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Optimization of Preparation Conditions for Activated Carbon from Date Stones by Chemical Activation using Response Methodology on Removal of Cr (VI) from Aqueous Solution

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ABSTRACT: *Aims:* the objective of this work was to evaluate the adsorption potential of date stones based activated carbon for Cr (VI) removal from aqueous solution. *Study design:* Date stones (DS), agriculture wastes, available in large quantity in Tunisia, were used to prepare a low cost activated carbon (DSAC) for removing Cr (VI) from aqueous solution. Chemical activation method using sulphuric acid was employed for the preparation of the DSAC. *Place and Duration of Study:* Chemical Engineering Department, National School of Engineers of Gabes, between January and June 2013. *Methodology:* Response Surface Methodology (RSM) called central composite design (CCD) was applied to correlate the preparation variables (activation temperature, activation time and impregnation ratio) to the percentage removal of Cr (VI) from aqueous solution. The influence of the studied parameters on the Cr (VI) removal was also investigated by using the analysis of variance (ANOVA) to identify the significant variables.Moreover, the batch adsorptions of Cr (VI) on activated carbon prepared at optimal conditions were carried out and the experimental data were analysed by Freundlich and Langmuir isotherms models. *Results:* The results obtained showed that the optimum conditions for preparing activated carbon from DS for Cr (VI) adsorption were activation temperature of 150°C, activation time of 20 h and impregnation ratio of 4.85:1(acid/DS, wt basis) which resulted in 97.25 removal of Cr (VI) from aqueous solution. It was observed that experimental values obtained were in good agreement with the values predicted by the model. The adsorption studies indicated that the equilibrium data for adsorption of Cr (VI) on the optimum activated carbon was well described by both the Freundlich and Langmuir isotherm models which yielded maximum adsorption capacity of 58.82 mg/g at pH 2.0. *Conclusion:* The DSAC seems to be a good adsorbent for the removal of Cr (VI) from wastewaters.

Keywords: activated carbon; central composite design; optimization; date stones; Cr (VI) removal.

INTRODUCTION

Chromium is one of the toxic heavy metal that is available in industrial effluents involved, leather tanning, textile dying, electroplating, cement industries and finishing industries [1]. It is present in wastewater mainly in Cr (III) and Cr (VI) oxidation states. Cr (VI) is considered to be potentially carcinogenic to humans because it's mutagenic and carcinogenic properties [2, 3] and is reported to be bioaccumulated into flora and fauna [4], creating ecological problems. The tolerance limit for the discharge of Cr (VI) into inland surface water is 0.1 mg/l and in potable water is 0.05 mg/l [5]. It is therefore essential to remove Cr (VI) from industrial effluents before discharging them into aquatic environment or onto land. Several methods of Cr (VI) removal have been developed such as reduction precipitation, electrochemical precipitation, ultrafiltration, ion exchange and reverses osmosis [6, 7]. However, most of these methods are expensive and ineffective for low Cr (VI) concentration [8]. In contrast adsorption technique is by far the most widely used [9]. The most common adsorbent is activated carbon [10, 11] but commercial activated carbons are very costly, then there is a need to produce a low cost adsorbent from cheaper and readily available materials which can be used economically on large scale. In recent years, many researchers have tried to produce activated carbons for removal of Cr (VI) from aqueous solutions using renewable and cheaper precursors such used tyres and saw dust[12] coconut coir pith

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[13] hazelnut shell [14] coconut shell [15] Wood Apple [16] neem leaves [17] treated saw dust [18] and almond shell [19]. Date stones were found as a good precursors to produce activated carbon for removal of various pollutants [20-27] .In Tunisia, Date stones is one of alternative material that is readily available. Any attempt to reuse this waste will be useful. So the objective of this work was to evaluate the adsorption potential of date stones based activated carbon for Cr (VI) removal from aqueous solution. The effects of three variables (activation time, activation temperature and H_2SO_4: date stones impregnation ratio) were investigated by using the Response Surface Methodology (RSM). The activated carbon preparations conditions were optimised by maximising Cr (VI) adsorption. Also, the batch adsorptions of Cr (VI) on activated carbon prepared at optimal conditions were carried out and the experimental data were analysed by Freundlich and Langmuir isotherms models.

