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ORIGINAL PAPER

Preparation of porous carbon from date palm seeds and process optimization

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Abstract The agricultural wastes like date palm seeds to be a suitable precursor for the preparation of porous carbon has been explored in the present work, utilizing phosphoric acid as the activating agent. The experimental methods reported in literature were chosen with certain modification in order to simplify the process. The process optimization was performed using the popular response surface methodology adopting a Box-Behnken design. Process optimization was performed to maximize the porous carbon Brunauer–Emmett–Teller (BET) surface area and the methylene blue (MB) adsorption capacity, with the process variables being the activation temperature, impregnation ratio (IR) and the activation time. The textural characteristics were assessed based on nitrogen adsorption isotherms, scanning electron microscopy, while the adsorption capacity was estimated using the MB adsorption. The optimized experimental conditions were identified to be an activation temperature of 500 °C, IR of 3.1 and activation time of 71.4 min, with the resultant porous carbon having BET surface area of 846.7 m^2/g and MB adsorption capacity of 445.7 mg/g. The popular Langmuir and Freundlich adsorption isotherm models were tested, and a maximum monolayer adsorption capacity of the MB was estimated to be 345 mg/g, which compares with the highest of MB reported in literature, evidencing the suitability of the porous carbon for adsorption of macro-molecular compounds.

Keywords Porous carbon · Methylene blue · BET surface area · Optimization

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Introduction

Porous carbon in its broadest sense is a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended intraparticulate surface area, which is useful as an adsorbent, and it can effectively remove organic and inorganic pollutants by the process commonly known as adsorption (Taghdiri and Zamani 2013; Behera et al. 2012). They are prepared using thermal decomposition of a variety of carbonaceous materials, usually from charcoal due to its low cost and availability (Ahmadpour and Do 1996; Bansal and Goyal 2005). It has large number of applications in liquid- and gas-phase adsorption processes, for removal of impurities, in drinking/waste water systems for reduction in organic pollutants and as a catalyst support in a variety of chemical synthesis (Gurrath et al. 2000; Mazyck and Cannon 2000; Walker and Weatherley 1998).

The physical properties and the chemical composition of the precursor, as well as the methods and process conditions employed for activation determine the yield, surface area, pore size distribution, surface functional groups and the adsorption properties of the porous carbon (László et al. 1997). The adsorption capacity of porous carbons are determined by their porous structure, but is strongly influenced by the chemical nature (Bansal and Goyal 2005). Any material that is carbonaceous and lignocellulosic in nature can be utilized as a precursor for the preparation of porous carbon. The two major methods of preparation of porous carbon are categorized as physical and chemical activation. Physical activation is a two-stage process in which precursors are carbonized in inert atmosphere prior to activation either with steam or CO_2 or combination of both. Chemical activation is a single-stage process, with the activating agents being phosphoric acid, nitric acid, zinc chloride,

K_2CO_3 and bases such as NaOH and KOH. The chemical activation slows down the formation of tar during thermal degradation of lignocellulosic material (Caturla et al. 1991) in the presence of dehydrating agent. Generally, it has been well documented that the activation temperatures are low, while the yield of porous carbon is high in chemical activation process as compared to physical activation (Lim et al. 2010). Phosphoric acid and zinc chloride have been used extensively in chemical activation process for biomass-based precursors, while KOH is utilized for coal-based precursors (Puziy et al. 2002). The chemical activation agents first degrade the cellulosic material, and the process of carbonization creates suitable pore structure as a result of dehydration (Azevedo et al. 2007). Phosphoric acid is preferred as compared to zinc chloride due to its non-polluting nature and is being widely used in pharmaceutical and food industries. In addition, phosphoric acid can be easily recovered by simply washing with water and can be reused in the process rendering it economically viable (Diao et al. 2002; Rodríguez-Reinoso et al. 1995; Srinivasakannan et al. 2004; Teng et al. 1998). Phosphoric acid imparts cation-exchange capacity, making it chemically stable both in acidic and base media in addition to its thermal stability (Puziy et al. 2002). Utilization of phosphoric acid as a suitable activating agent for the preparation of porous carbon from a variety of agricultural wastes has been well recorded in literature (Al-Qaessi and Abu-Farah 2010; Attia et al. 2008; Fierro et al. 2010; Girgis and El-Hendawy 2002; Guo and Rockstraw 2007; Haimour and Emeish 2006; Prahas et al. 2008; Zuo et al. 2005). However, it should be noted that the activation methods are different as majority of it reports single-stage activation with activation in inert conditions. The benefits of two-stage activation in the absence of inert media have been highlighted from the commercial production point of view as well as with respect to the quality of carbon (Lim et al. 2010) and also they highlighted the ability of process to generate high surface area mesoporous carbon with mean pore diameter of 3.2 nm.

