KOH-based porous carbon from date palm seed: preparation, characterization, and application to phenol adsorption
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ABSTRACT
The date palm seed being one of the major forms of biomass produced from the date industry in UAE, its potential to be an appropriate precursor for the preparation of porous carbon utilizing KOH as an activating agent is assessed in the present work. The porous carbon is prepared at an activation temperature of 600°C, impregnation ratio of 2, and activation duration of 1 hour, in an inert atmosphere using a conventional horizontal furnace. The resultant porous carbon has a Brunauer–Emmett–Teller surface area of 892 m²/g, pore volume of 0.45 cm³/g, and an average pore diameter of 1.97 nm. This porous carbon was used for adsorption studies at different initial concentrations (100–400 mg/l) and temperatures (30–50°C). The adsorption isotherm parameters for the Langmuir and Freundlich models were determined using experimental adsorption data and it was found that both Langmuir and Freundlich isotherms described well the adsorption behavior of phenol on porous carbon. The mono layer adsorption capacity was observed to be 333 mg/g, which is highest for the reported date palm seed biomass-based porous carbon. From the data obtained, it was concluded that the removal of phenol from aqueous solution by porous carbon prepared from date palm seed is a low-cost process with an extremely high performance.

Key words | date palm seed, Langmuir and Freundlich isotherm, phenol adsorption, porous carbon

INTRODUCTION
Phenol and phenolic derivatives are common organic chemicals that appear very frequently in wastewater from heavy chemical, petrochemical, pharmaceutical, paint, paper and pulp, and oil refining industries. Typically the refinery wastewater streams contain phenolic compounds in a wide range of concentrations, which need to be treated before the wastewater stream is discharged. These compounds are normally used as intermediates in the synthesis of pesticides, colors, plastics, insecticides, and many more substances. Improper treatment of these polluting compounds may produce a negative impact on human life and the environment by contaminating the soil and polluting the ground water. Furthermore, their toxicity may seriously affect microorganisms. Thus, the removal of phenolic compounds before discharging into surface water has become a priority in the management of wastewater treatment systems in chemical, petrochemical, and oil industries.

Existing phenol removal technologies are solvent extraction, distillation, adsorption, membrane separation, and electrochemical treatments (Busca et al. 2008). It appears that the adsorption of phenols by porous carbon is the best option over the other methods due to zero-sludge production and flexible process operation, as well as reduction in process costs. Porous carbon is most widely used in the adsorption process due to its chemical and mechanical stability, high degree of surface reactivity, and high adsorption capacity (Azargohar & Dalai 2005). In fact, the United States Environmental Protection Agency has recommended utilization of porous carbon as one of the best available technologies in removing organic pollutants. However, commercially available porous carbons are expensive and, hence, much of the research focus is on developing cost-effective high surface area carbon from inexpensive raw materials such as rice husk (Yalcin & Sevinc 2000), sawdust (Malik 2004), coconut
shell (Yang et al. 2010), and sugar-cane (Liou 2010). The physical and chemical properties of the porous carbon from date palm seeds can be tuned during the activation process as per effluent composition and the availability of date palm seeds in this region growing year by year, so this precursor can be utilized effectively to obtain high adsorption capacities comparative to commercial carbon.

Porous carbons are well known and widely used adsorbents in industries for a variety of separation applications. The current interest in porous carbon for the research community can be evidenced from the quantum of research reported in open literature on porous carbon, which accounts for nearly 30% of the overall research in the field of carbon. Generally, the porous carbon manufacturing methods are either based on physical activation which is basically gasification reactions of carbon with steam/CO₂/combination of both or based on the chemical activation methods which include dehydrating agents such as phosphoric acid, sodium hydroxide, potassium hydroxide, and zinc chloride. The precursors for the preparation of porous carbons could be either coal or lignocellulosic material or biomass-based materials. However, the characteristics of porous carbon highly depend on its precursor characteristics and the method of activation to produce the porous carbon (Suresh Kumar Reddy et al. 2012a, b). Among the available choice of impregnating agents, metal-based activating agents such as KOH are reported to be more suitable to produce highly microporous carbons, which have high adsorption capacities compared to other chemically activated porous carbons produced using agents such as phosphoric acid and zinc chloride (Zao et al. 2011). All authors have taken process variables such as activation temperature and KOH/biomass ratio as effecting process variables. But it seems activation time is one of the process variables among those process variables which was neglected in optimization of porous carbon development.

