

## Abatement of Cr (VI) from wastewater using a new adsorbent, cantaloupe peel: Taguchi $L_{16}$ orthogonal array optimization

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**Abstract**—Taguchi orthogonal design was applied for multivariate optimization of Cr (VI) abatement by cantaloupe peel powder (CPP), as a novel adsorbent, from industrial wastewater in a batch mode. Effective factors in the adsorption process, such as temperature, CPP dose, Cr (VI) concentration, wastewater pH, and contact time, were considered using an  $L_{16}$  orthogonal array design. The best conditions for adsorbing of Cr (VI) were determined by the Taguchi method and desirability approach as pH of 2, chromium concentration of 100 mg/L, contact time of 5 min, CPP dosage of 0.5 g/L, and wastewater temperature of 25 °C. Analysis of variance results indicated that the pH was the most important variable influencing the chromium removal percentage, and its contribution value was obtained 45.01%. The Langmuir model proved best fit for the experimental data and maximum adsorption capacity of Cr (VI) onto CPP was obtained 166.25 mg/g. The final part of the study includes an examination of the CPP through an analysis of the removal of chromium from real industrial wastewater. It can be concluded that the CPP presents a promising and efficient alternative for eliminating of Cr (VI) from industrial wastewaters.

Keywords: Cantaloupe Peel, Cr (VI), Industrial Wastewater, Optimization, Taguchi Method

### INTRODUCTION

Water resource pollution has emerged as a consistent threat to human beings and the environment owing to the abusive use and uncontrolled release of toxic substances [1,2] such as hexavalent chromium (Cr (VI)). The major sources of Cr (VI) pollution in the aquatic environment are wastewaters from electroplating and metallurgy, leather tanning, dyeing, metal finishing, and textile industries [1-4]. Hexavalent chromium species are highly toxic metals, and considered as priority pollutants because of their carcinogenic, mutagenic, and teratogenic properties [5,6]. As established by the US EPA, the concentration of Cr (VI) in wastewaters must be less than 0.05 mg/L prior to their discharge into the environment [2,3]. Various processes have been developed to treat the Cr (VI)-containing effluents, including chemical precipitation, ion exchange, membrane processes, and electrodialysis. Many of these techniques are significantly expensive and suffer intrinsic constraints such as the production of considerable amounts of mud [7,8]. However, the adsorption process in the removal of Cr (VI) from wastewaters is the most popular. Indeed, activated carbon is the most widely used adsorbent in the adsorption of Cr (VI). However, this adsorbent suffers limitations such as its impracticality when considering its use in

full-scale applications, or even low capacity for Cr (VI) removal. It is an expensive proposition to produce and regenerate the activated carbon, and there is at least 10-15% loss during conventional regeneration [2,6,9]. Moreover, to make the adsorption process more attractive and feasible, further research on novel low-cost adsorbents with higher adsorption capacity is necessary. This has fuelled growing research interest in the development of new and more effective adsorbents. However, the prices need to be lower than they are now.

Recently, agricultural waste materials have been extensively investigated for their abilities to depollute different pollutants from water and wastewaters [3,10,11]. These are locally available, present in abundance, and the large amount of surface functional groups evident, make various agricultural wastes appropriate options compared to expensive and synthetic ones [3,11]. Different agro-wastes like pistachio hull waste [3], sawdust [12], walnut hull [13], palm flower [14], rice straw [15], and banana peel as well as coir pith [16] have been studied for this purpose. Although, the Cr (VI) adsorption by agricultural waste materials has been widely reported, our literature survey in most of the peer reviewed journals indicated that adsorption study of Cr (VI) with cantaloupe peel as an adsorbent has not been investigated, and this is the first such study undertaken by the authors.

The adsorption process might be influenced by some variables such as pH value, adsorbent amount, adsorbate concentration, contact time, and temperature [17]. Therefore, to achieve the maximal removal of contaminants from water and wastewaters, it is impor-

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tant to undertake experimental design and optimize the process conditions. Numerous descriptive, relative, and quantitative statistical techniques have been applied to investigate the information obtained from engineering experiments [18-20]. The Taguchi method was originally seen as an effective statistical method [21]. In the Taguchi method, a small number of tests are done as the main effects of the design factors from a minimum number of experiments to obtain both information and create the optimized conditions [18]. In the design of the experiment using the Taguchi approach, a number of examinations are significantly minimized resulting in decreased experiment time and costs [20]. The Taguchi experiment design entails the use of the standard orthogonal array to study the testing procedures, therefore, examining the optimization of the process and determining the optimum value of the main influence parameters.

The aim of the present work was to apply Taguchi's statistical approach to optimize the Cr (VI) adsorption process by using cantaloupe peel as a novel adsorbent. Cantaloupe peel is an agricultural waste that is easily and abundantly available at no cost throughout Iran, especially the surrounding area of Hamadan city and is easily prepared and used. Therefore, a set of experiments based on the Taguchi approach was carried out to study the capacity of cantaloupe peel powder (CPP) to remove Cr (VI) under various conditions. The effects of different variables evaluated included those of wastewater pH, adsorbent dose, Cr (VI) concentration, and contact time on Cr (VI) adsorption in several levels. The isotherms data of

the adsorption process were also analyzed to comprehensively understand the Cr (VI) adsorption capacity of the CPP. The efficiency of the CPP was, in addition, investigated in terms of how effective it was in the removal of Cr (VI) from industrial wastewaters under optimized conditions.