Agricultural wastes are considered to be a very important feedstock as they are renewable as well as low-cost materials (Stavropoulos and Zabaniotou 2005). Date seeds are among such wastes and very few authors have reported utilization of date seeds as a precursor for the preparation of porous carbon (Banat et al. 2003; El-Naas et al. 2010a, b; Haimour and Emeish 2006; Hameed et al. 2009; Salman et al. 2011). Dates are abundantly available in United Arab Emirates (UAE), and their annual production capacity was reported to be 765,000 M tons in 2003, which constitutes 11 % of the global production. Date seeds have compact cellular structure and have comparatively low porosity. The chemical composition of date seed is reported to constitute of hemicellulose (23 %), lignin (15 %), cellulose (57 %) and ash (5 %) (Haimour and Emeish 2006).

Effluents from dyeing processes in the textile industries are known to contain color dye, heavy metals and surfactants that are stable to photo-degradation, bio-degradation and oxidizing agents (Garg et al. 2004; Kannan and Sundaram 2001; Malik et al. 2007). It has been a great concern to remove the synthetic dyes as they (or their degradation components) may be carcinogens and toxic that requires effective treatment system. Conventional methods that include precipitation, ion-exchange, membrane filtration and reverse osmosis have been applied for the removal of pollutants from wastewaters. However, these processes involve high investment and they are energy intensive (Demiral et al. 2008). The ever evolving and fast changing situation demands waste management mechanisms to be effective and economical. Adsorbents with large surface areas and appropriate pore size, which can adsorb large quantities of dye molecules, can potentially be a part of the integrated waste management system to meet the stringent environmental regulations (Chan et al. 2008).

The present work attempts to combine the pre-drying and semi-carbonization stage as single operation by prolonging the pre-drying stage until the mixture is bone dry, suitable for direct carbonization (second stage of activation), utilizing a self-generated atmosphere (SGA). The action of phosphoric acid on lignocellulosic material to cause chemical and structural changes at temperature starting as low as 50 °C is known (Zhang et al. 2009); however, the corresponding rates are low. Physically, this involves reconfiguration of the molecules resulting in the formation of a pasty mass (polymerization) followed by depolymerization resulting in dry material.

Process optimization of the process variables, activation temperature, activation time and IR on the Brunauer–Emmett–Teller (BET) surface area and methylene blue (MB) adsorption capacity uses response surface methodology (RSM) with Box-Behnken method (BBM). The objective functions for optimization are maximization of BET surface area and MB adsorption capacity. MB was chosen as the adsorbate, since it is a larger molecule with a molecular diameter of 0.8 nm and is accessible to pores that are larger than 1.3 nm (Valdés et al. 2002). However, the adsorptive capacities of porous carbons depend mainly on the precursor nature, the operating conditions of adsorption such as temperature, pH and the nature of adsorbate. This work had been taken place in The Petroleum Institute, UAE, during the year 2012–2013.

Materials and methods

The raw date seed from date processing industry in Unite Arab Emirates (UAE) was utilized as the precursor. They were first washed in 0.1 M HCl to remove dirt and greasy material on the seed surface, followed by repeated washing with distilled water to ensure all the impurities as well as the acid were removed. The seeds were dried in an air oven at 110 °C for 4 h. After drying, the seeds were crushed using mixer grinder to the powder form. 15 g of crushed date seeds of size 200–400 microns were taken as the precursor and mixed with H_3PO_4 (98 % of purity) of 60 % concentration, at a desired impregnation ratio (IR) (2–4). IR is defined as the grams of phosphoric acid/gram of dry date palm seed powder. The mixture was stirred for 5 h to ensure complete soaking of the precursor in phosphoric acid. After ensuring complete soaking of acid into the precursor, the mixture was dried in an air oven at 110 °C until it was completely dry and crisp. The dried powdery material was carbonized at a temperature ranging from 400 to 500 °C in the activation time range of 45–75 min, in a self-generated atmosphere. Upon completion of the experiment, the carbonized samples were cooled to the room temperature. The samples were washed repeatedly in batches, to ensure all the salts of phosphoric acid that were removed from the activated sample. This was ensured with the conductivity of filtrate lower than 50 µs. The washed product was then dried in air oven at 110 °C for overnight to ensure complete dryness. The yield of porous carbon was estimated based on the grams of dry porous carbon obtained to the grams of dry date palm seed powder utilized for activation. Methylene blue was used for the preparation of stock solution of concentration 1,200, 800 and 400 mg/l MB solution. The UV spectrophotometer was utilized at a wave length of 600 nm to determine the concentration of the MB solution before and after adsorption.