Hence, the present work attempts to utilize the abundant date palm seeds available in UAE as a precursor and KOH as the activating agent. Although a large variety of precursors have been tested to assess their suitability to be a potential precursor for the manufacture of porous carbon, work related to utilization of date palm seeds as a suitable precursor is limited. Among the work reported in the literature on utilization of date palm seeds by our research team, porous carbon was prepared using phosphoric activation and CO₂ activation (Suresh Kumar Reddy et al. 2012a, b) for elemental mercury and mercuric chloride applications. Some other researchers utilized date palm seeds as potential precursors for chemical oxygen demand (COD) removal from refinery wastewater (El-Naas et al. 2010) and for bentazon and carbofuran removal from pharmaceutical waste streams by developing porous carbon from date palm seed using KOH and CO₂ as an activating agent with reported Brunauer–Emmett–Teller (BET) surface area 765 m²/g and pore volume 0.43 cm³/g (Salam et al. 2011).

Evidenced from the lack of sufficient literature on utilization of date palm seeds as a suitable precursor, the present work attempts to assess its potential to be a suitable precursor for preparation of porous carbons and to utilize it for treatment of organic effluents. This is deemed necessary due to the large quantities of waste date seeds generated in the gulf region, which does not possess any significant value addition to industry.

The prime objective of the present work is aimed to investigate the following:

1. Preparation of porous carbon from date palm seeds as a precursor and KOH as an activating agent using literature reported process optimization conditions in view of maximization of BET surface area and % yield.
2. Assessment of the textural characteristics of optimized porous carbon to estimate BET surface area, pore volume, pore size distribution, and mean pore diameter using nitrogen adsorption isotherms and surface functional group studies using an Fourier transform infrared spectrometry (FT-IR).
3. Establishment of the phenol equilibrium adsorption isotherms and to test them with well-known adsorption isotherm models.

**EXPERIMENTAL**

**Preparation of porous carbon**

Date palm seeds received from local a farm in Abu Dhabi, UAE have been utilized as the precursor. The date palm seeds were washed with deionized water to remove the foreign materials and dried in an oven at 105 °C for 24 hours. The dry materials were ground to powder (particle size >500 μm) and were stored in a desiccator for further experiment.

The date palm seed precursors, crushed and sieved as stated in the above section, were utilized for KOH activation. Ten grams of date palm dust was taken as the precursor and mixed with KOH (40% by volume) solution at an impregnation ratio (KOH/biomass) of 2. The mixture was kept under stirred condition for 5 hours using a
magnetic paddle to ensure complete soaking of the KOH solution into the precursor. After ensuring complete soaking of KOH solution into the precursor, the mixture was dried in an oven at 105°C until it was completely dry and crisp. The dried powdery material was activated in a horizontal furnace at a temperature of 600°C for an activation time of 60 min, in an inert atmosphere using nitrogen flow of 150 ml/min (Fangyi et al. 2008). Upon completion of the experiment, the carbonized sample was cooled to room temperature in an inert atmosphere and washed repetitively with hydrochloric acid aqueous solution to remove ash present in the materials, followed by washing with distilled water several times until the pH of the filtrate was reduced to neutral. The final porous carbon was then dried in an oven at 105°C for 12 hours to ensure complete dryness and the yield of porous carbon was estimated based on grams of bone dry porous carbon obtained to grams of bone dry date palm seed taken for activation.

Adsorption procedure

Phenol was supplied by Sigma Aldrich and distilled water was used for the preparation of stock solution of concentrations 400, 300, 200, and 100 mg/l phenol solution. The ultraviolet (UV) light spectrophotometer was utilized at a wavelength of 269 nm to estimate the concentration of the phenol solution before and after adsorption.

Equilibrium batch adsorption experiments were conducted using Erlenmeyer flasks of 250 ml capacity. A fixed amount (0.1 g) of adsorbent was placed in each flask and a known concentration and volume (100 ml) of phenol (100, 200, 300, and 400 mg/l) was added to each flask. The bottles were kept in a shaker water bath, at different temperatures (30, 40, and 50°C) at 200 rpm. The experiments were continued at stable conditions for a period of 40 hours to ensure equilibrium between the solid (adsorbent) and the liquid phase (adsorbate). The amount of phenol adsorbed by the adsorbent was calculated using the formula

\[
q(e) = \frac{(C_0 - C_e)V}{W}
\]

where \(q(e)\) is the equilibrium adsorption (mg/g), \(C_0\) is the initial concentration of phenol solution (mg/l), \(C_e\) is the equilibrium concentration (mg/l), and \(W\) is the weight of adsorbent (g), respectively.

Several models have been published to describe the experimental data of adsorption isotherms, but of these models, the Langmuir and Freundlich models are the most frequently employed. These equations are given as provided below

**Langmuir isotherm model:**

\[
\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}
\]

**Freundlich model:**

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
\]

where \(C_e\) is the equilibrium concentration (mg/l), \(q_e\) is the amount adsorbed (mg/g), \(k_L\) and \(q_m\) are Langmuir constants, and \(k_F\) and \(n\) are Freundlich constants. Thus, in the present work, both models were used to describe the relationship between the amount of phenol adsorbed and the corresponding equilibrium concentration. The Langmuir (Langmuir 1916) assumes uniform and constant binding of the sorbate on the surface of the adsorbent. Unlike the Langmuir isotherm model, the Freundlich isotherm (Freundlich 1906) does not have any thermodynamic basis and does not offer much physical interpretation of the adsorption data.

