# Preparation of Activated Carbon from Date Stones:Optimization on Removal of Indigo Carmine from Aqueous Solution Using a two-Level Full Factorial Design

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**Abstract**—In this work date stones (SD), agriculture wastes, available in large quantity in Tunisia, were used to prepare a low cost activated carbon (DSAC) for removing Indigo Carmine (IC) from aqueous solution. Chemical activation method using $ZnCl_2$ was employed for the preparation of the DSAC. A 2-level full factorial design (FFD) was applied to correlate the preparation variables (activation temperature, activation time and impregnation ratio) to the removal of IC from aqueous solution. The influence of the studied parameters on the IC adsorption was also investigated by using the analysis of variance (ANOVA) to identify the significant variables. The results obtained showed that the optimum conditions for preparing activated carbon from DS for IC adsorption were activation temperature of 700°C, activation time of 120 min and impregnation ratio of 2:1 (Acid / DS, wt basis) which resulted in 298.1 mg/g adsorption capacity of IC from aqueous solution at pH 6.0. It was observed that experimental values obtained were in good agreement with the values predicted by the model. The DSAC seems to be a good adsorbent for the removal of anionic dyes in particular indigo carmine from wastewaters.

**Keywords**—Activated carbon, Full factorial design, Analysis of variance, Optimization, Date stones, Indigo carmine removal, Adsorption.

## INTRODUCTION

Many industries such as textile, paper, printing, leather, food, cosmetics, etc. use dyes to colour their final product and consume substantial volume of water [1, 2]. As a result, they generate a considerable amount of coloured wastewater. Discharge of this dye-containing-wastewater into environment can cause damage to the environment as dyes even in very low concentration are toxic to aquatic life [2- 4]. In addition, presences of colour substances in the water body may decrease the light transmission which decreasing the photosynthesis activity, leading to decrease growth of bacteria and hence decreasing the bio- degradation of impurities in water [4,5]. It has also been reported that many dyes and pigments have toxic as well as carcinogenic and mutagenic effects on aquatic life as well as humans [6,7].Therefore several physical, chemical and biological methods are available to remove dyes from wastewater before it safely discharged into environment [1,8-10]. Adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, flexibility, simplicity of design, ease of operation, and insensitivity to toxic pollutants and does not result in the formation of harmful substances [8, 11]. The most widely used adsorbent is an activated carbon because of its high surface area due to the presence of micro and meso pores [12]. However, commercial activated carbons are expensive so they may not be economical for wastewater treatment purpose. So, a number of studies have been performed using activated carbon prepared from agricultural wastes for the removal of dyes from aqueous solution [10]. Date stones, used in this study, are found to be a good source of activated carbons for removal of various pollutants [13 -21]. Basically, there are two different processes for production of activated carbon: physical and chemical activation [22-24]. The physical activation technique consists of carbonization of the precursor material followed by gasification of the resulting char in steam or carbon dioxide. The chemical activation technique involves carbonization of the raw material that has been impregnated with chemical reagent ($ZnCl_2$, $H_3PO_4$, KOH...). The chemical activation technique has more advantages over the physical activation technique since the chemical reagents enhance the yield and increase the surface area of the resulted product. $ZnCl_2$ is one of the most widely used chemical activating agents for the preparation of activated carbon. Among the most useful dyes, there is indigo carmine which is an anionic dye. It is one of the oldest dyes and still one of the most used in textile industry [25] for dyeing of denim and polyester fibres [26, 27]. It is usually used in food and cosmetics industries. Indigo carmine (IC) is considered as a highly toxic indigoid dye [28]. Contact with skin and eyes can cause permanent injury to cornea and conjunctiva [25] and if consumed by oral via may cause death [27].Several processes have been suggested for removal of Indigo Carmine and other dyes from wastewater including photochemical [30- 33] electrochemical [34, 36] biological [36,37] methods , electrocoagulation [38,39] and adsorption[ 26,40,41].