Equilibrium batch adsorption experiments were conducted using Erlenmeyer flasks 250 ml capacity. A fixed amount (0.1 g) of adsorbent was taken in each flask, and a fixed volume of MB solution with known concentration (400, 800 and 1,200 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 35 h to ensure equilibrium between the solid (adsorbent) and the liquid phase (adsorbate). The effect of pH was assessed by adjusting the pH of the liquid phase either with 0.1 M NaOH or with concentrated HCl to the desired pH. The pH of solution of the virgin MB solution was found to be 3.7 after adding porous carbon into the solution. The effect of pH was assessed at the liquid bath temperature of 30 °C at an initial concentration of MB at 800 mg/l.

The samples were analyzed at 77 K with an accelerated surface area and porosimetry system (Autosorb-1-C, Quantachrome). Prior to gas adsorption measurements, the carbon was degassed at 300 °C in a vacuum condition for a period of at least 2 h. Nitrogen adsorption isotherm was measured over a relative pressure (P/P_0) range from approximately 10^{-7} to 1. The BET surface area was calculated from the isotherms by using the BET equation. The Dubinin–Radushkevich (DR) method 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). FEG-250 SEM instrument (FEI, Holland) was employed at an accumulation voltage of 30 kV with 2.5 K magnification to estimate the surface pore structure of the porous carbon.

Response surface methodology using a Box-Behnken experimental design is a standard statistical tool widely used for the process optimization with minimum number of experiments (Gönen and Aksu 2008; Tan et al. 2008a). The process variables were the activation temperature (X_1), IR (X_2), and activation time (X_3), while the response variables being the BET surface area (Y_1) and MB uptake (Y_2). The Box-Behnken design recommends a minimum number of 15 experiments including the three repeat runs for optimizing the process parameters (Bezerra et al. 2008). The upper and lower limits of the variables were provided in Table 1, where '−1' represents the low level, '+1' for the high level and '0' for the center point. Table 2 shows the experimental conditions, for which the experiments were conducted along with the results. The upper and the lower limits were fixed based on the extensive literature analysis on the process conditions as well as based on the preliminary experimental runs. An empirical second-order polynomial model relating the three process variables to response variable as represented below was utilized,

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i,j=1}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{n} \beta_{ii} X_i^2 \tag{1}$$

where Y is the predicted response, β_0 is the constant, β_i is the linear coefficient, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients and X_i, X_j are the coded values of the process variables. The results of experiments were analyzed using statistical computing software MINITAB-15 utilizing the model equation and the analysis of variance (ANOVA).

Table 1 High and low levels of factors

Factor	Low level (−1)	Center point (0)	High level (+1)
Activation temperature (X_1) (°C)	400	450	500
Impregnation ratio (X_2)	2	3	4
Activation time (X_3) (min)	45	60	75

Table 2 Experimental data

Run	X_1 (°C)	X_2	X_3 (min)	Y_1 [BET surface area (m^2/g)]	Y_2 [MB number (mg/g)]
1	400	2	60	428	300
2	500	2	60	820	326
3	400	4	60	651	363
4	500	4	60	860	374
5	400	3	45	550	295
6	500	3	45	838	320
7	400	3	75	713	308
8	500	3	75	812	470
9	450	2	45	430	250
10	450	4	45	665	291
11	450	2	75	630	310
12	450	4	75	598	365
13	450	3	60	653	382
14	450	3	60	654	381
15	450	3	60	653	375