## MATERIALS AND METHODS

### 1. Preparation of the Adsorbent

The cantaloupe peel mass samples were obtained from a local farm in the Hamadan province, Iran. Prior to its use, the cantaloupe peel waste was sun-dried in the ambient air for five days. The dried mass was finally powdered in a hammer micromill (Parsazma model, Iran) and was sorted according to size using a high-vibration screen. The adsorbent size for all the experiments was <0.85 mm.

### 2. Designation and Optimization of Adsorption Experiments

The choice of the influencing factors and their levels in the design of an experiment is often a significant phase. Accordingly, five operating parameters including pH, dosage of CPP, initial concentration of Cr (VI), contact time, and temperature were selected to investigate the removal of target contaminants from aqueous solutions via different experimental runs. The influence factors and their corresponding levels are tabulated in Table 1.

Minitab-16 software was employed in the Taguchi design as was the appropriate orthogonal array. The  $L_{16}$  orthogonal array, based

**Table 1. Control factors and their levels used for design of experiments in this study**

Designation	Explanation	Level <sub>1</sub>	Level <sub>2</sub>	Level <sub>3</sub>	Level <sub>4</sub>
A	Contact time (min)	5	10	20	30
B	Contaminant concentration (mg/L)	25	50	100	200
C	CPP dose (g/L)	0.1	0.25	0.5	1
D	pH	2	4	6	8
E	Temperature (°C)	20	25	30	35

**Table 2. The S/N ratio of each experiment resulted from different arrangement of factors and their levels**

Run	$L_{16}$ orthogonal array (arrangement of different level)					Average of MAE (%)	S/N ratio
	Column 1 (A)	Column 2 (B)	Column 3 (C)	Column 4 (D)	Column 5 (E)	Column 6	Column 7
1	1	1	1	1	1	96	39.82
2	1	2	2	2	2	97	39.73
3	1	3	3	3	3	70	36.83
4	1	4	4	4	4	50	33.97
5	2	1	2	3	4	42	32.43
6	2	2	1	4	3	40	31.91
7	2	3	4	1	2	98	39.99
8	2	4	3	2	1	97	39.91
9	3	1	3	4	2	62	35.84
10	3	2	4	3	1	96	39.82
11	3	3	1	2	4	48	33.61
12	3	4	2	1	3	95	33.45
13	4	1	4	2	3	50	33.45
14	4	2	3	1	4	90	31.83
15	4	3	2	4	1	97	39.91
16	4	4	1	3	2	90	39.08

on afore mentioned operating parameters was also selected for the experiment. Table 2 shows the experimental runs undertaken on combining Table 1 and the L<sub>16</sub> orthogonal array.

We applied the signal-to-noise (S/N) ratio to evaluate the experimental data. Generally, three kinds of S/N ratio analysis such as the higher the better, lower-better (LB), and the nominal the best may be applicable [21]. As this work aims at understanding maximum adsorption efficiency of the target contaminant, the S/N ratio analysis chosen was the higher the better (Eq. (1)) [20].

$$\text{Signal-to-noise} = -10 \log_{10} \left[ \frac{1}{n} \sum \left( \frac{1}{\text{MAE}_i} \right)^2 \right] \quad (1)$$

The adsorption experiments were optimized at the desired pH value, contact time, and CPP dosage levels using the necessary CPP in a 250 mL stoppered, conical flask containing 50 mL of the test solution. The initial solutions with different concentrations of Cr (VI) were prepared by proper dilution from stock 1,000 mg/L Cr (VI) standards. The desired amount of the CPP was then added and the content in the flask shaken by an electrically thermostatic reciprocating shaker at 120 rpm. The performance of the batch tests was assessed as MAE (%). MAE of the target contaminant was calculated as follows:

$$\text{MAE}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

To conclude the optimum conditions for the adsorption experiments, we used the relationship between each parameter and their percentage (%) contribution to the adsorption of chromium onto CPP, the analysis of mean (ANOM), and the analysis of variance (ANOVA) [22,23].

### 3. Analytical Methods and Adsorbent Characterization

All analytical measurements were performed according to the methods specified by the American Public Health Association [24]. All the experiments were conducted in duplicate to guarantee the reproducibility of the results, and the average value has been reported herein. The nomenclature section describes the parameters and constants of all the equations used in this research work.

The surface area, average pore diameter, and pore volume of CPP were determined using the N<sub>2</sub>-BET method using the Belsorp Mini 2. The surface functional groups of the CPP were determined using the Fourier transform infrared (FTIR) spectroscopy with a Nicolet spectrometer. The pH of zero point of charge (pH<sub>zpc</sub>) of CPP was determined according to the pH drift procedure [25]. All chemicals used were of analytical grade and purchased from Merck Co.