MATERIAL AND METHODS

Materials

All the chemicals used are of the analytical grade. Stock solutions of Cr (VI) was prepared by dissolving appropriate amounts of $K_2Cr_2O_7$ (Prolabo, 99.5% purity) in distilled water. This solution is diluted as required to obtain solutions containing 5 or 10 mg/L of Cr (VI).

Adsorbent Preparation

The stones were first washed with water to remove impurities, dried at 105°C for 24h, crushed and sieved. Fraction with average particle size of about 500 µm was selected for this study. 10 g of dried stones were well mixed by stirring with sulphuric acid solution at different impregnation ratios (1.5- 4.85) and heated for different activation times (10-30 h) at different temperatures (100-200°C). At the end of activation time the samples were withdrawn from furnace and allowed to cool. For the removal of residual H_2SO_4, the samples were repeatedly washed with distilled water until the pH of washing solution reached 6.0-6.5. After that, the samples were dried at 105°C for 24h, crushed, sieved and stored in tightly closed bottles. Particles with size between 0.5 to 0.63 µm were used for adsorption experiments.

Adsorption Studies and Analytical Method

The adsorption tests were performed at fixed parameters (contact time of 10h, initial Cr (VI) concentration of 5 mg/l, and adsorbent dose of 0.2g/ L at pH 2.0) .The mixture was agitated at 200 rpm at 25 °C until equilibrium was reached. The residual concentration of Cr (VI) solution was determinated by the diphenilcabazide colorimetric method on a visible spectrophotometer (model DR 2000) at a wavelength 540 nm [28]. The adsorption capacity q (mg/g) and removal efficiency were calculated according to the equations (1) and (2) respectively:

$$q_{\max}(mg/g) = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$Removal(\%) = \frac{(C_i - C_t)}{C_i} * 100 \quad (2)$$

Where C_0 and C_e were the concentrations of chromium (VI) initially and at equilibrium, V is the volume of solution and m is the amount of adsorbent.

Design Experiments

In this work, a standard Response Surface Methodology (RSM) design called central composite design (CCD) was employed to study the various process parameters for preparing the activated carbon. The CCD is suitable for exploration a quadratic response surface and it helps to optimise the effective parameters with a minimum number of experiments and also to analyse the interaction between the parameters [29-33]. Generally the CCD consists of three kinds of runs which are the 2^n factorial runs, 2n axial runs and n_c center runs (replicates), where n is the number of variables. In this work the activated carbons were prepared by chemical activation method using sulphuric acid. Therefore the preparation variables investigated were activation temperature X_1, activated time X_2 and activation ratio X_3 indicating that altogether 20 experiments as calculated from the following equation:

$$N = 2^n + 2n + n_c = 2^3+2*3+6 =20 \quad (3)$$

Where N is the total number experiments required.

These three variables together with their respective ranges chosen based on literature [34-

39] and preliminary studies are reported in Table I.

Table I
Independent Variables and their Coded Levels for the Central Composite Design

Variables (factors)	*Code values*	*Coded variable levels*				
		+α	*+1*	*0*	*-1*	*-α*
Activation Temperature (°C)	X_1	234.1	200	150	100	65.9
Activation time (h)	X_2	36.82	30	20	10	3.18
Impregnation ratio IR	X_3	4.85	4	2.75	1.5	0.65

The center points are used to determine the experimental error and the reproducibility of the data. The axial points are located at (±α, 0, 0), (0, ± α, 0) and (0, 0, ± α) where α (1.682) is the distance of the axial point from center and makes the design rotatable. The experimental runs sequence was randomized in order to minimize error as result of the effects of the uncontrolled factors. The response selected was the percentage removal of Cr (VI) from aqueous solution (Y). This response was used to develop an empirical model which correlated the response to the three preparation variables using a second-degree polynomial equation as given by:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + (\sum_{i=1}^{n} b_{ii} X_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (4)$$

Where Y is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and X_i, X_j are the coded values of the activated carbon preparation variables. The experimental data obtained were analysed using a statistical software design Expert version 7.0.0 (STATE-EASE Inc; Minneapolis, USA) for regression analysis to fit the second degree polynomial equation and also for the analysis of variance.

RESULTS AND DISCUSSION

Development of Regression Model Equation

Table II shows the complete design matrixes together with the response values obtained from the experimental work.

