site of the tea leaves. So, it can be concluded that pH is more significant factor as compared to the initial chromium concentration in adsorption efficiency.

3.2.2. Effect of pH and dried biomass of tea leaves (adsorbent) on chromium removal efficiency:

Fig. 6 explains that as the mass of dried tea leaves increased from 1 g to 2 g, the adsorption efficiency also got increased due to enhanced surface area for adsorption of chromium(VI). With the decrease of the pH, removal efficiency of chromium increases as more positive charges on the adsorbent surfaces now interact strongly with more anionic part of the chromate salt ($Cr_2O_7^{2-}$). So, it can be inferred that pH and mass of dried tea leaves (adsorbent) are both significant factors in removal efficiency of chromium.

3.2.3. Effect of pH and agitation speed on chromium removal efficiency:

Fig. 7 explains that as the pH get decreased from 9 to 5, removal efficiency of chromium increased due to the increase

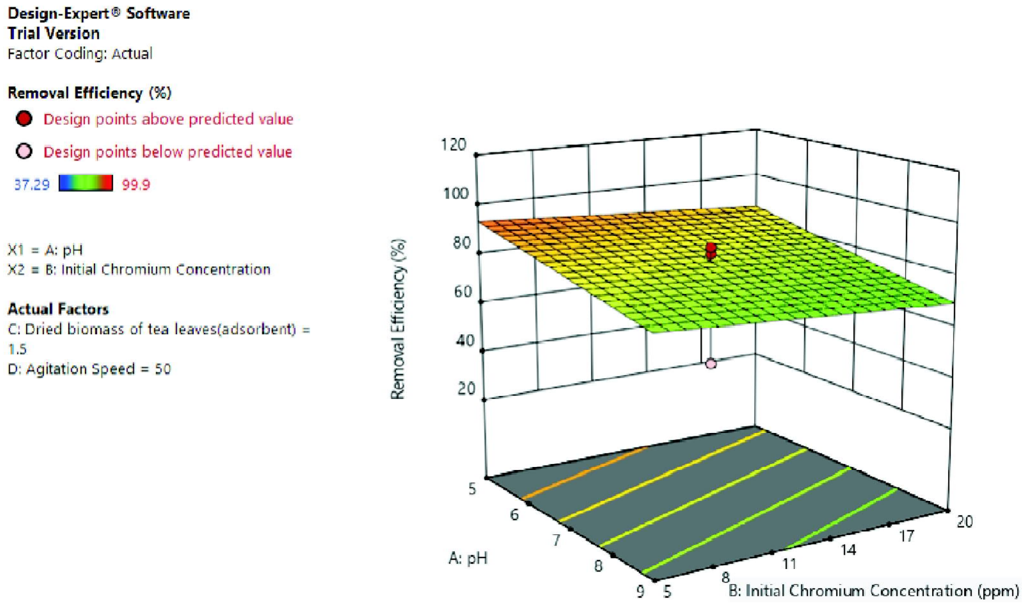


Fig. 5. Response surface 3D plot indicating the effect of interaction between initial chromium concentration and solution pH with removal efficiency.