## RESULTS AND DISCUSSION

### 1. Adsorbent Characteristics

The N<sub>2</sub> adsorption-desorption isotherms are given in Fig. 1 and the pore size distributions indicated in Fig. 2. The isotherms have two distinctiveness sections (P/P<sub>0</sub> < 0.8 and P/P<sub>0</sub> > 0.8). Surface area and total pore volume of the CPP were obtained from N<sub>2</sub> adsorption isotherm. BET-specific surface and total pore volume on the adsorbent were 1.04 m<sup>2</sup>/g and 0.0002 cm<sup>3</sup>/g, respectively. Analysis of data showed in Fig. 2 indicated that the size of pores of CPP is less than 20 nm. Therefore, based on International Union of Pure and Applied Chemistry (IUPAC) classification, this adsorbent can

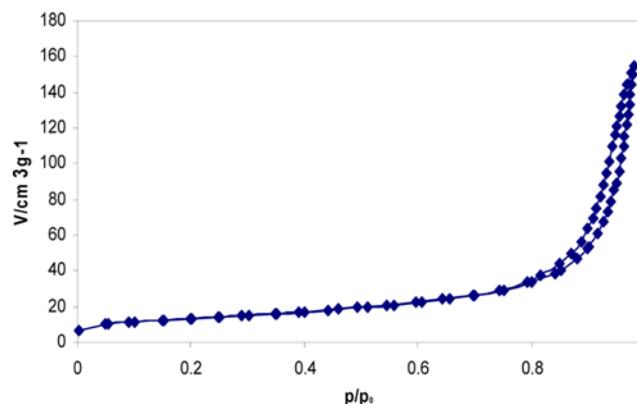


Fig. 1. N<sub>2</sub> adsorption/desorption isotherm of CPP.

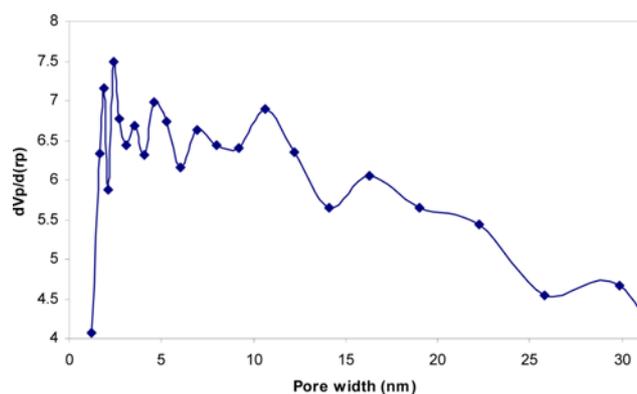


Fig. 2. Pore size distribution of CPP.

be categorized as a microporous sorbent [26].

### 2. Optimum Conditions

The mean of the duplicated of measurement adsorption of efficiency and S/N ratio for each test condition is shown in Table 2. Maximum values of the S/N ratios between the 16 runs are highlighted in Table 2. Referring to Table 2 indicates that maximum value of S/N ratio is in run 7. The analysis of mean (ANOM) statistical approach has developed to predict the optimum conditions [20]. Primarily, the mean of the S/N ratio (M<sub>S/N</sub>) of each factor at a certain level has been determined through the experiment (Eq. (3)).

$$M_{S/N} = M_{\text{Factor}-I}^{\text{Level}-i} = \frac{1}{n_{Iij-1}} \left[ \left( \frac{S}{N} \right)_{\text{Factor}-I}^{\text{Level}-i} \right] \quad (3)$$

The M<sub>S/N</sub> results as a response table for the tested factors and cor-

Table 3. Response table for M<sub>S/N</sub> ratios for the tested factors and corresponding levels

Level	Control factors				
	A	B	C	D	E
1	<b>37.59</b>	35.39	36.11	<b>40.14</b>	36.68
2	36.06	35.83	36.38	38.67	<b>37.04</b>
3	35.69	<b>37.59</b>	<b>36.81</b>	36.28	33.91
4	36.07	36.61	36.11	35.41	32.97
Delta	1.91	2.2	0.71	6.9	1.63
Rank	<b>1</b>	<b>3</b>	<b>3</b>	<b>1</b>	<b>2</b>

**Table 4. Fractional sum of squares and percentage contribution of each tested factor on adsorption chromium onto CPP**

Factors	Df	SS <sub>F</sub>	SS <sub>T</sub>	F <sub>value</sub>	V <sub>E</sub>	P (%)
Contact time (min): A	3	1834	1278	8.004	0.001752	8.54%
Concentration (mg/L): B	3	1108	1369	10.629	0.000435	8.08%
Dose (g/L): C	3	1221	1742	2.122	0.137564	23.03%
pH: D	3	3307	2436	156.419	4.59E-12	45.01%
Temperature (°C): E	3	1729	1243	6.996	0.003209	15.34%

responding levels are indicated in Table 3. Subsequently, the higher  $M_{SN}$  as better characteristic was selected optimum conditions of each parameter as evaluated in the Taguchi method. Finally, to undertake the confirmation optimum run under optimal predicted conditions, the examination carried out was duplicated.

