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Research Article
Adsorption of Acenaphthene Using Date Seed Activated Carbon

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Abstract

Background and Objective: Discharge of emerging pollutants in water bodies is increasing with industrial growth. Polycyclic aromatic hydrocarbons (PAHs), which are organic compounds that are carcinogenic, bio-accumulative and do not break down easily in our environment, are frequently found in wastewaters. The objective of this study is to utilize locally available cheap/waste material specifically date seeds for the removal of PAHs from wastewater. **Materials and Methods:** In this study, waste date seeds were used for preparation of granular activated carbon (GAC) and applied for removal of PAH's (specifically acenaphthene) from aqueous phase by setting up of batch experiments which has not been applied has been investigated. The removal efficiencies were compared against GAC available commercially made of coconut shell. In a preliminary study, equilibrium time and optimum GAC dosage were determined in batch experiments using commercial GAC. The efficiency of our produced GAC compared to commercial GAC at different initial PAH's concentration (16-40 µg L^{-1}) have been studied at 25°C temperature. **Results:** Results showed that GAC produced from date seeds out performed commercial GAC. Nonlinear regression analysis were performed for Langmuir and Freundlich models and it was found that Freundlich model has the closest fit for the data. **Conclusion:** The relative simplicity and low cost of producing our date seed GAC makes it an alternative to other available commercial GAC in the market for the removal of acenaphthene. However, it should be noted that our batch experiments were done at different initial pollutant concentration and didn't take into consideration effects of variations in GAC mass, time and temperature on the adsorption process.

Key words: Date seed, activated carbon, polycyclic aromatic hydrocarbons, acenaphthene

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Discharge of emerging pollutants in water bodies is increasing with industrial growth. Polycyclic aromatic hydrocarbons (PAHs), which are organic compounds that are carcinogenic, bio-accumulative and do not break down easily in our environment, are frequently found in wastewaters[1]. Removal of these contaminants is required from wastewater by treatment for the safe reuse of the treated wastewater or its disposal.

Acenaphthene is one of those PAHs. This pollutant has been removed from wastewater using physiochemical, biological and combined biological physiochemical treatment processes[2-5]. Among those methods, adsorption by granular activated carbon (GAC) is considered inexpensive, environmentally friendly and effective[6].

The GAC is produced from natural carbonaceous materials such as peat, coal and coconuts by several processes that include high temperatures approaching 800°C and steam[7]. Date seeds are waste material which is generated locally (in Saudi Arabia) in large quantities. This material can be used to prepare GAC in a more economical way. To our knowledge, GAC prepared from date seeds has not been studied for removal of acenaphthene from water.

The specific objectives of the study were: (1) To determine adsorption capacities of activated carbon prepared from date seeds for selected PAHs (Acenaphthene), (2) To compare adsorption capacities of GAC prepared from date seed with commercially available GAC. Analysis of selected pollutant (Acenaphthene) was carried out using GC-MS.

The study was composed of three phases: In phase-1, GAC was prepared from date seeds. In phase-2, a preliminary adsorption reactor was operated to determine equilibrium time and optimum GAC mass using commercial GAC. In the final phase, adsorption reactor was operated to compare date seeds GAC and commercial GAC adsorption capacities.

MATERIALS AND METHODS

The study was carried out during the year 2016 at Department of Civil Engineering, King Abdul Aziz University, Jeddah, Kingdom of Saudi Arabia.

Granular activated carbon (GAC): In this study commercial GAC made of coconut shell (manufactured by Multiply Industrial Co., Ltd. Model No. M85C) and GAC prepared from date seeds were used.

Preparation of GAC from date seed: The seeds of dates used in this study were of variable sizes. After removal from the fruit, they were washed and left to dry. Activation was done through placing the dry date seeds (430 g) in a crucible covered by sand (595 g) and heated in a furnace oven at 800°C for 2 h. The resulting product of date seeds (109 g) were separated from the sand and then placed in crucible and heated in a steam sterilizer for 2 h at 120 C. The resulting product was then crushed and sieved in mesh # 40 (425 µm) and mesh # 8 (2.36 mm).

Preparation of artificial wastewater: A stock solution composed of PAH's (Acenaphthene) with a concentration of 1000 mg L^{-1} in acetone acetate was prepared. Two milliliters was taken from stock solution and added in 10 mL methanol to get a working solution of 200 mg L^{-1} which was stored in a refrigerator for further use.