Results and discussion

Box-Behnken method was used to construct a polynomial regression equation in order to analyze the correlation between the process variables and the response variables. The porous carbon BET surface area was found to vary from 428 to 860 m^2/g, while the MB uptake was found to vary from 250 to 470 mg/g, respectively, as shown in Table 2. The final empirical models in terms of BET surface area (Y_1) and MB number (Y_2) were given by Eqs. (2) and (3),

$$Y_1 = 652.6 + 23.61X_1 + 58.14X_2 + 33.68X_3 + 92.21X_1^2 - 55.14X_2^2 - 45.92X_1X_2 - 47.15X_1X_3 - 66.7X_2X_3 \tag{2}$$

$$Y_2 = 379.39 + 36.63X_1 + 34.7X_2 + 37.08X_3 - 21.21X_1X_2 - 34.37X_1X_3 - 50.05X_2^2 - 25.2X_3^2 \tag{3}$$

The appropriateness of model equation in predicting the experimental responses can be assessed based on the coefficient of determination (R^2). The R^2 for BET surface area of porous carbon was estimated as 0.97, while that of MB uptake was estimated as 0.96, validating the appropriateness of the model. The coefficients of model equation along with significance of each of the model parameters were analyzed for BET surface area and MB, respectively. The lower the value of p or the higher the value of F or t (F test or t test), the significant were the model parameters. The quadratic parameter X_3^2 is insignificant over BET surface area, while the interaction parameters X_2X_3 and quadratic parameters X_1^2 are insignificant on the MB uptake. A test on appropriateness of the model is mandatory as it is used to optimize the process. The validity of model in addition to R^2 is based on the ANOVA.

Analysis of variance is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model (Huiping et al. 2007). The model F value of 21.58 and $p > F$ of 0.002 indicate the validity of the model for BET surface area. The model F value of 14.7 and $p > F$ value of 0.004 as well imply the appropriateness and validity of the model for MB uptake. From the ANOVA results, it can be concluded that the model predictions using Eqs. (2) and (3) are satisfactory and that the model can be utilized to identify the optimum process conditions.

BET surface area

Brunauer–Emmett–Teller surface area is an important parameter which determines the adsorption capacity of porous carbon. In general, higher the BET surface area, higher will be the adsorption capacity provided the pore size are suitable to the adsorbing molecule. The effect of activation temperature, IR and activation time on BET surface area (Y_1) is presented in this section. All the three parameters show significant positive effect toward BET surface area. Figure 1 shows a 3D surface plot showing effect of activation temperature and IR on BET surface area, whereas Fig. 2 shows 3D response surface plot of the effect of activation temperature and activation time on BET surface area. The BET surface area shows an increasing trend with the increase in activation temperature and IR. The increase in BET surface area with the increasing IR possibly indicates the rate limiting step to be IR. An increase in IR further contributes to the acid reacting with lignocellulose, contributing to the increase in the porosity of the carbon or the BET surface area. In the case of porous carbon preparation from cotton stalk using phosphoric acid, Girgis and El-Hendawy (2002) observed that there has been an increase in IR, which results a significant increment in the BET surface area. An increase in activation temperature is well known to increase the rate of reaction, which contributes to the widening of pore structure which as a result increases the BET surface area. It is very well known in the literature that with the increase in activation temperature, the BET surface area increases significantly. For sorghum as a precursor in the preparation of porous carbon, Diao et al. (2002) observed that an increase in the BET surface area resulted in an increase in activation temperature in the range of 400–500 °C. As can be seen from the Fig. 1, the surface area is highest at an activation temperature of 500 °C and IR of 3. Activation time is also expected to contribute to increase in the extent

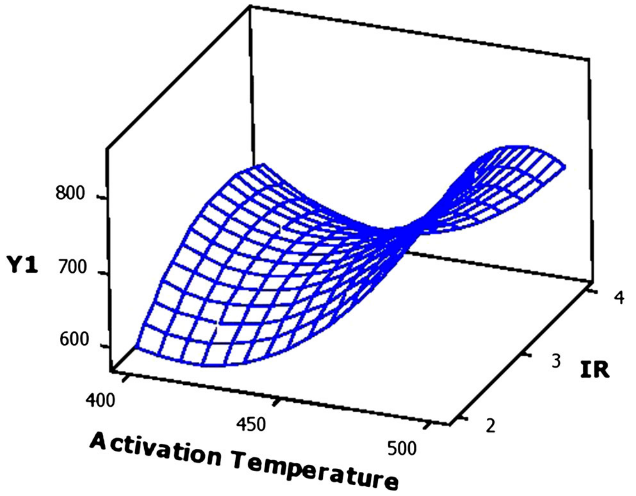

Fig. 1 3D-surface plot of activation temperature and impregnation ratio on BET surface area (Y1)

