Optimization study of preparation Iraqi grape seeds activated carbon for cadmium ion removal from aqueous solution

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Abstract

Porous activated carbon prepared from Iraqi grape seeds (GS) using physical activation method, consisted of carbon dioxide (CO_2) gasification. Based on the central composite design (CCD), two factor interaction (2FI) and quadratic models were respectively employed to correlate the activated carbon preparation variables. The effects of the activation temperature and activation time on the activated carbon yield and cadmium removal were investigated. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The optimum conditions for preparing activated carbon from Iraqi grape seeds were found to be activation temperature of 237.38 °C and activation time of 0.58 h. The grape seeds activated carbon yield was found to be 19.94% while the removal of Cd (II) was found to be 86.85%.

Keywords: Grape seeds; Optimization; Activated carbon; Adsorption; Cadmium ion.

المفاضلة الرياضية المختبرية لتحديد أفضل الظروف لتحضير الكاربون المنشط لبذور العنب لأغراض إزالة ايون الكادميوم من المحاليل السائلة

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الخلاصة

تم تحضير الكربون المنشط المسامي من بذور العنب العراقية (GS) باستخدام طريقة التنشيط الفيزيائي، والمتضمن استخدام ثاني أوكسيد الكربون للتنشيط مع التسخين المطلوب وبالزمن المحدد للتنشيط. استنادًا إلى برامجيات التصميم المركب المركزي(CCD) ، والمتضمن برامجيات تخص تحضير الكربون المنشط مختبريا لدراسة أفضل ظروف التحضير المختبري فقد تم استخدام نماذج تفاعل عوامل تحضير الكاربون المنشط الأساسية (2FI) ونماذجها التربيعية على التوالي لربط متغيرات تحضير الكربون المنشط من حرارة وزمن تنشيط مع نسبة ومعدل التحول (Yield) للكاربون المنشط ونسبة الازالة (Removal) للكادميوم.

تم دراسة تأثير درجة حرارة التنشيط ووقت التنشيط على معدل انتاج الكربون المنشط (باعتماد بذور العنب العراقي كمادة بادئة للتحضير) وازالة الكادميوم من المحاليل السائلة (كأحد العناصر الثقيلة الملوثة للبيئة) عبر البرامجيات أعلاه (CCD) ومن خلال التفاعل الرياضي لهذه العوامل مع المخرجات. من خلال استعراض نتائج تحليل التباين(ANOVA) ، تم تحديد العامل الأكثر تأثيرًا في كل استجابة للتصميم التجريبي وتم تثبيت الظروف المثلى لتحضير الكربون المنشط من بذور العنب العراقية والتي اشارت نظريا الى درجة حرارة تنشيط مساوية الى 237.38 درجة مئوية ووقت تنشيط يساوي 0.58 ساعة. كما وجد أن معدل انتاج الكربون المنشط لبذور العنب بلغ 19.94٪ بينما كانت نسبة إزالة الكادميوم 86.85٪

الكلمات المفتاحية: بذور العنب، الكربون المنشط، الامتصاص الكيميائي، أيون الكادميوم.

1. **Introduction:**

The presence of heavy metals and other toxic ploy aromatic hydrocarbons and trace elements in tobacco smoke is a major concern. Notably, lead (Pb), arsenic (As), chromium (Cr), nickel (Ni), and cadmium (Cd) are usually associated with its adverse health effects. Heavy metals can pass from tobacco to the smoke and smoke condensate [1].

Lead and cadmium, particularly, both of which have long half-lives (10–12 years), accumulate in tissues and fluids following smoke exposure. Biomonitoring studies reveal that smokers have substantially higher lead and cadmium levels than nonsmokers. Bioaccumulation of metals has also been demonstrated in nonsmokers, who are chronically exposed to secondhand smoke [2].

Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust at an average concentration of about 0.1 mg/kg. The highest level of cadmium compounds in the environment is accumulated in sedimentary rocks, and marine phosphates contain about 15 mg cadmium/kg [3]. Cadmium is frequently used in various industrial activities. The major industrial applications of cadmium include the production of alloys, pigments, and batteries [4]. Although the use of cadmium in batteries has shown considerable growth in recent years, its commercial use has declined in developed countries in response to environmental concerns.

Several chemical and physical technological solutions have been used and developed to remove high concentrations of each potential toxic heavy metal from wastewater. These methods are chemical precipitation, ion exchange, membrane filtration, electrochemical treatment technologies, adsorption, etc. Adsorption techniques have gained popularity recently due to their efficiency in the removal of pollutants; in addition adsorption produces high quality products and is an economically feasible process [5]. Adsorption is considered to be superior compared to other techniques due to its low cost, availability, simplicity of design, high efficiency, ease of operation biodegradability and ability to treat pollutants in more concentrated form [6].