**Structural characteristics of porous carbon**

The BET surface area, along with the pore size distribution, was estimated using the standard nitrogen adsorption isotherm obtained by an Autosorb 1-C adsorption apparatus (Quanta Chrome Instruments, FL, USA). Prior to analysis, the samples were first dried in an oven at 130°C overnight and were quickly placed in the sample tube. The tube was then heated to 170°C and was evacuated for 4 hours until the pressure was less than 10⁻⁴ Torr. The BET surface area was calculated from the isotherms using the BET equation (Suresh Kumar Reddy et al. 2012a, b). The Dubinin–Radushkevich equation was used to calculate the micropore volume. The total pore volume was calculated from nitrogen adsorption data as volume of liquid nitrogen at a relative pressure of approximately 0.99–1 (Lyubchik et al. 2002). FT-IR spectra of various samples were recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions using KBr as the diluent to identify the functional groups in the activated carbon. The samples were loaded into the sample holder and scanned in the mid-IR region, viz. 100–4,000 cm⁻¹ to generate the spectrum. A pellet made of nearly the same amount of KBr was used as the background.

**RESULTS AND DISCUSSION**

**Characterization of porous carbon**

Figure 1 shows the adsorption desorption isotherm of N2 at –196 K for a sample prepared at the optimum conditions. A
sharp increase in the adsorption curve at a $P/P_0$ value of 0.1 is indicative of the fact that micropores are being filled. However, increase in adsorption with increase in relative pressure beyond 0.1 and the formation of a hysteresis loop indicate a type-IV isotherm which is typical for mesoporous solids, displaying capillary condensation. A sharp increase in the adsorption capacity at high relative pressure close to 1 further strengthens the type-IV isotherm. The presence of a hysteresis loop at a $P/P_0$ value of 0.4 corresponds to a type-IV isotherm, which characterizes a mesoporous nature, with bottle neck-type pores. The steep increase in the isotherm at a relative pressure of 0.8 or above indicates development of wider pores and is possibly due to the capillary condensation in the mesopores (Prahas et al. 2008). It has been reported that porous carbon prepared at a high impregnation ratio and activation temperature possesses characteristics of a type-IV isotherm, indicating the presence of micro- along with large amounts of mesopores (Baquero et al. 2003). The porous carbon yield was estimated to be 24.5% and the BET surface area of the porous carbon was estimated as 892 m$^2$/g, with average pore volume of 0.45 cm$^3$/g and average pore diameter of 1.97 nm. The carbon obtained in this work is much better than the reported results (El-Naas et al. 2010), maybe due to the synthesis-optimum process conditions.

To further investigate their surface chemistries, FT-IR spectra of porous carbon are presented in Figure 2. The FT-IR spectrum of the precursor shows the presence of functional groups such as alkene, ester, aromatic, ketone, alcohol, hydroxyl, ether, and carboxyl. This is in accordance
with the date palm seeds composed of cellulose, hemicellu-
lose, and lignin (Suresh Kumar Reddy et al. 2022a, b). The
spectrum of porous carbon shows IR bands around 3,400–
3,600 cm$^{-1}$ which are attributed to the $\text{–OH}$ vibration
stretching of hydroxyl groups involved in hydrogen bonding,
possibly due to adsorbed water (Salam et al. 2011). The band at
2,400 cm$^{-1}$ is attributed to C–H stretching vibrations in aliphatic
structures, 1,640 cm$^{-1}$ is ascribed to the olefin functional
groups and the one at 1,150 cm$^{-1}$ to the stretching vibration of the aromatic ring (methoxy-O-CH$_3$) (Suresh
Kumar Reddy et al. 2022a, b). The peak at 750 cm$^{-1}$ pertains
to C–H out-of-plane bending in benzene derivatives. The phenol
adsorption advances through donor–acceptor formation; the primary active groups are carbonyl and basic
groups (Gundogdu et al. 2012).

Adsorption isotherm

Numerous factors are known to have significant effects on
the adsorption of phenol, which include pH of solution,
type of carbon, carbon surface functionalities, mineral con-
tent of carbon, and addition of electrolytes. In addition, it
is known that the phenols do partly get adsorbed irreversibly
due to polymerization by oxidative coupling reaction. Irre-
spective of this fact, it is general practice to assess the
phenol adsorption capacity of the carbon as it serves as an
important indicator to assess its ability for wastewater treat-
ment applications (El-Naas et al. 2010). Hence the present
work attempts to assess the equilibrium adsorption capacity
of the carbon prepared using KOH activation under optim-
ized process conditions and to compare it to the literature
reported values (El-Naas et al. 2010).

