# Characterization and application of nanotube activated carbon prepared from Iraqi zahdi date seeds

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## Abstract

Nanotube activated carbon (NAC) prepared from Iraqi zahdi date seeds (ZDS) using physiochemical activation (KOH treatment and carbon dioxide gasification). The effects of the activation temperature, activation time and chemical impregnation ratios on the carbon yield. The optimum conditions for preparing nano activated carbon from Iraqi Zahdi date seeds were found to be activation temperature of 750.0 $^{o}$C, activation time of 70 min and chemical impregnation ratio of 2.1. The carbon yield was found to be 19.0%.

It was found that surface area and pore characteristics using the Brunauer-Emmett-Teller (BET) Surface area is 1000 $m^2$/ g and diameter of inner smelters is 2.16 nm (mesoporous) in the activated carbon molecule.

The nano activated carbon prepared for the removal of Phenol compounds (PCs) from aqueous solution by the adsorption process was found to contain, in general, large pore sizes. The higher activation temperature and KOH-char impregnation ratio (IR) applied is believed to be responsible for activated carbon characteristics which gave better outputs at least when compare to those being used commercially. However, the high surface areas and total pore volumes of the prepared activated carbon were believed to be due to the method of the activation process employed in this work which was a combination of both chemical and physical activating agents of KOH and $CO_2$. Pore development during the carbonization process is an important step because it enhances the surface areas and pore volumes of the activated carbon by promoting the diffusion

of KOH and $CO_2$ moles into the pores thus increasing the KOH-C and CO2-C reactions; a process responsible for generating more pores in the activated carbon.

***Keywords:*** Nano tube activated carbon; Adsorption; Date seeds; Optimization; Phenol compounds.

**توصيف وتطبيق الكربون المنشط للأنابيب النانوية المحضرة من بذور التمر الزهدي العراقي**

**الخلاصة**

الكربون النانوي المنشط (NAC) المحضر من بذور تمر الزهدي العراقية (ZDS) باستخدام التنشيط الفيزيائي الكيميائي) معالجة KOH وتغويز ثاني أكسيد الكربون .(آثار درجة حرارة التنشيط ووقت التنشيط ونسب التشريب الكيميائية على محصول الكربون. تم العثور على الظروف المثلى لإعداد الكربون المنشط نانو من بذور التمر العراقي الزهدي لتكون درجة حرارة التنشيط من 750.0 درجة مئوية ، ووقت التنشيط 70 دقيقة ونسبة التشريب الكيميائية 2.1. تم العثور على محصول الكربون ليكون 19.0 ٪.

وقد وجد أن مساحة السطح وخصائص المسام باستخدام Brunauer-Emmett-Teller (BET) تبلغ مساحة السطح 1000 م 2 / جم ويبلغ قطر المصاهر الداخلية 2.16 نانومتر (ميسبوري) في جزيء الكربون المنشط.
تم العثور على الكربون المنشط نانو أعد لإزالة مركبات الفينول (PC) من محلول مائي بواسطة عملية الامتزاز لاحتواء ، بشكل عام ، أحجام المسام الكبيرة. يُعتقد أن درجة حرارة التنشيط الأعلى ونسبة تشريب KOH-char (IR)المطبقة هي المسؤولة عن خصائص الكربون المنشط التي أعطت مخرجات أفضل على الأقل عند مقارنتها بالخصائص المستخدمة تجاريًا. ومع ذلك ، يُعتقد أن المساحات المرتفعة والسطح الكلي لحجم الكربون المنشط المحضر يرجع إلى طريقة عملية التنشيط المستخدمة في هذا العمل والتي كانت مزيجًا من عوامل التفعيل الكيميائية والفيزيائية لكل من KOH و .CO2 تعتبر عملية تطوير المسام أثناء عملية الكربنة خطوة مهمة لأنها تعزز المساحات السطحية وأحجام مسام الكربون المنشط من خلال تشجيع نشر شامات KOH و CO2 في المسام وبالتالي زيادة تفاعلات KOH-C و CO2-C ؛ عملية مسؤولة عن توليد المزيد من المسام في الكربون المنشط.
**الكلمات المفتاحية**: نانو أنبوب الكربون المنشط. الامتزاز؛ بذور التمر الاقوي؛ مركبات الفينول.