Preliminary batch experiment: Preliminary batch experiments were conducted to determine equilibrium time and optimum GAC mass using commercial GAC made of coconut shell (manufactured by Multiply Industrial Co., Ltd. Model No. M85C). This was done using constant influent concentration of PAH's (Acenaphthene) at 40 µg L^{-1} (0.1 mL of working solution in 0.5 L) was selected taking into consideration acenaphthene solubility in water at 25°C is 4,500 µg L^{-1}[8]. The experiments were performed at different time intervals i.e., 30, 90 and 180 min and at different dosage of GAC i.e., 1, 3 and 6 g in the flasks.

To perform batch experiments, GAC was added into a 500 mL screw cap Erlenmeyer glass flask then 500 mL of distilled water was added. Then 100 µL (40 µg L^{-1}) of PAH's (Acenaphthene) was added from the working solution, then Teflon tape and a screw cap were used to seal it, the flasks were placed in an incubator shaker for the desired time at 150 rpm and 25°C. The whole amount of sample (from adsorption experiments 250 mL) was filtered by using a filter flask, filter paper and a suction pump where the pump was used to pass the sample through the filter paper into the filter flask. Afterwards, the sample passed through a solid phase extraction (SPE) cartridge (Hypersep C18, 500 mg/6 mL from Thermo Scientific-USA) at a rate of 7 mL min^{-1} using a suction pump. The cartridge was conditioned by 5 mL methanol followed by 5 ml di-ionized water before extraction. The compounds were eluted from the solid phase with 10 mL cyclohexane, a splitless injection of the extract was made into a GC equipped with a high-resolution fused silica capillary column that was interfaced to a mass spectrometer (single Quadruple from Bruker Platonic). The analytes were separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical GC/MS conditions. The MS was operated in SIM mode for quantitation. The GC/MS was calibrated by standards prepared in cyclohexane. The concentration of each analyte was calculated using its integrated area and the external standard technique.

The adsorbed amount of acenaphthene at equilibrium, q_e (µg g^{-1}) was calculated by the following expression[9]:

$$q_e = \frac{V}{M}\left(C_o - C_e\right) \quad (1)$$

where, C_0 and C_e (µg L^{-1}) are the initial and equilibrium concentration of PAH's solution, respectively. V (L) is the volume of the solution and m (g) is the mass of adsorbent used.

Adsorption percentage: The adsorption percentage of both commercial and date seeds GAC at different initial concentrations of selected pollutant (Acenaphthene) were calculated by the following expression[9]:

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

where, C_o and C_e are initial and final concentration of pollutants respectively.

Adsorption isotherms: Based on the results from the preliminary batch experiment, conditions were adjusted here accordingly where optimum time was fixed at 100 min and GAC was fixed at 3 g in a 250 mL flask instead of 6 g GAC in a 500 mL flask (to reduce cost and materials used) with different influent concentrations (40, 32, 24 and 16 µg L^{-1}) for both date seeds GAC and commercial GAC. The preliminary batch experiment procedure was repeated for both commercial GAC and GAC prepared from date seeds with these new conditions.

Theoretical: From the experiments information on the adsorption capacity of the adsorbent was obtained. The adsorption isotherms describe how PAH's (Acenaphthene) interact with adsorbents and express the surface properties and affinity of the adsorbent. The adsorption isotherms generally fits the Freundlich or Langmuir model[10-13].

Freundlich model: The Freundlich model assumes a heterogeneous surface with a non-uniform distribution of adsorption over the surface of adsorbent. The Freundlich model can be expressed by the following equation[10-12]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where, q_e is the amount adsorbed at equilibrium (µg g^{-1}), K_F is the Freundlich adsorption capacity parameter (µg g^{-1}) (L µg^{-1})1/n, C_e is the concentration of adsorbate at equilibrium (µg L^{-1}) and 1/n is the Freundlich adsorption intensity parameter. Freundlich constants K_F and n values can be determined from nonlinear regression using Excel Solver.

Langmuir model: Langmuir model assumes that the maximum adsorption capacity consists of a monolayer adsorption, that the adsorption energy is distributed homogeneously over the adsorbent surface and that there are no interactions between adsorbed molecules. Langmuir equation is expressed by the following equation[10,12,13]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_e, q_{max}, K_L and C_e are the amount adsorbed at equilibrium (µg g^{-1}), maximum adsorption capacity (µg g^{-1}), Langmuir constant (L µg^{-1}) and the concentration of adsorbate at equilibrium (µg L^{-1}), respectively. q_{max} and K_L values can be determined from nonlinear regression using Excel Solver.