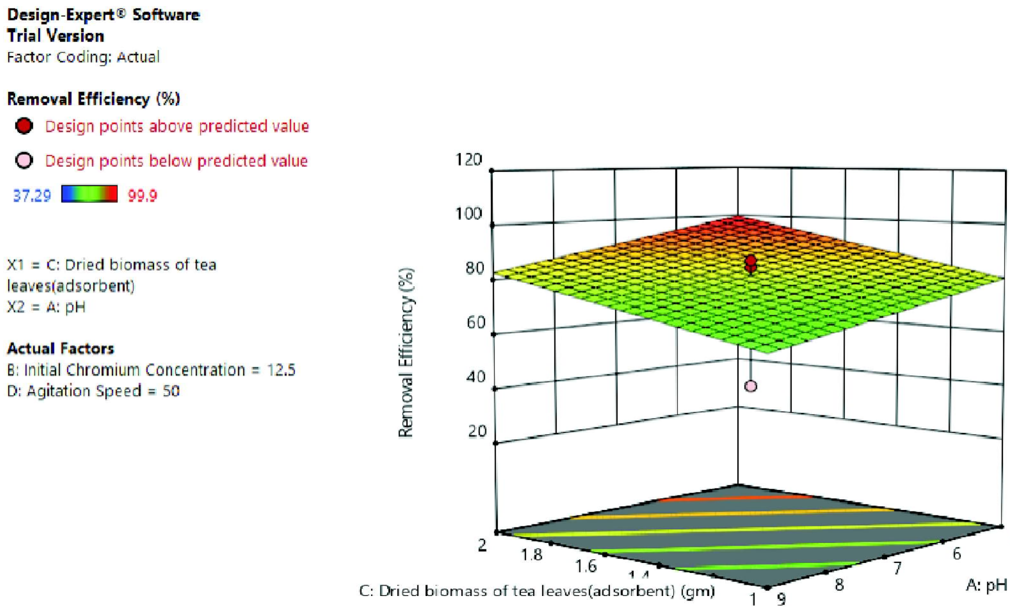


Fig. 6. Response surface 3D plot indicating the effect of interaction between adsorbent biomass and solution pH with removal efficiency.

of positively charged ions on the adsorbent surface which bind strongly with more anionic part of the chromate salt ($Cr_2O_7^{2-}$). Agitation speeds on the other hand, did not have much influence on the removal efficiency of the chromium. So it can be deduced that pH is more dominant factor as compared to the agitation speed in adsorption efficiency.

The optimized value of the process parameters for best chromium adsorption (84.57%) was obtained after running

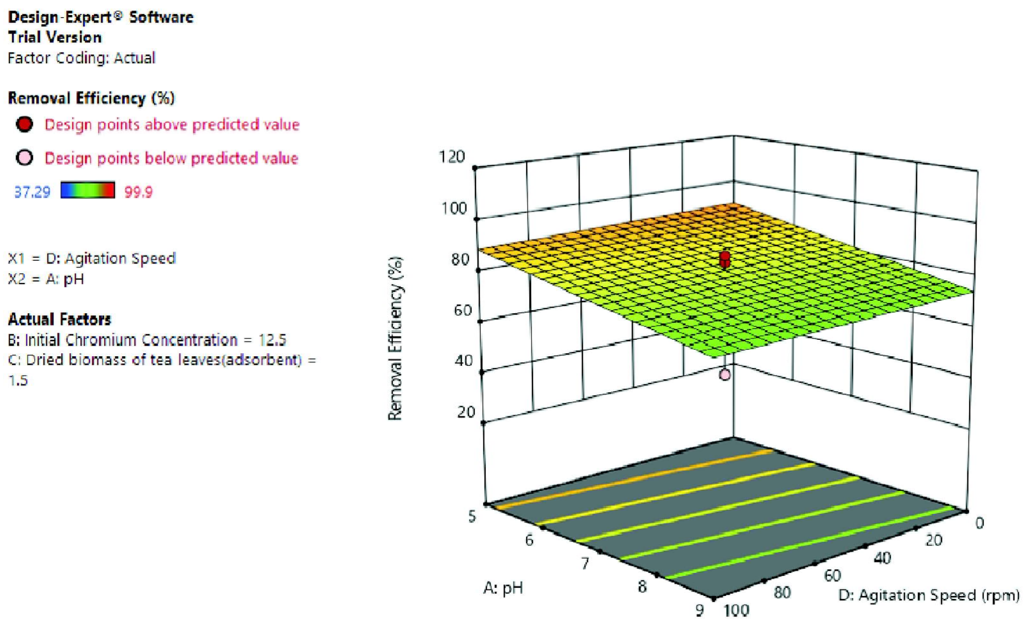


Fig. 7. Response surface 3D plot indicating the effect of interaction between agitation speed and solution pH with removal efficiency.