This research is aimed at optimizing preparation parameters for production of activated carbon from date stones which is abundantly available as waste material in Tunisia, for adsorption of indigo carmine. $ZnCl_2$ was chosen as activating reagent, since it resulted in high surface areas and high yield [10, 15] .Some of the most important preparation conditions: activation temperature, chemical impregnation ratio IR and activation time were optimized using response surface methodology RSM, an experimental design technique which is a useful tool in studying interactions between two or more variables [42-48].

## EXPERIMENTAL

### Adsorbate

Indigo Carmine (Fig.1), which is also commonly known as Acid Blue 74 or Food Blue 1 is a dark blue, water-soluble powder. Its molecular formula is $C_{16}H_8O_8N_2S_2Na_2$ and molecular weight is 466.36 g/mol. For the present study Indigo Carmine was obtained from Labosi (colour index: 73015) and used as received without further purification. Solutions were prepared by dissolving requisite quantity of the dye in distilled water.


**Fig. 1. The molecular structure of indigo carmine (IC).**

### Preparation of the activated carbon

The date 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 300µm was selected for this study. The dried stones were soaked in $ZnCl_2$ solution with a different impregnation ratios (0.25- 2.00) for 24 h at 110 °C. The dried mixture were put into a furnace and heated for different activation times (30-120 min) at different temperatures (400-700°C) under a constant $N_2$ (99.99%) flow of 120 $cm^3$/min. Then, the produced activated carbon was repeatedly washed with 0.1 mol/L HCl followed by hot distilled water until the pH of washed solution reached 6.7-7. Finally, the product was dried at 110 °C for 24 h, ground and sieved to a particle size of 125 µm for further studies.

**Adsorption studies and analytical method**

The adsorption tests were performed at fixed parameters (contact time of 24h, initial IC concentration of 100 mg/l, and adsorbent dose of 0.2g/l at pH 6.0) .The mixture was agitated at 200 rpm at 25°C. The residual concentration of IC solution was determined spectrophotometrically on a visible spectrophotometer (HACH DR/2000) at a wavelength of 610 nm. The adsorption capacity $q_{max}$ (mg/g) was calculated according to the equations (1):

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

Where $C_0$ and $C_e$ were the concentrations of IC (mg/L) initially and after 24h, V is the volume of solution (L) and m is the amount of dry adsorbent used (g).

**Design of experiments by a two-Level Full Factorial Design**

In order to optimize an activated carbon preparation, three factors influencing the process: impregnation ratio, activation temperature and activation time must to be studied. But the studying of the each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time. Factorial design is applied to reduce the total number of experiments in order to achieve the best overall optimization of the process. The basic experimental design is to input all factors at two-levels, called 'high' and 'low' in experimental terms or represented by the coded levels of '+1' and '−1'. For any experiment with k number of factors each at two-levels, a full factorial design will have $2^k$ runs. This study used a three factors full factorial design. The levels and ranges of the studied process parameters ($X_1$ - activation temperature, $X_2$ – activation time and $X_3$ –impregnation ratio) affecting IC removal employed in the experiment are given in Table 1 with 11 runs to model the date stones activated carbon production process. The data ranges were selected based on the preliminary results and the literature.

**Table. 1. Independent variables and their coded levels for the two-Level FFD**

| *Variables (factors)* | *Code Values* | *Coded variable levels* | | |
|---|---|---|---|---|
| | | +1 | 0 | -1 |
| Activation Temperature(°C) | $X_1$ | 700 | 550 | 400 |
| Activation Time(min) | $X_2$ | 120 | 75 | 30 |
| Impregnation Ratio IR | $X_3$ | 2 | 1.125 | 0.25 |

Response for IC adsorption capacity was used to develop an empirical model which correlated the response to the three preparation variables employing.

The general mathematical model developed by using factorial design is as follow (44):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_1X_3 + b_6X_2X_3 + b_7X_1X_2X_3 \qquad (2)$$

Where Y is the response and the b terms are parameters to be determined with $b_0$ is the global mean and bi represents the other regression coefficients.