RESULTS AND DISCUSSION

Influence of contact time and adsorbent mass in preliminary batch experiment: It was observed that the effect of contact time and adsorbent mass has direct correlation with removal capacity where increase of contact time and adsorbent mass reduces effluent concentration of acenaphthene as shown on Fig. 1. The removal of pollutant (Acenaphthene) was rapid in the initial stage of the contact time and gradually decreased with lapse of time, only in GAC mass of 6 g it reached equilibrium. For GAC, the removal of acenaphthene increased significantly with the increase of GAC mass in a shorter amount of time.

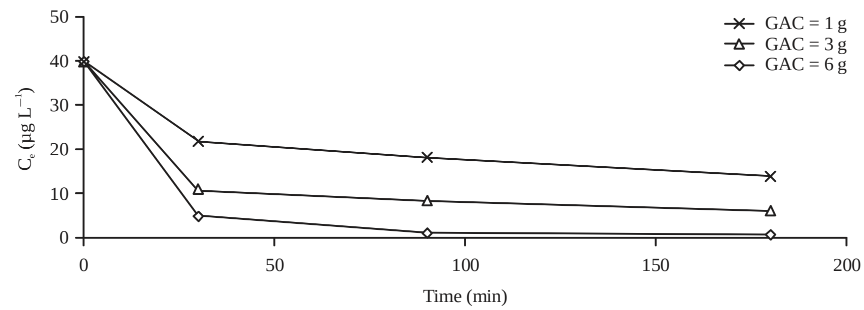

Fig. 1: Effect of contact time on effluent acenaphthene concentration

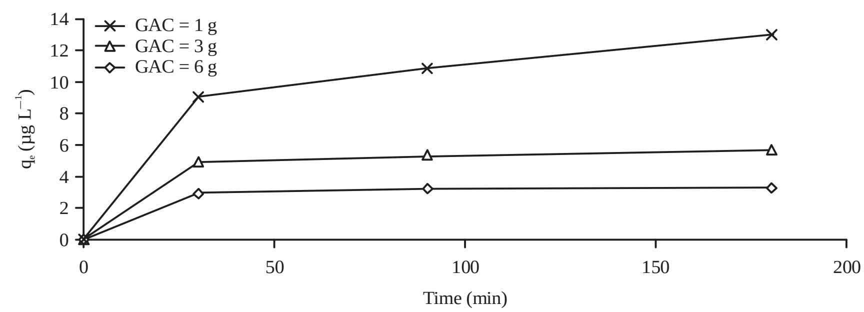

Fig. 2: Effect of contact time on adsorption capacity of acenaphthene

Selection of equilibrium time and optimum GAC Mass from preliminary batch experiment: Optimum contact time for acenaphthene was found to be 100 min. The equilibrium time considered for further work has been taken as 100 min to ensure steady state. As for optimum GAC mass, it was found to be 6 g in a 500 mL sample.

Influence of contact time on acenaphthene adsorption in preliminary batch experiment: The adsorption isotherm (q_e versus time) was depicted in Fig. 2 which showed that the adsorption capacity increased with increasing of contact time and eventually attained a constant value except when GAC mass was low at 1 g where adsorption capacity continued to increase.

Removal percentage of acenaphthene in batch experiment: To study the influence of date seeds GAC on the removal of acenaphthene compared to commercial GAC, experiments were performed with the following conditions: 150 rpm at 25°C with fixed GAC mass of 3 g both date seeds GAC and commercial GAC and a fixed 100 min duration (based on preliminary batch experiments) using different initial pollutant (Acenaphthene) concentrations of 40, 32, 24 and 16 µg L^{-1} in a 250 mL sample.

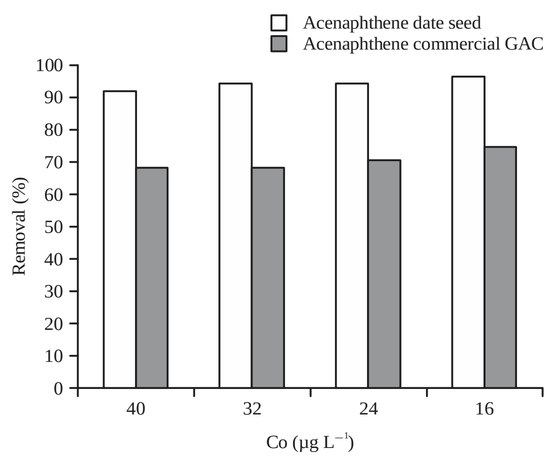

Fig. 3: Effect of initial concentration on removal % of acenaphthene using date seeds GAC and commercial GAC

The outcomes of date seed produce from GAC were better than commercial GAC by approximately 34% as shown in Fig. 3. In this study removal percentage for both date seed and commercial GAC decreased with the increase of initial concentration (96.99-92.2%) and (75.09-68.39%), respectively similar to Alade *et al.*[14,15] studies where flamboyant pod back, rice husk, milk bush kernel shell were used to produce GAC to remove acenaphthene.