## 1. Introduction

The presence of phenol and chlorinated phenol in industrial wastewater stream is stringently regulated at low limit of concentration before it could be discharged to the environment. Since phenolic substances are toxic and harmful to human and aquatic life, the removal of these pollutants from waste effluent becomes environmentally important. Additionally, phenol has been classified as one of the primary pollutants. Several methods have been proposed in literatures on techniques for removal phenolic

compounds from wastewater such as photo catalytic, microbial degradation, chemical-biological oxidation and catalytic oxidation process [1-3]. However, the adsorption process appears to be the most applicable method for removing trace amount of contaminant from wastewater effluent [4,5].

However, the adsorption onto activated carbon has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design. However, commercially available activated carbons are still considered expensive. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [6].

A major challenge in activated carbon production from new precursors is to produce very specific carbons which are suitable for certain applications. The most important characteristic of an activated carbon is its adsorption capacity which is highly influenced by the preparation conditions. Meanwhile, in assessing the effect of the preparation conditions on quality attributes, the use of an adequate experimental design is particularly important. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more variables [7]. Optimization of experimental conditions using RSM has been widely applied in various processes including preparation of activated carbons [8]. Date Palms grows well in most parts of world especially in Iraq, expectedly, large and abundant quantity of date seeds are naturally generated by this process, which presently are underutilized and are often buried in rows within the date palm plantations and date industrial.

The objective of this research was to optimize the preparation conditions of activated carbon from Iraqi zahdi date seeds and its consequent application to remove phenol compounds based on RSM experimental design approach.

## 2. Experimental

*2.1.Phenolic compounds*

The adsorbate: phenol (> 99.5%) and 3-chlorophenol (> 95%) were purchased from Merck, Germany; their physical properties are summarized in Table 1.

Table 1, Physical Properties of the Phenolic Compounds

| **Component** | **Phenol** | **3-Chloro phenol** |
|---|---|---|
| **Molecular weight** | **94.11** | **128.56** |
| **Boiling point** | **181.4** | **214** |
| **Specific gratify** | **1.071** | **1.268** |
| **Solubility in water** | **8.2** | **2.6** |

*2.2.Preparation and characterization of activated carbon*

Iraqi zahdi date seeds used as precursors for preparation of nanotube activated carbon. The precursors were firstly washed with water to remove dirt from its surface and subsequently dried overnight at 100 $^{o}$C. The dried precursors were crushed to the size (1- 6 mm) and then carbonized at 600 $^{o}$C under purified nitrogen with flow of 150 $cm^3$/min for 2 h in a stainless steel vertical tubular reactor placed in a tubular furnace (the heating rate was fixed at 10 $^{o}$C/min). The char produced was then soaked in potassium hydroxide (KOH) solution with different impregnation ratios (KOH: char). The mixture was then dehydrated in an oven overnight at 100 $^{o}$C to remove moisture and then activated under carbon dioxide $CO_2$ atmosphere at different temperatures using stainless steel vertical tubular reactor placed in a tubular furnace (the heating rate was fixed at 10$^{o}$C/min). Once the final temperature was reached, the gas flow was switched over from nitrogen to $CO_2$ while activation was held for varying periods of time. The activated product was then cooled to room temperature and washed with hot distilled water, hydrochloric acid solution (0.1M) and hot distilled water until the pH of the washed solution reached 6 –7 .