## RESULTS AND DISCUSSION

### Development of regression model equation

The design matrix as well as predicted and experimental responses is given in Table 2. Run 9-11 at center points were conducted to determine the experimental error and the reproducibility of the data. It was found that The IC removal was varied from 25.4 to 298.1mg/g and the most active carbon was produced when the activation temperature was 700°C for 120 min and $ZnCl_2$ to carbon mass ratio was 2.0: 1($ZnCl_2$: DS).

**TABLE 2. Experimental Design matrix for preparation of DSAC**

| *Run Number* | *Activated carbon preparation variables* | | | *Response IC removal Y(mg/g)* | |
|---|---|---|---|---|---|
| | Activation temperature X1(°C) | Activation time X2 (min) | Impregnation ratio X3 (W/W) | Actual | predicted |
| 1 | 400 | 30 | 0.25 | 25.4 | 33.88 |
| 2 | 700 | 30 | 0.25 | 58.25 | 49.78 |
| 3 | 400 | 120 | 0.25 | 31.2 | 22.72 |
| 4 | 700 | 120 | 0.25 | 157.9 | 166.38 |
| 5 | 400 | 30 | 2.00 | 33.4 | 24.92 |
| 6 | 700 | 30 | 2.00 | 48.6 | 57.1 |
| 7 | 400 | 120 | 2.00 | 121.2 | 129.68 |
| 8 | 700 | 120 | 2.00 | 298.1 | 289.62 |
| 9 | 550 | 75 | 1.125 | 93.9 | 96.76 |
| 10 | 550 | 75 | 1.125 | 98.3 | 96.76 |
| 11 | 550 | 75 | 1.125 | 100.1 | 96.76 |

From table 2, it can be seen that the adsorption capacity value depended highly of preparation conditions and ranged from 25.4to

298.1. The higher adsorption capacity was obtained in the case of 700°C of activation temperature, 120mmin of activation time and 2 of impregnation ratio. The results were analyzed using Design Expert® 7.1.6 software and along with the main effects the interactions of different factors were determined. The mathematical regression model for the 8 runs factorial design is given by:

$$\mathbf{Y= 96.76+ 43.96\, X_1+55.34\, X_2+28.57X_3 +31.94\, X_1\, X_2 +4.07\, X_1\, X_3 +28.98\, X_2\, X_3} \qquad \mathbf{(3)}$$

The positive sign in front of the terms indicates a synergetic effect. So it can be concluded that all factors studied are synergistic.

As shown by figure 1 the $R^2$ value is 0.99 which is considered high, indicating that the predicted values of the response from the model are in agreement with the actual experimental data for IC removal.