Table 3 indicates that adsorption of Cr (VI) onto CPP is optimized at a contact time of 5 min, initial concentration 100 mg/L, temperature 25 °C, CPP dose 0.5 g/L, and pH 2. Accordingly, further evaluation of the data in Tables 2 and 3 indicates that the dosage of CPP decreases from 1 to 0.5 g/L. Adsorption processes are generally a surface phenomenon; therefore, adsorption efficiency can be significantly affected by surface area and available active sites due to the amount the mass of adsorbent. Thus, from economic point of view, the optimization of adsorbent dosage and the best-required mass of adsorbent for scale-up and designing of large-scale equipment is necessary. The calculations indicated that the adsorbed pollutant was reduced per unit mass of the adsorbent by increasing the adsorbent. One possible reason could be due to overlap of active sites at higher adsorbent masses leading to reduced effective surface area required for adsorption [1,25]. The other plausible reason for this phenomenon is that some of active adsorption sites may remain unsaturated. Refs [2,9,26] stated that lack of increase in adsorption in proportion to the adsorbent dose was because the adsorption density increased at higher concentration of adsorbent due to the competition among chromium to access the active areas of the CPP surface. Moreover, higher doses of the adsorbent per unit volume of wastewater resulted in the adsorbent surface overlapping and aggregation of the adsorbent molecules, and consequently the total surface and the pollutant adsorption decreased. The reason is that the aggregation of the adsorbent molecules increases the diffusion path during the pollutant diffusion on the adsorbent surface, and this in turn decreases the adsorption efficiency. Nonetheless, this result indicated that the CPP had high affinity to adsorb of chromium at a relatively low concentration as compared with other adsorbent have been evaluated by other researcher. Moussavi and Barikbin [3] report experiments where 97% of chromium was removed from a solution containing 100 mg/L Cr (VI) after 60 min of contact time with 5 g/L of pistachio hull. Rao et al. [27] observed 85% removal of 100 mg/L Cr (VI) with 4 g/L of bagasse after a contact time of 90 min. Bhattacharya et al. [28] observed that after 4 h of contact time, 80.7 and 84.3% chromium had been removed from a 50 mg/L solution with 5 g/L of sawdust and 10 g/L neem bark, respectively. Bonsal et al. [29] reported formaldehyde-treated rice husk with dosage of 20 g/L removed 76.5% of Cr (VI) from a 100 mg/L solution.

These results suggest that, from an engineering perspective, the CPP is a promising low-cost adsorbent for Cr (VI) removal due to

its availability, economic costs, and higher removal efficiencies compared to the frequently investigated agricultural wastes.

### 3. Percentage of Contribution

The analysis of variance (ANOVA) was statistically evaluated to determine of the percentage contribution (P) of each parameter in the adsorption of Cr (VI) onto CPP.

The percentage contribution of each factor on the removal of chromium by CPP was obtained by substituting the factorial sum of squares (SS<sub>F</sub>), the total sum of square (SS<sub>T</sub>) and the variance of error (V<sub>E</sub>) in the following equation [20]:

$$P(\%) = \frac{SS_F - (DOF_A \times V_E)}{SS_T} \times 100 \quad (4)$$

P values of each of the influential parameters on chromium adsorption by the CPP are indicated in Table 4.

Table 4 shows that P% of each factor on the chromium adsorption onto the CPP is in the following order: the pH of solution (45.01%), the dose of adsorbent (23.03%) the temperature of the solution (15.34%) the time of contact (8.54%), and the initial concentration of chromium (8.08%). This data indicates that the adsorption of chromium onto CPP is considerably influenced by the solution pH as compared to other selected parameters. According to data in Table 2, when the pH of the solution is 2, around 96, 98, 95, and 90% of chromium is removed in run 1, run 7, run 12, and run 14 shown in column 4 (D) (highlighted numbers), respectively, and the mean of all these runs is 95%. These results reveal that the Cr (VI) adsorption onto CPP is a pH-dependent process.

The wastewater pH governs the speciation of metals and the dissociation of active functional sites on the adsorbent. Hence, metal adsorption is critically linked with the solution pH [2,3]. Not only do different metals show different pH optima for their adsorption, but they may also vary from one kind of adsorbent to another [30, 31]. As illustrated in Table 4, under the predicated optimum conditions proposed, 99.5% the Cr (VI) removal efficiency was attained and this further decreased when the solution pH (in runs 4, 5, 11, and 14 shown in Table 2) increased consequently leading to a notable decrease in the removal efficiency to 45% (average). Attaining the maximum Cr (VI) adsorption at pH 2 is of great importance from the point of view of the application, since the wastewater generated in chromium-plating plants is typically acidic. This overcomes the necessity of further pH manipulation for maximizing the adsorption process, which in turn makes the treatment more cost-effective. According to information provided in Refs [2,3,32,33] most researchers have similarly reported attaining the maximum Cr (VI) adsorption onto different adsorbents in the acidic pH range.