Figure 3 shows the equilibrium adsorption isotherm of
phenol uptake by the porous carbon at three different tem-
peratures of 30, 40, and 50 °C. A decrease in the phenol
uptake with increase in temperature could be attributed to the
exothermic nature of the adsorption process, which is
well in concurrence with the general understanding of the
adsorption process. An increase in the water adsorption
capacity of porous carbon is reported to increase with tem-
perature, as well as change the hydration grades of species
dissolved in aqueous solution. The interaction energy of
phenol–water changes with increasing temperature as the
water adsorption by the carbon greatly modifies the
phenol adsorption mechanism. Therefore, since a significant
portion of active sites are occupied by water molecules, they
will weaken $\pi-\pi$ interactions, which are primary bonding
mechanisms of phenol on activated carbon and the donor–
acceptor complex formations (Gundogdu et al. 2012).

Langmuir and Freundlich isotherm models were
employed to identify an appropriate adsorption isotherm
model. Figures 4 and 5 show the Langmuir and Freundlich
isotherms, respectively, in comparison to the experimental
data at 30, 40, and 50 °C. The suitability of the models can
be judged by the $R^2$ values which can be seen in Table 1
along with other parameters. The Langmuir equation is
reported to be suitable for homogeneous surfaces while
the Freundlich equation is suitable for highly heterogeneous
surfaces often giving a good representation of adsorption
data over a restricted range of concentrations (Suresh
Kumar Reddy et al. 2014). The equilibrium adsorption data
in the present work were found to match the Langmuir iso-
therm model, possibly due to the less heterogeneous nature
of the porous carbon. The nature of adsorption expressed in
terms of dimensionless factor $R_L$ was found to be 0.131,
which suggests that the adsorption was favorable. The maxi-
num monolayer adsorption capacity was estimated to be
333 mg/g and was relatively high and on a par with the
adsorption capacities reported in the open literature (El-
Naas et al. 2010).

The maximum phenol adsorption capacity of 333 mg/g

corresponds to porous carbon with a BET surface area of
892 m$^2$/g, with average pore volume of 0.45 cm$^3$/g and aver-
age pore diameter of 1.97 nm. It is well known that
matching the pore size of adsorbent with the size of the
adsorbate molecule is important to maximize the adsorption
capacity. The phenol molecular diameter is in the range of
approximately 0.8–1.0 nm. The average pore diameter of
the porous carbon is approximately two times that of
phenol, which means that it is easy for phenol to diffuse
into the inner pores of the porous carbon and to get
adsorbed on the internal surfaces. Thus, the range of pore sizes is appropriate for phenol to adsorb and is an important factor in the adsorption process.

Table 2 shows the maximum phenol adsorption capacity of various porous carbons prepared from different precursors. The adsorption capacity of the carbon prepared in the present work favorably compare with the highest of the reported values (El-Hendawy et al. 2001; Sulaymon & Ahmad 2008; Ahmaruzzaman 2008; El-Naas et al. 2010). The adsorption capacity strongly depends on the porous nature as well as the favorable surface functional groups in addition to the adsorption process conditions such as pH, electrolyte, and temperature. Hence, a wide variation in the adsorption capacity is expected depending on the source of porous carbon and the process methods. Although the surface area of the porous carbon prepared in the present work is of lower range, nevertheless adsorption capacity is favorable, owing to the nature of favorable functional groups, minerals, etc. (Maarof et al. 2004).
Temperature (°C) the adsorption capacity of phenol.

CONCLUSIONS

The effectiveness of porous carbon locally prepared from date palm seeds for the uptake of phenol from synthetically prepared aqueous solution wastewater was evaluated. The porous carbon prepared under the optimum process conditions is estimated to have a pore volume of 0.45 cm³/g, an average pore diameter of 1.97 nm, and a micropore volume of 43%, and has adsorption capacity comparable to other adsorbents, which proves that date palm seed can be considered as a low-cost alternative to commercial porous carbons for the removal of phenols from refinery wastewater. The textural characteristics of the porous carbon prepared at optimized conditions are predominantly micropores, with meager mesopore evidence from hysteresis loop. From FT-IR studies it can be revealed that porous carbon contains favorable functional groups for enhancing the adsorption capacity of phenol.

The Langmuir isotherm model described well the adsorption behavior of phenol on porous carbon and the mono layer adsorption capacity observed to be 335 mg/g. The dimensionless factor R_l was found to be 0.131, which suggests that the adsorption system is favorable. As part of our future work, various lignocellulosic biomasses utilized for porous carbon preparation with this method, testing phenol adsorption capacity, and studying physical characteristics of these materials can be discussed.

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