Activated carbons obtained from various from agricultural wastes, such as banana stalk [7], date stone [8], twigs tamarisk trees [9] olive seeds [10], banana bunch fruits [11], eucalyptus trees [12], oil palm frond [13], sunflower seeds husks [14], pomegranate trees [15], willow legs [16], date seeds [17], oil palm frond [18], oil palm shell [19], and fruits seeds like grape seeds. Iraqi grapes are widely planted hardwood in Iraq and other countries. The grape trees is widely planted in Baghdad, Karbala, Diyala, Babylon, Salahuddin, Kirkuk, Dahuk, Erbil and Sulaymaniyah governorates, where it grows well thanks to suitable climatic condition and soils. Grape production provides employment and income for hundreds of thousands of families. Grapes are used to produce syrup, raisins, vinegar, fresh grape juice, and alcoholic drinks [20].

It was found that using response surface methodology (RSM) has been to be a useful tool to study the interactions of two or more variables in production of activated carbon for different applications. The adsorption capacity and activated carbon yield are highly influenced by the preparation conditions [21]. The focus of this research was to optimize the experimental conditions to prepare high yield grape seeds activated carbon for high removal of cadmium ion Cd (II) from aqueous solutions at the optimum conditions using central composite design (CCD) software.

2. Materials and Methods

2.1. Materials

Grape seeds (GS) collected from Iraqi local markets used as starting materials for preparation activated carbon as adsorbent.

2.2. Adsorbate

Technical grade of Cadmium Cd (II) of 1000 mg/l concertation supplied from Scharlaw Chiemi, S. A., Barcelona – Spain, was used as an adsorbate.

2.3. Preparation of activated carbon

Grape seeds used as precursors for preparation of activated carbon were washed thoroughly to remove the dirt's and deposits on their surfaces and dried in oven at 100 ^oC for 24 h to remove moisture. The dried grape seeds were crushed and screened to particle size of 1-2 mm and weight the amount used for preparation activated carbon, then carbonized under purified nitrogen with flow of 150 cm^3/min in a box furnace. The heating rate was fixed at 10 ^oC/min. Once the final temperature was reached to 237.38 ^oC, the nitrogen gas flow was switched to CO_2 flow of 150 cm^3/min and activation was held for different period of 0.58 h. Once the activation time is over the heating element automatically shut down by furnace programmer and the CO_2 was switched to nitrogen flow manually of 150 cm^3/min to laboratory temperature. The grape seeds activated carbon prepared (GSAC) was collected and weight to calculate the yield.

2.4. Design of experiments for preparation grape seeds activated carbon

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables. A standard design called a central composite design (CCD) was applied in this work to study the variables for preparing the activated carbons. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [21]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (five replicates). The activated carbon were prepared using physical activation method by varying the preparation variables using the CCD. The activated carbon preparation variables studied were (x_1) activation temperature and (x_2) activation time. These two variables together with their respective ranges were chosen based on the literature and preliminary studies. Activation temperature and activation time are the important parameters affecting the characteristics of the activated carbon produced [21]. The number of experimental runs from the central composite design (CCD) for those two variables consists of four factorial points, four axial points and five replicates at the center points indicating that altogether 13 experiments were required, as calculated from equation 1:

$$N = 2^n + 2n + n_c = 13 \quad \dots (1)$$

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. Each response (Y_i) for carbon yield and Cd (II) removal was used to develop an empirical model, which correlated the response to the preparation process variables using a second degree polynomial equation as given by equation 2.

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

where Y is the predicted activated carbon yield or Cd 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 Cd (II) removal variables.

The activated carbon was derived from grape seeds by physical activation method which involved by gasification with CO_2. The parameters involved in the preparation were varied using the response surface methodology (RSM). The variables studied were x_1, activation temperature and x_2, activation time. These two variables together with their respective ranges were chosen based on the literature and the results obtained from the preliminary studies where the activation temperature and activation time were found to be important parameters affecting the characteristics of the activated carbon produced. 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 Y_1 activated carbon yield, Y_2 removal of Cd.

2.5. Activated carbon yield

The experimental activated carbon yield was calculated based on the following equation (3):

$$\%Yield = \frac{w_c}{w_o} \times 100 \quad ... \quad (3)$$

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

2.6. Removal of Cd (II) studies

Batch adsorption was performed using 200 ml of cadmium solution with different initial concentrations of (25, 20, 15 and 10 mg/l) was placed in a 250 ml Erlenmeyer flasks. 0.30 g of the prepared activated carbon (GSAC), was added to the flask and kept in an isothermal shaker (120 rpm) at 30 ^{o}C until equilibrium was attained. The concentrations of Cd ion in solution before and after adsorption were determined using atomic absorption spectrophotometer (AAS Shimadzu, Japan). The percentage removal of cadmium at equilibrium was calculated by the following equation (4):

$$\%\ Removal = \frac{(C_o - C_e)}{C_o} \times 100 ..(4)$$

where C_o and C (mg/l) are the concentration of Cd at initial and at equilibrium.