Peak Cr (VI) adsorption at pH 2 can be explained by considering the fact that the pH of the solution influences both the surface

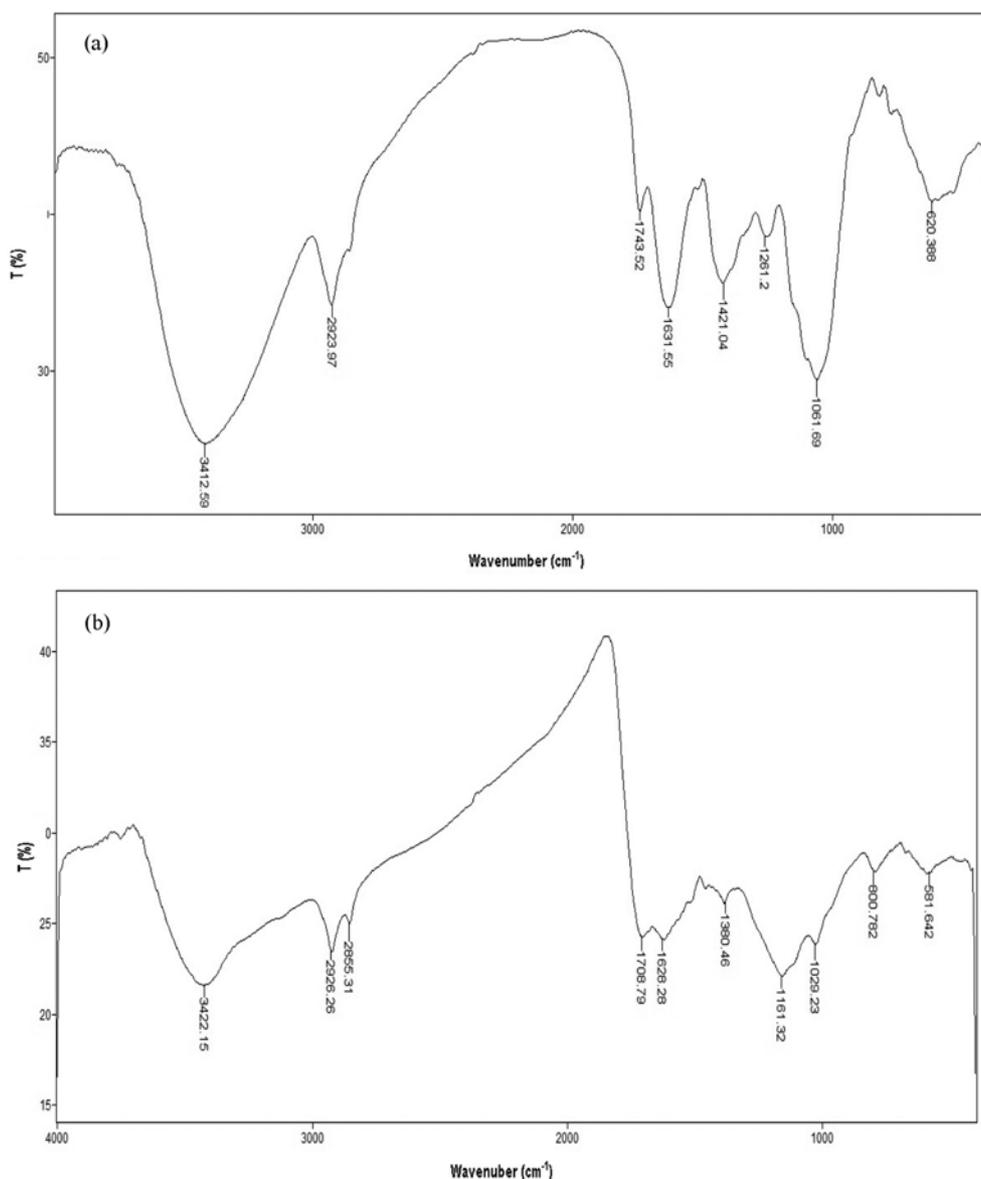


Fig. 3. FTIR spectrum of CPP before (a) and after (b) adsorption of Cr (VI) at wave numbers from 400 to 4,000  $\text{cm}^{-1}$ .

charge of the CPP and the dominant species of chromium in the solution. According to the literature [32,33], various Cr (VI) species such as  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are in the solution as a function of pH. In acidic conditions,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  are predominant, whereas at basic pH, the dominant species is  $\text{CrO}_4^{2-}$  [33]. Since all Cr (VI) species are anionic, as the pH increases, the  $\text{H}^+$  concentration decreases and the surface charge of the adsorbent becomes negative, which prevents the retention of the chromium species. This justifies a decrease in Cr (VI) adsorption as the pH increases in the media. Numerous researchers have arrived at the same conclusion [2,3,8,33]. Further, the  $\text{pH}_{\text{zpc}}$  of the CPP has been found to be 4.5, implying that the surface of the CPP is positively charged at  $\text{pH} < 4.5$  and negatively charged at  $\text{pH} > 4.5$ . At pH values higher than 4.5 the negatively charged surface of the CPP has been seen to repel the negatively charged chromate ions, whereas at lower pH it has attracted and bound them. Therefore, the maximum adsorption capacity of CPP was recorded when the pH was 2. To further evaluate

the mechanism of the adsorption processes, the functional groups on the CPP involved in the biosorption of Cr (VI) were determined using the FTIR spectrum.