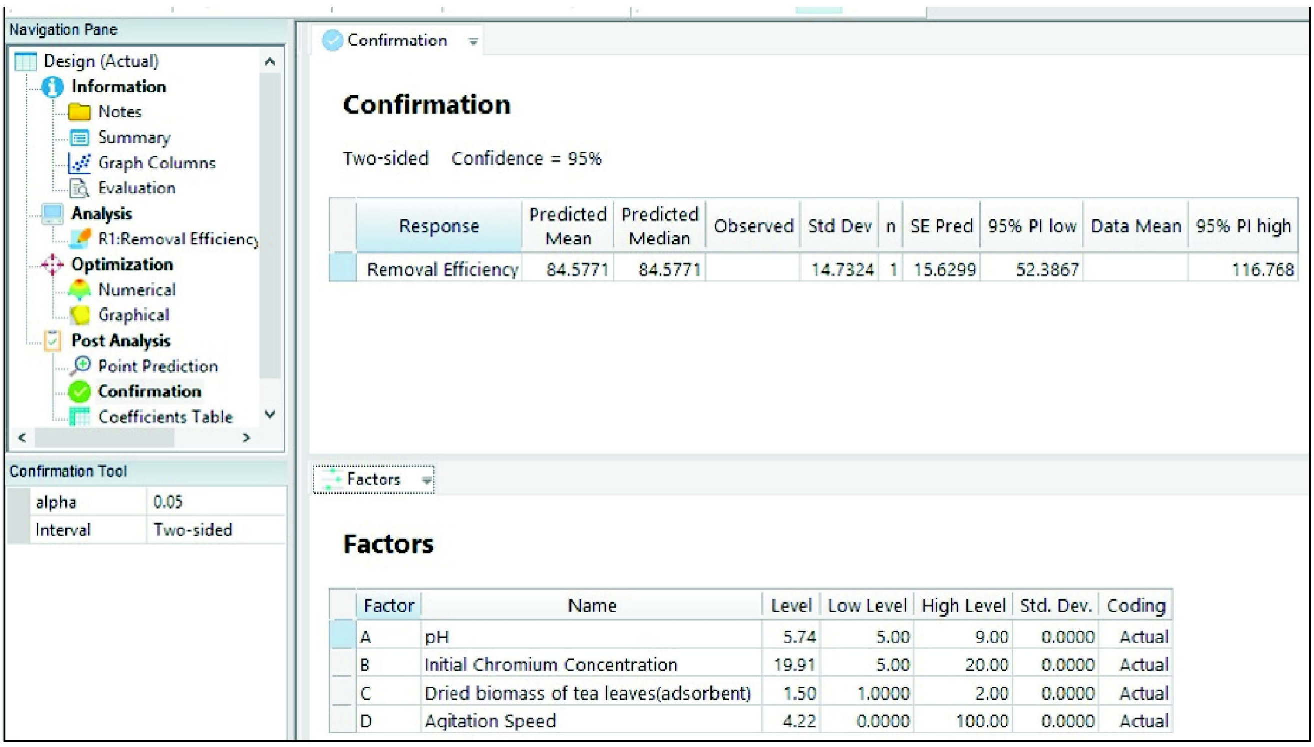


Fig. 8. Screenshot showing confirmation record of the optimized condition for maximum removal efficiency of chromium(VI) obtained by the Linear model.

the set of 30 experiments designed by Design Expert Software as given in Table 4.

Table 4. Optimized value of the parameters for chromium(VI) removal

Parameters	Optimized values
pH	5.7
Initial chromium concentration (mg/L)	19.9
Agitation (rpm)	4.2
Weight of dried biomass (g)	1.5

The final equation for this Linear model is:

Removal efficiency =

88.43904 – 4.25021×pH – 0.456833×Initial chromium concentration + 19.79417×Dried biomass of adsorbent – 0.024042×Agitation speed.