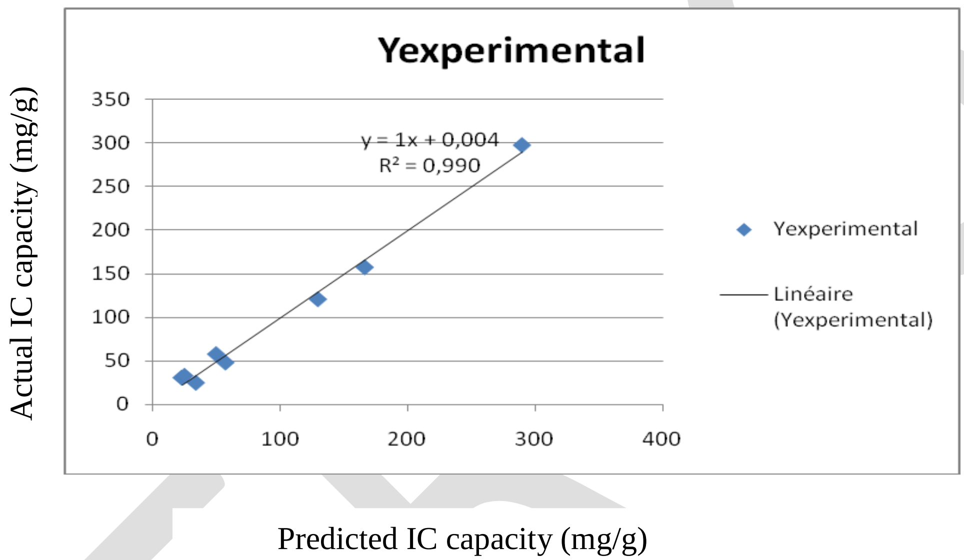



**Fig. 2. Correlation between the experimental and predicted values for IC removal**

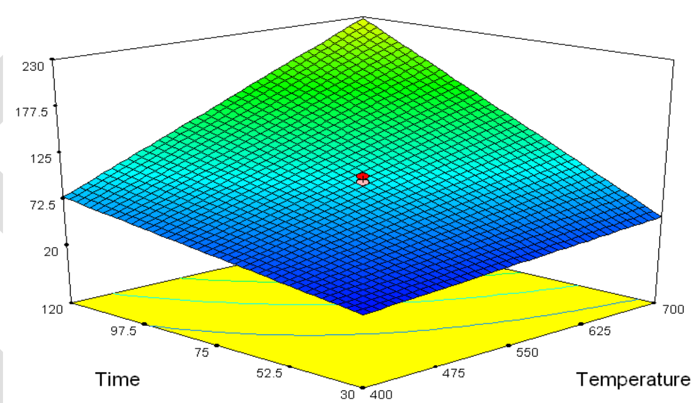
**Analysis of variance**

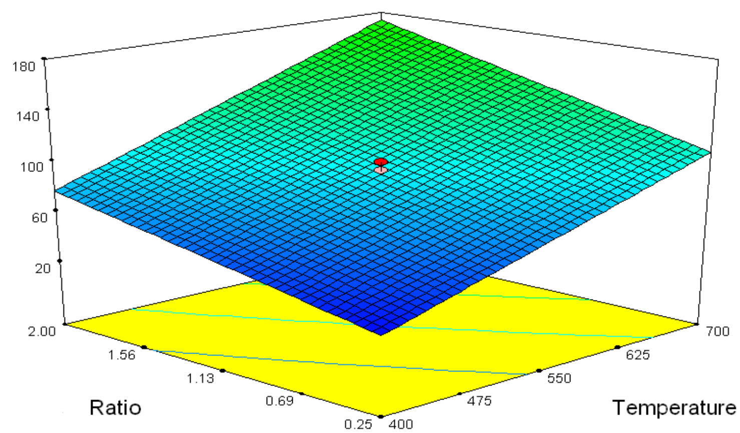
The validity of the model was further justified through analysis of variance (ANOVA).Results obtained are reported in Table3. The higher of F-test value and the lower of P-value, the higher the significance of corresponding coefficient. Values of P less than 0.05 indicate that the model termsare significant. From table 3, it can be seen that the prediction of the model is significant with F-value of 51.62 and Prob › F less than 0.0001. $X_1$, $X_2$, $X_3$, $X_1X_2$, $X_1X_3$ and $X_2X_3$ were significant model terms to the response. However, the effects of activation temperature: $X_1$ and time: $X_2$ were greater than impregnation ratio: $X_3$ on IC removal.

Fig.3 shows the three – dimensional response surface which was constructed to demonstrate the effect of the significant variables on IC removal. It was observed from this figure that the activation time and the temperature imposed greater effect on IC removal than impregnation ratio. At higher values of these factors, the removal of IC becomes more extensive. The activation temperature is an important parameter in shaping the pore structure of DSAC. At higher activation temperature and at longer activation time, the removal of volatile matters from DS becomes more extensive, resulting in a higher IC adsorption.

**Table. 3. ANOVA for response model for IC removal by DSAC.**

| Source | Sum of squares | Degree of freedom | Meansquare | F value | Prob > F |
|---|---|---|---|---|---|
| Model | 61505.01 | 6 | 10250.84 | 51.62 | 0.0041 |
| $X_1$ | 15457.22 | 1 | 15457.22 | 77.83 | 0.0031 |
| $X_2$ | 24503.45 | 1 | 24503.45 | 123.38 | 0.0016 |
| $X_3$ | 6529.39 | 1 | 6529.39 | 32.88 | 0.0105 |
| $X_1X_2$ | 8163.23 | 1 | 8163.23 | 41.10 | 0.0077 |
| $X_1X_3$ | 132.44 | 1 | 132.44 | 0.67 | 0.4740 |
| $X_2X_3$ | 6719.30 | 1 | 6719.30 | 33.83 | 0.0101 |
| Residual | 595.80 | 3 | 198.60 | - | - |