The FTIR spectrum of CPP before and after the adsorption of Cr (VI) was also obtained (Fig. 3). The evaluation of the spectrum before (fresh) and after adsorption of the chromium (i.e., Cr (VI) loaded) indicated changes in the functional groups on the adsorbent. The majority of the changes occurred in bands between 3,340-3,450, 2,924-2,855, and 600-1,708  $\text{cm}^{-1}$  that matched the hydroxyl groups (-OH), C-H bending, carbonyl group stretching C=O, C-O stretching functional groups and N-H bending, respectively [3,12]. Therefore, the change in -OH, -CH, C-O, and N-H functional groups suggests that their groups were the essentially active groups involved in the adsorption of Cr (VI) onto CPP. The main changes are seen in the band between 3,300-3,345  $\text{cm}^{-1}$  after the adsorption of Cr (VI), which indicates electrostatic attraction between protons of symmetric and asymmetric C-H and O-H functional groups on the CPP

surface with anionic chromium in solution. Thus, the results suggest that the chemisorption may be a predominant mechanism in the Cr (VI) adsorption process when using the CPP. However, the presence of polar groups on the surface of CPP indicates that some Cr (VI) may be also removed by complexation of Cr (VI) with functional groups and surface precipitations.

#### 4. Selection of Best Adsorption Isotherm of Cr (VI) Adsorption onto CPP

Analysis of the isotherm data is critical to determine the maximum capacity of the adsorbent, the appearance of the surface properties, and to develop an equation for purposes of effectively designing columns. Accordingly, isotherm data obtained were fitted by four most commonly used isotherms including the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin.

The equilibrium study was obtained by mixing for the appropriate time interval, the different initial concentrations of the solution (25-250 mg/L) of the corresponding ion with a fixed mass of the optimum adsorbent (0.5 g/L) at optimum pH=2. The amount of adsorbed Cr (VI) at equilibrium was calculated from a simple mass balance equation as follows [6]:

$$q_e(\text{mg}_{\text{adsorbed}}/\text{g}_{\text{CPP}}) = \frac{V}{M} \times (C_0 - C_e) \quad (5)$$

The linear forms of applied isotherms equations and the calculated adsorption isotherm parameters for Cr (VI) adsorption onto the CPP are given in Table 5. As demonstrated in Table 6, the adsorption of Cr (VI) onto CPP is fitted with the Langmuir isotherm models having the highest values of the correlation coefficient ( $R^2$ ). Apart from the correlation coefficient, the applicability of the isotherm equations was further evaluated by comparing residual root mean square

**Table 5. Isotherm details of chromium adsorption onto CPP**

Isotherm model	Parameters	
Langmuir : $\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}}$	$K_L$	0.0058
	$q_{max}$	166.25
	$R_L$	0.077
	$R^2$	0.998
	RMSE	5.70
	$X^2$	0.26
Freundlich : $\ln q_e = \ln k_f + n^{-1} \ln C_e$	$K_F$	80.35
	$1/n$	0.4
	$R^2$	0.956
	RMSE	24.35
	$X^2$	28.24
Dubinin-Radushkevich: $\ln q_e = \ln q_m - K_{DR} \varepsilon^2$	$K_{DR}$	0.004
	E	11
	$R^2$	0.856
	RMSE	29.63
	$X^2$	42.48
Temkin : $q_e = B_T \ln A_T + B_T \ln C_e$	$B_T$	8
	$A_T$	3.23
	$R^2$	0.942
	RMSE	16.45
	$X^2$	5.55

**Table 6. Adsorption of Cr (VI) from electroplating plant as real wastewater by CPP**

Properties	Unit	Value	
		Found	After adsorption
Cr (VI)	mg/L	41.5	0.041
pH	-	4.1	5.6
TDS	mg/L	6121	5671
Color	-	Dark green	Slightly green
$\text{SO}_4^{2-}$	mg/L	405.8	381.9
$\text{Cl}^-$	mg/L	24.5	21.5
$\text{NO}_3^-$	mg/L	90.8	88.3
$\text{NH}_4^+$	mg/L	23.3	20.2
$\text{Ni}^{2+}$	mg/L	0.82	0.4
$\text{Zn}^{2+}$	mg/L	0.52	0.43

error (RMSE) and the chi-square test ( $X^2$ ), which can be described as [34]:

$$\text{RMSE} = \sqrt{\frac{1}{n-2} \sum_{i=1}^N (q_{e,meas} - q_{e,calc})^2} \quad (6)$$

$$\chi^2 = \sum_{i=1}^N \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,calc}} \quad (7)$$