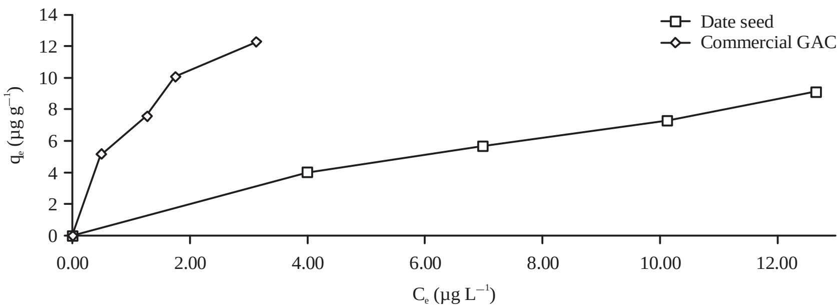

Fig. 4: Effect of effluent concentration on the adsorption of acenaphthene onto both date seeds GAC and commercial GAC

Table 1: Isotherm constants for adsorption of PAH's onto date seeds and commercial GAC

	Date seeds GAC						Commercial GAC					
	Freundlich constants			Langmuir constants			Freundlich constants			Langmuir constants		
Absorbent pollutant	n	K_F (L g^{-1})	R^2	q_{max} (µg g^{-1})	K_L (L µg^{-1})	R^2	n	K_F (L g^{-1})	R^2	q_{max} (µg g^{-1})	K_L (L µg^{-1})	R^2
Acenaphthene	2.11	1.82	0.975	4.34	0.75	0.960	1.37	0.35	0.989	6.15	0.04	0.979

Adsorption isotherms and modeling in batch experiment: Effect of effluent pollutant (Acenaphthene) concentration on adsorption capacity for both commercial GAC and our produced date seeds GAC was shown in Fig. 4. The produced date seeds GAC performed better than commercial GAC. Effluent concentration was significantly lower and adsorption capacity were higher for date seed GAC compared to commercial GAC as shown in Fig. 4.

To determine information on the mechanism and properties of the adsorption process, experiment results of acenaphthene adsorption on date seeds activated carbon and commercial activated carbon were fitted to the Freundlich and Langmuir models (Eq. 3 and 4). Freundlich and Langmuir constants were determined from using Eq. 3 and 4 in nonlinear form (Table 1) for both date seeds GAC and commercial GAC by utilizing Excel Solver.

Although coefficient of determination (R^2) (Table 1) of both non-linear equations (Eq. 3 and 4) were considerably well obtained. The Freundlich model exhibited a better fit to the adsorption data than the Langmuir model, this was in agreement with Alade *et al.*[14,15] studies.

For Freundlich model, the constants n and K_F reflect the adsorption intensity and capacity, respectively. It's stated in various literatures that when n is ranged between 1 and 10, the adsorption could be considered favorable and the adsorbent surface as heterogeneous[16,17]. Our n values fit into this range (Table 1) and date seeds GAC have a higher n value than commercial GAC for selected pollutant (Acenaphthene). Furthermore n value for our date seed GAC (2.11) is higher than n values from Alade *et al.*[14,15] studies (ranging from 1.04-1.45) where flamboyant pod back, rice husk, milk bush kernel shell were used to produce GAC to remove acenaphthene. As for K_F, the higher its value the higher the adsorption capacity, here our date seeds GAC was better than commercial GAC.

CONCLUSION

In batch experiments, the produced date seed GAC proved that it's significantly better than commercial GAC in removing acenaphthene (34%). It can be considered as an alternative to other available commercial GAC in the market for the removal of acenaphthene. However, it should be noted that the current batch experiments were done at different initial pollutant concentration and didn't take into consideration effects of variations in GAC mass, time and temperature on the adsorption process.

SIGNIFICANCE STATEMENT

This study discover the use of waste date seeds generated locally (in Saudi Arabia) in large quantities to produce granular activated carbon (GAC) that can be beneficial for the removal of PAH's (specifically acenaphthene). This study will help researchers to uncover the feasibility of using date seed GAC to remove acenaphthene from waste water which was not been investigated previously and encourage date manufacturers to utilize date seed waste instead of throwing it away.

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