3.3. Imaging by Scanning Electron Microscope (SEM):

SEM was performed with dried biomass of tea leaves (adsorbent) before and after adsorption in optimized condition obtained through RSM. SEM provides microscopic images which contain information about the sample's surface topography and composition.

SEM image reveals that the adsorbent before adsorption had very irregular or uneven rough surfaces as shown in Fig. 9. After adsorption the surfaces of the adsorbent became much smoother indicating adsorption of chromium on the surface as shown in Fig. 10. The smoothening effect arises due to insertion of chromium in the pores present on the surfaces.

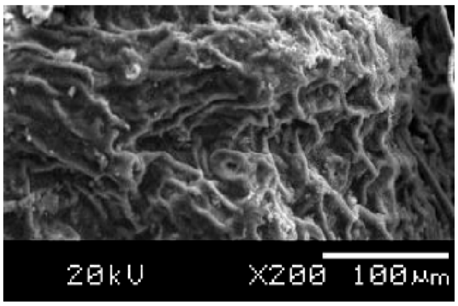


Fig. 9. SEM image of dried biomass of dried tea leaves before adsorption.

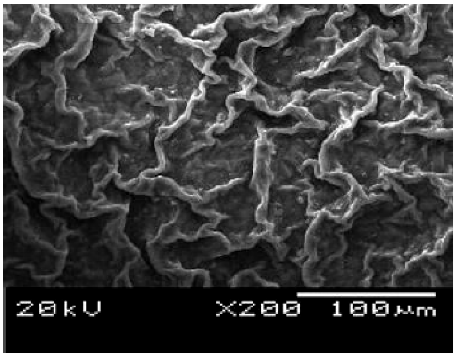


Fig. 10. SEM image of dried biomass of dried tea leaves after adsorption.

4. Conclusions

This study demonstrates that dried mass of tea leaves is a promising adsorbent for the removal of chromium(VI) ions from aqueous solutions. It offers several advantages including cost-effectiveness, high efficiency and minimization of chemical/biological sludge. In countries where there is a rush of rapid industrial development coupled with lack of awareness about metal toxicity, there is an urgent need for developing an economical and eco-friendly technology that satisfies demands for heavy metal removal when other conventional methods fails. The major finding in the present study is that adsorption efficiency increases with increase in dried biomass and decrease in pH. Increase in initial chromium concentration (from 5 ppm to 20 ppm) and agitation speed (rpm) does not have much effect on the removal efficiency of the chromium. The optimized conditions as obtained from our experiment fit the nature of the effluent in many leather industries. It can therefore be concluded that dried mass of tea leaves (*Camellia sinensis*) is an effective alternative biomass for the removal of chromium(VI) from effluent coming from the leather industries.

The adsorption efficiency of chromium(VI) by dried tea leaves biomass were compared with previously reported natural biosorbents as shown in Table 5[15]. The maximum removal efficiency of tea leaves in the present study at pH 5 was found to be 84.57%, which is comparable with the adsorption efficiency of many other natural biosorbents. The maximum removal of chromium(VI) as shown in the previous studies were carried out at a pH range of 1–2. Decreasing

Table 5. Comparative study of adsorption efficiency of different biosorbents for chromium(VI)

Natural biosorbents	Solution pH	Maximum removal efficiency (%)
Coconut shell	1.5	83
Saw dust	1	99.9
Neem leaves	4.1	67.5
Banana peels	3	96
Bamboo waste	2	98.28
Groundnut hull	2	82
Grape leaves activated carbon	1.5	89.5
Tea leaves	5	84.57

the pH from 5 to 1 in our work, would favour the protonated form of the functional group present on the tea leaves surface, which would facilitate more adsorption of chromium(VI) in the form of chromate salt ($Cr_2O_7^{2-}$), thereby increasing the removal efficiency. This modification in the present work could make tea leaves as a better alternative to many natural adsorbents.

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