The experimental results revealed that the values of the RMSE and the chi-square test in the Langmuir isotherm were lower than the other models, confirming that the Langmuir isotherm better represented the adsorption of Cr (VI) onto CPP. This data suggests that the adsorption of Cr (VI) occurred on a monolayer (the adsorbed layer is one molecule in thickness) as assumed in its formulation of the Langmuir model onto an adsorbent surface. This experimental data is in agreement with available data in literature [2,3,6,13,14, 32,33]. A dimensionless separation factor or equilibrium constant  $R_L$  [23,25], expressed as  $R_L = 1/(1 + K_L C_0)$  was also used to further the evolution of a favorable Langmuir isotherm model. The value of  $R_L$  represents the adsorption situations to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) [25]. Based on the Langmuir constant, the value of this parameter ( $R_L$ ) for Cr (VI) adsorption with CPP falls between 0 and 1, which confirms that Cr (VI) adsorption with this adsorbent is favorable under the conditions selected in this study. With reference to Table 6, it may be said that the Temkin isotherm ( $R^2 = 0.942$ ) fits the adsorption of Cr (VI) on CPP, well.  $B_T \ln A_T$  as the Temkin adsorption potential obtained from the fitted Temkin model, that greater than 8 kJ mol<sup>-1</sup> [2,3], confirming that the bonding of Cr (VI) ions on the CPP surface is very strong [3,25]. Isotherm experimental data were further interpreted by a D-R isotherm to distinguish between the physical and chemical adsorptions. The analysis of data with the D-R isotherm showed that the energy (calculated by  $E = 1/\sqrt{2K_{DR}}$ ) of the Cr (VI) adsorption process onto CPP was 11 kJ/mol. Values of E explain that the adsorption mechanism is based on ion-exchange or physical adsorption [3,26]. As indicated in Table 6, the value of E lies between the typical range of bonding energy for chemisorption (8-16 kJ/mol) [1], and demonstrates that in the adsorption of Cr (VI) onto CPP, ion-exchange and chemisorption plays a significant role. This data reconfirms the results obtained from the pH study. The

maximum adsorption capacity ( $q_{max}$ ) of Cr (VI) onto CPP was 166.25 mg/g (Table 5); this rate is better than those displayed by other adsorbents that have been tested for the adsorption of Cr (VI) in Refs [2, 3,8,10-14,32,33]. From this observation, it may be suggested that Cr (VI) was favorably adsorbed onto CPP and it is definitely a suitable adsorbent owing to its high adsorption capacity, abundant availability at very low costs, and its status as an economic adsorbent for the uptake of Cr (VI) from industrial wastewater.

### 5. Abatement of Cr (VI) from Real Wastewater by CPP

The analytical applicability of CPP was tested for the abatement of Cr (VI) from real industrial wastewater. For this, a sample of real wastewater was obtained from a local electroplating plant. The wastewater properties are shown in Table 6. In this section, Cr (VI) adsorption from real wastewater (without any adjustment) was carried out under the optimized conditions such as: CPP dosage of 0.5 g/L, temperature (25±2 °C), stirring speed 120 rpm, and contact time 5 min. As presented in Table 6, removal values of Cr (VI) 99.9% were obtained in the electroplating wastewater. On the other hand, after a contact time of 5 min, the initial concentration of the electroplating wastewater reached 0.041 mg/L. Therefore, the US EPA standard, 0.05 mg/L [3], for the discharge of wastewater containing chromium into surface waters was met. Because wastewater generated in electroplating plants is typically acidic, attaining maximum Cr (VI) adsorption at a low pH is advantageous because the pH of wastewater does not need to be adjusted for efficient adsorption. Furthermore, the final pH of the wastewater at the end of the experiment was increased to around neutral value (Table 6). Control of the pH (during the experiments and the effluent) at an optimal value is critical to attaining maximum performance. However, the results indicate that the adjustment of pH during adsorption onto CPP is unnecessary, which reduces the overall cost of treatment. Results given in Table 6 indicate that in addition to efficient adsorption of Cr (VI), the CPP improved other characteristics of the wastewater. Thus, the CPP has been demonstrated as a potential and cost-effective adsorbent for the removal of Cr (VI) from industrial wastewaters.

### CONCLUSIONS

This work revealed that the microporous adsorbent, CPP, could be applied as low-cost adsorbent for eliminating the Cr (VI) from industrial wastewaters. The results also indicated that the Taguchi method gives a suitable approach for optimization of removal percentage of Cr (VI) by the CPP. According to the Taguchi method, the solution pH had the greatest contribution (45.01%) in the Cr (VI) adsorption by the CPP. The Langmuir model showed the best fit compared to Freundlich, Temkin, and D-R models. The maximum adsorption capacity of Cr (VI) onto the CPP was attained at 166.25 mg/g. Treatment of electroplating wastewater by the CPP revealed that the Cr (VI) concentration reduced to levels lower than the designated standards for effluent discharge. Consequently, cantaloupe peel powder has been seen as a proficient and cost-effective waste material for treating chromium-laden wastewaters.

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### NOMENCLATURE

- $A_T$  : Temkin isotherm equilibrium-binding constant [L/g]  
 $B_T$  : Temkin isotherm constant [mg/g]  
 $C_e$  : equilibrium concentration [mg/L]  
 $C_{ini}$  : chromium (VI) initial concentration [mg/L]  
 $DOF_R$  : represents the degree of freedom for each factor  
 $m$  : represents the number of experiments carried out  
 $K_{DR}$  : Dubinin-Radushkevich isotherm constant [mol<sup>2</sup>/kJ<sup>2</sup>]  
 $K_L$  : Langmuir isotherm constant [L/mg]  
 $M$  : mass of CPP [g]  
 $n$  : represents the number of repetitions  
 $n_{ij}$  : represents the number of appearances of factor I in the level i  
 $q_e$  : amount of chromium (VI) adsorbed per gram of CPP at equilibrium [mg chromium (VI)/gCPP]  
 $q_{e, meas}$  : experimentally measured  $q_e$  value [mg/g]  
 $q_{e, calc}$  : calculated  $q_e$  value [mg/g]  
 $V$  : solution volume [L]  
 $\epsilon$  : Dubinin-Radushkevich isotherm constant [J/mol]