Table II
Experimental Design Matrix for Preparation of DSAC

	Activated carbon preparation variables			*Response*
Run Number	*Activation temperature X_1(°C)*	*Activation timeX_2 (h)*	*Impregnation ratio IR X_3 (W/W)*	*Cr(VI) removal, Y (%)*
1	100	10	1.5	38.32
2	200	10	1.5	32.16
3	100	30	1.5	51.24
4	200	30	1.5	39.68
5	100	10	4	68.17
6	200	10	4	54.86
7	100	30	4	89.18
8	200	30	4	79.14
9	65.9	20	2.75	58.21
10	234.1	20	2.75	46.17
11	15	3.18	2.75	28.20
12	150	36.82	2.75	53.16
13	150	20	0.65	40.94
14	150	20	4.85	97.25
15	150	20	2.75	59.85
16	150	20	2.75	64.45
17	150	20	2.75	66.12
18	150	20	2.75	68.45
90	150	20	2.75	65.56
20	150	20	2.75	63.45

It can be seen from table II that the optimum percentage removal of 97.25 was obtained at 150°C of activation temperature, 20h of activation and 4.85 of impregnation ratio.

According to the sequential model sum of squares, the model was selected based on the highest order polynomial where the additional terms were significant.

The final empirical formula models for the removal of Cr (VI) (Y) in terms of coded factors (parameters) after excluding the insignificant terms is represented by following equation:

$$Y = 64.54 - 4.49\,X_1 + 7.89\,X_2 + 16.45\,X_3 - 3.72\,X_{21} - 7.79\,X_{22} + 2.26\,X_{23} + 3.11\,X_2X_3 \quad (5)$$

It can be seen that the coefficient of X_2 and X_3 are higher than others. This indicates that time and impregnation ratio have higher effect on Cr (VI) removal, also the positive sign of these terms indicating that increasing time and impregnation ratio increasing the removal of Cr (VI). The negative sign of X1 indicating that decreasing temperature increases amount of Cr (VI) adsorbed. The interaction effect between X_2 and X_3 was found to be moderate.

The quality of the model developed was evaluated based on the correlation coefficient (R^2) value. The closer the R^2 value to unity, the better the model will be as this will give predicted values which are closer to the actual values for the response. As shown by fig. 1, the R^2 value is 0.983, which is considered high, indicating that there was a good agreement between the experimental and the predicted values for the Cr (VI) removal as suggested by the model.

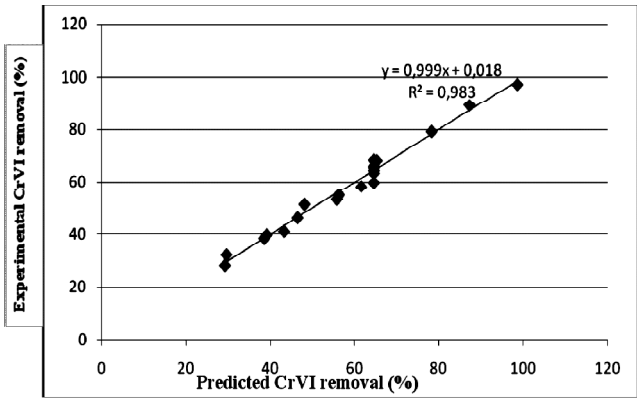

Figure 1: Correlation between the experimental and predicted values for Cr (VI) removal

Analysis of Variance

The validity of the model was further justified through analysis of variance (ANOVA).Results obtained are reported in table 3.The higher of F-test value and the lower of P-values, the higher the significance of corresponding coefficient. Values of P less than 0.05 indicate that the model terms are significant.

From table 3, it can be seen that the prediction of the model is significant with F-value of 70.13 and Prob › F less than 0.0001. In this case, X_1, X_2, X_3, X_2X_3, X_1^2, X_2^2 and X_3^2 were significant model terms to the response.

Fig. 2 shows the three dimensional response surface which was constructed to demonstrate the effect of two significant variables on Cr(VI) removal. It was observed from this figure that the activation time and the activation ratio imposed greater effect on Cr (VI) removal than the activation temperature. At higher values of these factors, the removal of Cr (VI) becomes more extensive. Similar results were obtained by NAWABANNE and IGBOKWE [32].