*2.3.* **Adsorption studies**

A 1000 ppm adsorbate stock solution was prepared by dissolving a desire amount of solute in deionized water in a volumetric flask. Single component experimental test was conducted conventional batch mode system. The stock solution was then dilute to 8 different solute concern ranges between 25-200 mg/l in 250 ml volumetric flask. 0.2 g of NAC was added to a series of 2 glass-stopper flasks filled with 200 ml diluted

solutions. The glass-stopper flasks were then placed in water bath shaker and shaken at 120 rpm and constant temperature of 30°C until equilibrium co was attained. At desired time interval. The concentrations of PCs solutions before and after adsorption were determined using a double beam UV–Vis spectrophotometer (UV-1700 Shimadzu, Japan).

The percentage removal of PCs at equilibrium was calculated by the following equation:

$$\%\ Removal = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where $C_o$ and $C_e$ (mg/l) are the concentration of PCs at initial and at equilibrium, respectively [9].

*2.4. Activated carbon yield*

The experimental activated carbon yield was calculated based on the following equation:

$$\%Yield = \frac{w_c}{w_o} \times 100 \quad (2)$$

where $w_c$ and $w_o$ are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

*2.5. Design of experiments for preparation of activated carbon*

The various process parameters for preparing the activated carbon was studied with a standard response surface methodology (RSM) design called a central composite design (CCD). This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters [10]. Generally, the CCD consists of a $2^n$ factorial runs with 2n axial runs and $n_c$ center runs (six replicates).

The activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The activated carbon preparation variables studied were (i) $x_1$, activation temperature; (ii) $x_2$, activation time and (iii) $x_3$, KOH: char impregnation ratio. These three variables together with their respective

ranges were chosen based on the literature and preliminary studies. Activation temperature, activation time and chemical impregnation ratio are the important parameters affecting the characteristics of the activated carbons produced [12]. The number of experimental runs from the central composite design (CCD) for the three variables consists of eight factorial points, six axial points and six replicates at the centre points indicating that altogether 20 experiments were required, as calculated from equation 3:

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

where $N$ is the total number of experiments required and n is the number of process variables.

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The two responses ($Y_1$) were activated carbon yield and pesticides removal ($Y_i$). Each response was used to develop an empirical model which correlated the response to the three preparation process variables using a second degree polynomial equation [11] as given by equation 4:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (4)$$

where $Y$ is the predicted activated carbon yield or the removal response, $b_o$ 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 or pesticides removal variables.

The activated carbon was derived from these precursors by physiochemical activation method which involved the use of KOH treatment and followed by gasification with $CO_2$. The parameters involved in the preparation were varied using the response surface methodology (RSM). The three variables studied were:

(i) $x_1$, activation temperature

(ii) $x_2$, activation time

(iii) $x_3$, KOH/char impregnation ratio (IR)

These three variables together with their respective ranges were chosen based on the literature and the results obtained from the preliminary studies where the activation temperature, activation time and IR were found to be important parameters affecting the characteristics of the activated carbon produced [7]. The most important characteristic of an activated carbon is its adsorption uptake or its removal capacity which is highly influenced by the preparation conditions. Besides, activated carbon yield during preparation is also a main concern in activated carbon production for economic feasibility. Therefore, the responses considered in this study were:

(i) $Y_1$ activated carbon yield
(ii) $Y_2$ removal of bentazon
(iii) $Y_3$ removal of carbofuran
(iv) $Y_4$ removal of 2,4-D

## *3.* Results and discussion

### *3.1. Preparation of IZDSAC using DOE*

The complete design matrix for the yield response of nanotube activated carbon prepared from IZDS with the three response values, carbon yield and PCs (phenol and 3-chlorophenol) removal, which included in the experimental works Table (not shown) 15-20 runs at the center point were conducted to determine the experimental error and the reproducibility of the data.