3. Results and discussion

3.1. Preparation of (GSAC) using DOE

The complete design matrix for the yield response of activated carbon prepared from grape seeds (GSAC) with the removal of cadmium ion from aqueous solution include 13 runs as shown in Table . Five runs from them at the center point were conducted to determine the experimental error and the reproducibility of the data. The yield of activated carbon and the removal of Cd were influenced not only by the preparation variables, but also depended on the type and nature of the original precursors, as different precursors would have different physical and chemical characteristics.

Table (1) Complete design matrix for the yield response of activated carbon prepared from grape seeds (GSAC) with the removal of cadmium ion

No.	Block	Temperature ^{o}C	Time hr	Yeild %	Removal %
1	Block 1	118.93	0.75	16.0	77.0
2	Block 1	331.07	0.75	18.5	85.0
3	Block 1	150.00	1.00	17.7	90.1

4	Block 1	150.00	0.50	18.8	89.0
5	Block 1	225.00	0.75	19.5	88.0
6	Block 1	225.00	0.75	19.5	88.0
7	Block 1	225.00	0.75	19.5	88.0
8	Block 1	300.00	1.00	17.0	87.0
9	Block 1	225.00	0.40	20.0	90.0
10	Block 1	225.00	1.10	15.0	83.0
11	Block 1	225.00	0.75	19.5	88.0
12	Block 1	300.00	0.50	18.3	88.0
13	Block 1	225.00	0.75	19.5	88.0

3.2. Grape seeds activated carbon yield

The experimental data revealed that the activation time have the greatest effect on the ESAC yield response and gave the highest F value of 12.68. The Analysis of variance (ANOVA) results shows the interaction between activation temperature and activation time effect on the prepared activated carbon GSAC yields as shown Table 2.

Table (2) ANOVA for response surface quadratic model for GSAC yield

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob > F
Model	22.36	5	4.47	5.05	0.0280
X_1	0.68	1	0.68	0.77	0.4091
X_2	11.21	1	11.21	12.68	0.0092
X_1^2	6.70	1	6.70	7.57	0.0284
X_2^2	5.10	1	5.10	5.77	0.0474
X_1X_2		1		0.011	0.9183

Figure (1) shows the three-dimensional response and the interaction effects between the parameters considered on the yield of GSAC. In general, GSAC yield was found to increase with increasing of activation temperature and to decrease with increasing activation time.

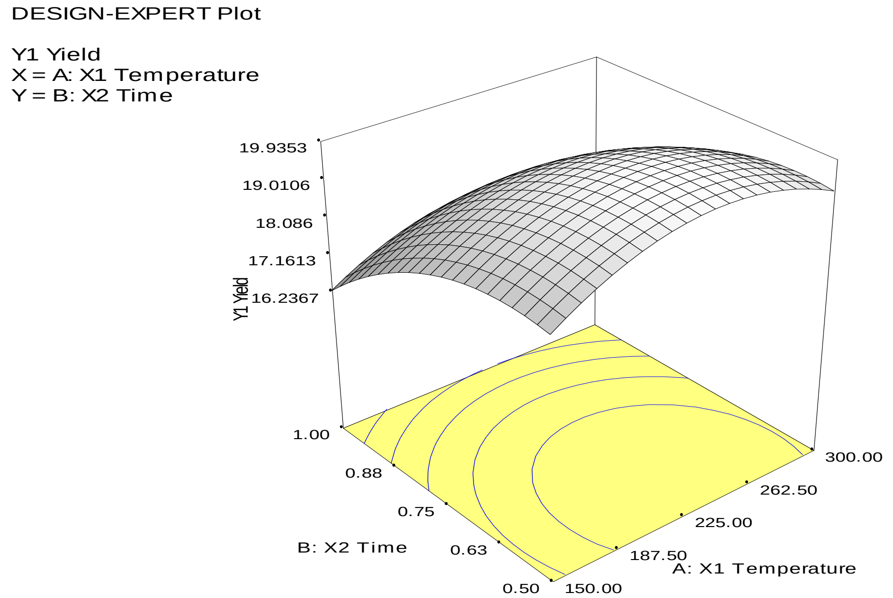

Figure (1) Three-dimensional response on the yield of GSAC, the variables activation temperature and activation time

3.3. Optimization of operation parameters

In order to optimize the preparation conditions for activated carbons fro Iraqi grape seeds for the purpose of removal pollutants as cadmium from aqueous solution used, the targeted criteria was set as maximum values for the two responses of activated carbon yield (Y1) and Cd removal (Y2) while the values of the three variables (activation temperature activation time) were set the within the range of values studied. It was found that the optimum preparation activation temperature and activation time needed were 237.38 ^{o}C and 0.58 h.

Conclusion

Iraqi grape seeds were used as precursor to prepare porous activated carbon with sufficient yield of carbon and high cadmium removal. A central composite design was conducted to study the effects of two activated carbon preparation variables, which were the activation temperature and activation time on the activated carbon yield and the removal of cadmium. Through analysis of the response surfaces derived from the models, the GSAC yield was found to decrease with increasing activation time and increase with increasing activation temperature. The optimum conditions for prepare GSAC was obtained using 237.38 ^{o}C activation temperature and 0.58 h activation time.

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