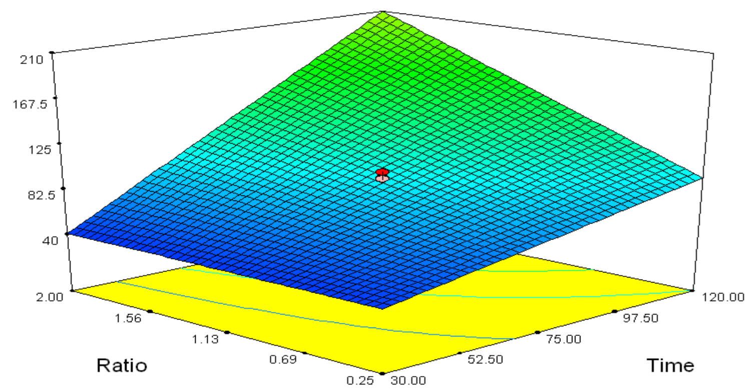



**Fig. 3. Three dimensional response surface plot for IC adsorption**

**Process optimization**

One of the main aims of this study was to find the optimum process parameters at which activated carbon produced will have a high IC removal. The optimized conditions were an impregnation ratio of 2.0 g/g, an activation temperature of 700 ºC and an activation time of 120 min. In such optimal combination of parameters, the adsorption of IC reached approximately 300 mg/g. The insignificant error for the IC removal as presented in table 4 showed that the experimental data was in good agreement with the predicted data which can indicated the success of the process of optimisation exercise.

**Table 4. Model validation**

| *Temperature (°C)* | *Activation time (h)* | *Impregnation ratio (IR)* | *$q_{IC}$ (mg/g)* | | |
|---|---|---|---|---|---|
| | | | Experimental | Predicted | Error (%) |
| 700 | 2 | 2 | 298.1 | 289.61 | 2.85 |

**Comparison with others adsorbents**

Table 5 compares the adsorption capacities of different adsorbent used for removal of IC. The value of q in this study is larger than those in most previous works. This suggests that the IC can be easily adsorbed by the DSAC.

**Table 5. Comparison of activated carbons prepared from various raw materials and the optimum conditions of IC removal.**

| *Precursor* | *Preparation conditions* | *q (mg/g)* | **Source** |
|---|---|---|---|
| Delanie regia | - | 115 | 40 |
| mytilus edulis shells | - | 40.41 | 49 |
| chitin | - | 5.78 | 50 |
| chitosan | - | 71.82 | 50 |
| Commercial A C | - | 57.32 | 41 |
| silk yarn | 0.5 M HCl (room temperature, 0.5 h) | 15.06 | 51 |
| Rice husk ash | | 29.28 | 27 |
| Hen Feathers | hydrogen peroxide (30% w/v) ,24 h | 1494.68 | 52 |
| Citrus reticulata peels | 20 % formaldehyde ,10 % urea, 3 h. | 71.07 | 53 |
| modified $TiO_2$ nanoparticles | CetyltriMeammonium bromide 0.08M,1 h | 106.24 | 54 |
| De-oiled soya | $H_2O_2$, 24h | 174.88 | 28 |
| Bottom ash | $H_2O_2$, 24h | 78.81 | 28 |
| **Date Stones** | $ZnCl_2$ (700°C, 2 h, 2g/g) | 298.10 | This study |

## CONCLUSION

Date stones were used as precursor to produce an activated carbon with high indigo carmine removal from aqueous solution. A 2-level full factorial 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 700 °C, activation time of 120 min and impregnation ratio of 2.The maximum adsorption capacity obtained is 298.1 mg/g, which is higher than the most others adsorbents. The present study shows that activated carbon prepared from date stones can be used as a good adsorbent for the removal of indigo carmine from aqueous solutions.

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