Table 3
For Response Surface Quadratic Model for Cr (VI) Removal

Source	*Sum of squares*	*Degree of freedom*	*Mean square*	*F value*	*Prob > F*
Model	6061.71	9	673.52	70.13	< 0.0001
X_1	275.32	1	275.32	28.67	*0.0003*
X_2	849.46	1	849.46	88.45	*< 0.0001*
X_3	3695.46	1	3695.46	384.78	*< 0.0001*
X_1X_2	0.57	1	0.57	0.059	*0.8129*
X_1X_3	3.96	1	3.96	0.41	*0.5351*
X_2X_3	77.19	1	77.19	8.04	*0.0177*
X_1^2	199.20	1	199.20	20.74	*0.0011*
X_2^2	873.92	1	873.92	90.99	*< 0.0001*
X_3^2	73.54	1	73.54	7.66	*0.0199*
Residual	96.04	10	9.60	-	-

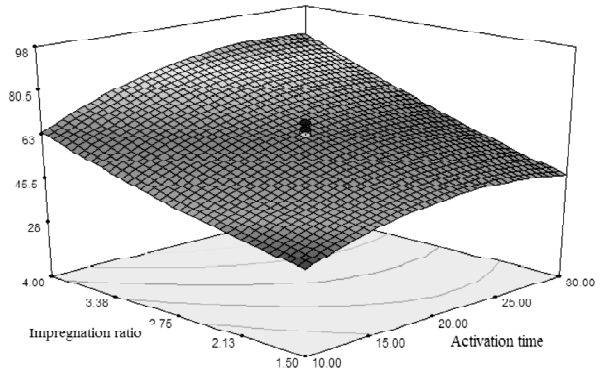

Figure 2: Three dimensional response surface plot for Cr (VI) removal (Activation time /impregnation ratio)

Process Optimization

One of the main aims of this study was to find the optimum process parameters at which activated carbon will have a high Cr (VI) removal. The optimum response was obtained by using 150°C, 20 h and 4.85 of activation temperature, activation time and impregnation ratio respectively. The insignificant error for the Cr (VI) removal (1.37%) as presented in table IV showed that the experimental data was in good agreement with the predicted data.

Table IV
Model Validation

Temperature (°C)	*Activation time (h)*	*Impregnation ratio (IR)*	*Cr (VI) removal (%)*		
			Experimental	*Predicted*	*Error (%)*
150	20	4.85	97.25	98.6	1.37

Isotherm Studies

The equilibrium adsorption isotherm is important in the design of adsorption systems. Two commonly used isotherm models, Langmuir and Freundlich have been applied to describe the adsorption of Cr (VI) onto the activated carbon prepared at optimal conditions (DSAC). The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 values.

Langmuir (Eq. 4) and Freundlich (Eq. 5) given below, have been applied to describe the adsorption of Cr (VI) onto the (DSAC).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

$$Lnq_e = \frac{1}{n} LnC_e + LnK_F \quad (7)$$

Where q_e and C_e are the amount of adsorbate adsorbed per unit weight of adsorbent and equilibrium concentration of adsorbate remained in solution, respectively. In Eq. 6, q_{max} indicates the theoretical monolayer adsorption capacity (mg g^{-1}) and K_L is the equilibrium constant (L mg^{-1}). In Eq. 7, K_F is the Freundlich constant and 1/n is the adsorption intensity. The essential characteristic of the Langmuir isotherm can be expressed in terms of dimentionless equilibrium R_L which defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$) or favorable ($0 < R_L < 1$).

The adsorption isotherms for Cr (VI) were studied using initial concentration of an adsorbent between 0.05 g/L and 0.35 g/L at Cr (VI) initial concentration of 10 mg/L. The experimental data were fitted to the isotherm models and graphical representations of these models are presented in Fig. 3 and 4. The slope and the intercept of each linear plot in these figures are used to calculate Langmuir and Freundlich parameters which are listed in table V along with associated correlations. Based on the correlation coefficient R^2, it can be concluded that the adsorption of Cr (VI) on DSAC at 25°C was described well by both of Langmuir and Freundlich isotherm models. The adsorption process was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by 1/n values of Freundlich which was less than one.In addition, DSAC has adsorption capacity q_{max} (58.82 mg/g) which demonstrates that DSAC has high adsorption ability toward Cr (VI).