### REFERENCES

1. J. Acharya, J. N. Sahu, C. R. Mohanty and B. C. Meikap, *Chem. Eng. J.*, **149**, 249 (2009).
2. G. Ghanizadeh, G. Asgari, A. M. Seid Mohammadi and M. T. Ghanian, *Fresenius. Environ. Bull.*, **21**, 1302 (2012).
3. G. Moussavi and B. Barikbin, *Chem. Eng. J.*, **162**, 900 (2010).
4. D. H. Kumar Reddy, S. M. Lee and K. Seshiah, *Environ. Eng. Res.*, **17**, 125 (2012).
5. S. Kalidhasan, P. A. Gupta, V. R. Cholleti, A. Santhana Krishna Kumar, V. Rajesh and N. Rajesh, *J. Colloid Interface Sci.*, **372**, 98 (2012).
6. G. Asgari, A. R. Rahmani, J. Faradmal and A. M. Seid Mohammadi, *J.R.H.S.*, **12**, 53 (2012).
7. W. S. Shin, K. Kang and Y. K. Kim, *Environ. Eng. Res.*, **19**, 15 (2014).
8. G. Asgari, B. Ramavandi, L. Rasuli and M. Ahmadi, *Desalin. Water. Treat.*, **51**, 6020 (2013).
9. A. R. Keshtkar and M. A. Hassani, *Korean J. Chem. Eng.*, **31**, 295 (2014).
10. G. V. Vamsi Aditya, B. P. Pujitha, N. C. Babu and P. Venkateswarlu, *Korean J. Chem. Eng.*, **29**, 71 (2012).
11. M. Hamdi Karaoglu, S. Zor and M. Ugurlu, *Chem. Eng. J.*, **159**, 106 (2010).
12. M. A. Wahab, S. Jellali and N. Jedidi, *Bioresour. Technol.*, **101**, 5075 (2010).
13. X. S. Wang, Z. Z. Li and S. R. Tao, *J. Environ. Manage.*, **90**, 729 (2009).
14. R. Elangovan, L. Philip and K. Chandraraj, *Chem. Eng. J.*, **141**, 111 (2008).
15. H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li and W. Xia, *J. Hazard. Mater.*, **150**, 452 (2008).
16. K. M. S. Sumathi, S. Mahimairaja and R. Naidu, *Bioresour. Technol.*, **96**, 316 (2005).
17. Y. A. Aydın and N. D. Aksoy, *Chem. Eng. J.*, **151**, 194 (2009).
18. G. Zolfagharia, A. Esmaili-Sari, M. Anbia, H. Younesi, S. Amir-mahmoodi and A. Ghafari Nazari, *J. Hazard. Mater.*, **192**, 1055

- (2011).
19. J. N. Sahu, J. Acharya and B. C. Meikap, *J. Hazard. Mater.*, **172**, 818 (2009).
  20. S. H. Sadeghi, V. Moosavi, A. Karami and N. Behnia, *J. Hydrol.*, **448-449**, 180 (2012).
  21. G. Taguchi, *Introduction to quality engineering*, McGraw-Hill New York, USA (1990).
  22. C. S. Chou, R. Y. Yang, J. H. Chen and S. W. Chou, *Powder Technol.*, **199**, 271 (2010).
  23. N. J. Cox, J. Warburton, A. Armstrong and V. J. Holliday, *Earth Surf. Proc. Land.*, **33**, 39 (2008).
  24. APHA (American Public Health Association), *Standard methods for the examination of water and wastewater*, 20<sup>th</sup> Ed, APHA, AWWA, WEF, Washington DC, USA (1998).
  25. G. Asgari, B. Roshani and G. Ghanizadeh, *J. Hazard. Mater.*, **217-218**, 132 (2012).
  26. G. Ghanizadeh and G. Asgari, *React. Kinet. Mech. Catal.*, **102**, 142 (2011).
  27. M. Rao, A. V. Parwate and A. G. Bhole, *Waste Manage.*, **22**, 830 (2002).
  28. A. K. Bhattacharya, T. K. Naiya, S. N. Mandal and S. K. Das, *Chem. Eng. J.*, **137**, 541 (2008).
  29. M. Bansal, U. Garg, D. Singh and V. K. Garg, *J. Hazard. Mater.*, **162**, 320 (2009).
  30. R. S. Singh and M. K. Mondal, *Korean J. Chem. Eng.*, **29**, 1787 (2012).
  31. H. Seo, M. Lee and S. Wang, *Environ. Eng. Res.*, **18**, 45 (2013).
  32. A. El Nemr, *J. Hazard. Mater.*, **161**, 141 (2009).
  33. J. R. Memon, S. Q. Memon, M. I. Bhangar, A. El-Turki, K. R. Hal-lam and G. C. Allen, *Colloids Surf., B.*, **70**, 237 (2009).
  34. K. Y. Foo and B. H. Hameed, *Chem. Eng. J.*, **156**, 10 (2012).