The final empirical models in terms of coded factors (parameters) after excluding the insignificant terms for activated carbon yield ($Y_1$) phenol removal ($Y_2$) and 3-chlorophenol removal ($Y_3$) are given in Equations 5 to 7, respectively.

$$Y_1 = 17.90 - 4.79x_1 - 1.96\,x_2 - 1.865x_3 - 2.18\,x_1^2 - 0.66\,x_2^2 + 0.72\,x_3^2 - 1.56\,x_1x_2 + 0.36\,x_1x_3 + 1.16\,x_2x_3 \quad (5)$$

$$Y_2 = 93.44 + 4.45\,x_1 + 3.34\,x_2 + 9.49\,x_3 - 1.05\,x_1^2 - 0.36\,x_2^2 - 7.20\,x_3^2 - 4.62\,x_1\,x_2 - 4.00\,x_1x_3 - 3.70\,x_2\,x_3 \quad (6)$$

$$Y_3 = 94.27 + 4.29\,x_1 + 1.93\,x_2 + 8.03\,x_3 - 1.77\,x_1^2 - 0.055\,x_2^2 - 5.76\,x_3^2 - 2.75\,x_1\,x_2 - 3.50\,x_1x_3 - 3.72\,x_2\,x_3 \quad (7)$$

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value. The $R^2$ values for equations (5-7) were 96.25, 88.49, 88.97 and 90.70%, respectively. 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. The $R^2$ of 0.9625 for equation (5) was considered relatively high, indicating that there was a good agreement between the experimental and the predicted in the carbon yield. The $R^2$ of 0.885, 0.890 and 0.907 for equations 6 and 7, respectively were considered high, indicating that there was agreement between the experimental and the predicted in the removal of phenol and 3-chlorophenol from this model.

*3.2. IZDS activated carbon yield*

The carbon yield was found to be 19.0%, the experimental investigations revealed that the activation temperature has the greatest effect on the activated carbon yield. This was indicated by the response showing the highest F value of 152.05 as would be observed from ANOVA results. In general, the yield of prepared carbon was found to decrease with increasing activation temperature, activation time and IR. An increase in temperature would increase the release of volatiles as a result of intensification in dehydration and elimination reaction which would also increase the C-KOH and C-$CO_2$ reaction rate, thereby resulting in decreasing carbon yield [13]. An increase in activation time also would cause more volatile matters to be released which lead to a decrease in carbon yield. Since KOH would promote the oxidation process, it therefore means that with higher IR, the gasification of surface carbon atoms would be the predominant reaction, leading to an increase in the weight loss of carbon [14]. .

*3.3. Phenol and 3-chlorophenol removal onto prepared activated carbon*

The experimental observation for both the IR and activation temperature revealed that they have significant effects on the response of phenol and 3-chlorophenol removal onto prepared activated carbon, whereas activation time showed the least effect on this response. The quadratic effect of IR was also higher compared to the quadratic effects of activation temperature and time on the same response. The interaction effects between $x_1$, $x_2$ and $x_3$ on the response of phenol and 3-chlorophenol removals were found to moderate.

It was observed that the removal of PCs on prepared activated carbon generally increased with increasing activation temperature and IR. This is due to the formation of micropores caused by an increase in the activation temperature and also the development of porosity of the activated carbons prepared by KOH activation which is associated with gasification reaction. Similar results have been obtained by other researchers [15].

### *3.4. Effect of Initial Concentration of PCs on Adsorption*

The adsorption of phenol and 3-chlorophenol onto prepared activated carbon at the optimum conditions reached the equilibrium condition after adsorption time. The percentage removal of phenol" at the equilibrium time was almost 89%, whereas 97% for 3-chlorophenol.

## *4.* Conclusions

Iraqi zahdi date seeds were used as precursor to prepare an activated carbon with high surface area, sufficient yield of carbon and high phenol compounds removal with carbon yield of 19.0%. The optimum conditions for preparation of activated carbon using central composite design were found to be activation temperature of 750 $^{o}$C, activation time of 70 min and chemical impregnation ratio of 2.1. Activation temperature was found to have the greatest effect on carbon yield. Phenol and 3-chlorophenol were found to adsorb strongly onto Iraqi zahdi date seeds activated carbon.

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