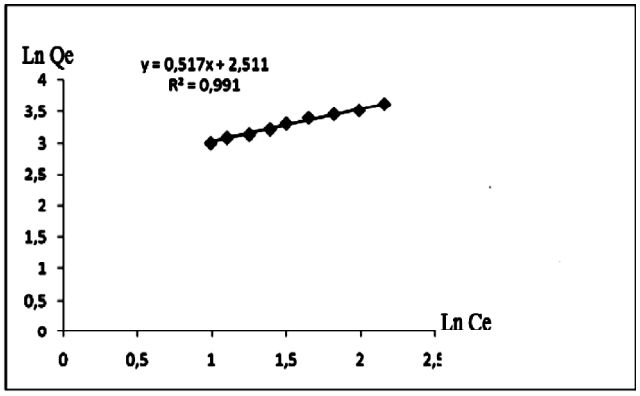

Figure 3: Freundlich isotherm for the adsorption

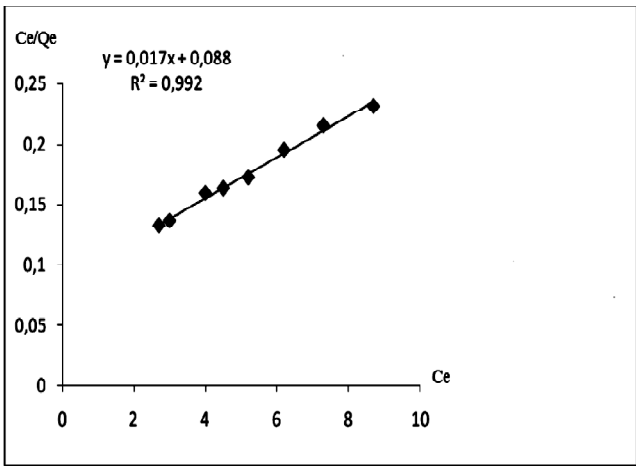

Figure 4: Langmuir isotherm for the adsorption

Table V
Langmuir and Freundlich Models Parameters for the Adsorption of Cr(VI) onto the DSAC at 25°C

Model	*Langmuir*				*Freundlich*		
Prameter	$K_L(l/mg)$	$q_{max}(mg/g)$	R^2	R_L	K_F	$1/n$	R^2
	0.93	58.82	0.992	0.097	12.32	0.52	0.991

Comparison with others Adsorbents

Table 5 compares the adsorption capacities of different adsorbent prepared by activation with sulphuric acid and used for removal of Cr (IV). The value of q_{max} in this study is larger than those in most previous works. This suggests that the Cr (VI) can be easily adsorbed by the DSAC.

Table VI
Comparison of Activated Carbons Prepared from Various Raw Materials and the Optimum Conditions of Cr (VI) Removal

Precursor	*Preparation conditions*	q_{max} *(mg/g)*	*Source*
Olive Stones	600°C,3h	71.0	34
Tamarind Seeds	110°C,5h	29.1	33
Wood Apple	110°C, 24 h	13.0	16
Ground nut husk	150 °C,24 h	7.0	33
Hazelnut shell	150°C,24 h	170.0	14
Cornelian cherry (CC)	200°C, 24 h	21.0	33
Apricot stone (AS)	200°C,24 h	34.7	39
Almond shells (ASC)	200°C, 24 h	20.0	19
Tridax procumbens	160 5°C	9.7	33
Gingelly oil cake	140-160°C, 24 h	30.58	40
Palmyra palm fruit seed	200°C,10h	32.14	41
Pterospermum acerifolium fruit capsule	Room temperature, 24 h	76.92	42
Commercial activated carbon	-	54.64	43
Peach kernel	160 ± 5, 8 h	47.5	44
Nutshell	160 ± 5, 8 h	46.64	44
Aquacarb207EA" work	150-155°C, 24 h	7.0	45
Date Stones	150°C, 20 h	58.82	this study

CONCLUSIONS

Date stones were used as precursor to produce an activated carbon with high Cr (VI) removal from aqueous solution. A central composite design was conduct to investigate the effects of three activated carbon preparation factors: activation temperature, activation time and impregnation ratio. The optimum condition was activation temperature of 150°C, activation time of 20 h and impregnation ratio of 9.6. Langmuir and Freundlich isotherms described well the process isotherm. The maximum adsorption capacity obtained from Langmuir isotherm model is 58.82 mg/g, which is higher than the most others low cost adsorbents. The present study shows that activated carbon prepared from date stones can be used as a good adsorbent for the removal of Cr (VI) from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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