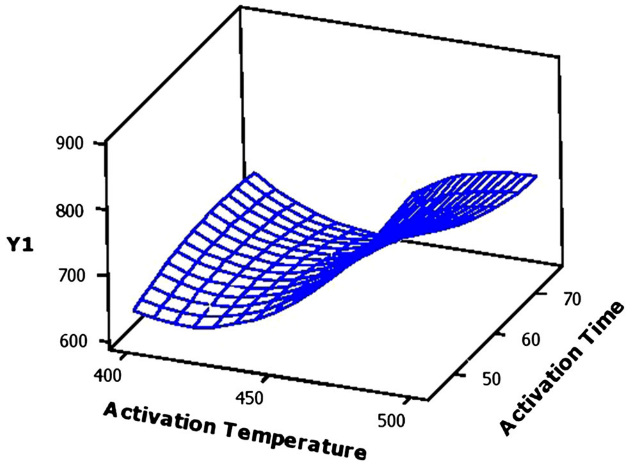

Fig. 2 3D-surface plot of activation temperature and activation time on BET surface area (Y1)

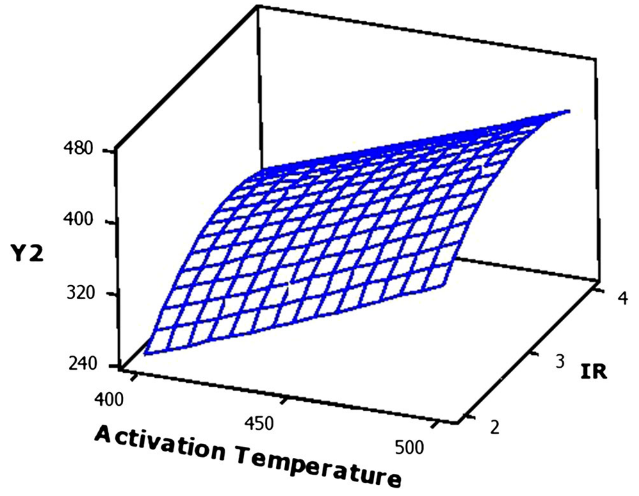

Fig. 3 3D-surface plot of activation temperature and impregnation ratio on activated carbon MB number (Y2)

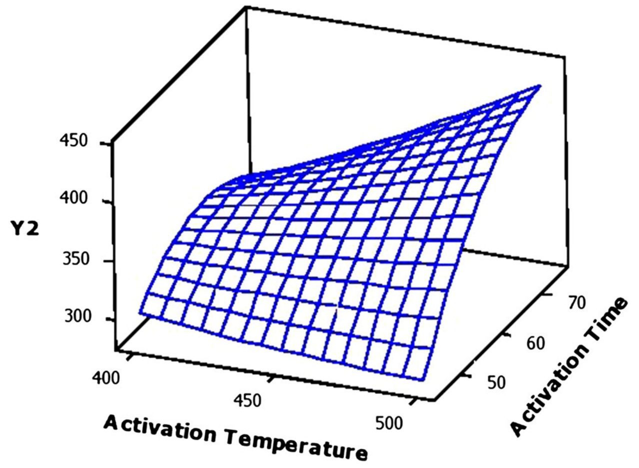

Fig. 4 3D-surface plot of activation temperature and activation time on activated carbon MB number (Y2)

of reactivity, which contributes to the increase in BET surface area. The longer activation period gives acid more time to react with the precursor which constitutes toward the hydration reaction and swelling of the internal structure which facilitates the impregnating agent to react with the interior of the particle. A combination of high activation temperature and activation time seems to be having critical effects in generating structural changes facilitating large surface areas.

Methylene blue uptake

Referring to ANOVA results, activation temperature, IR and activation time showed significant effects on the adsorption of MB. Figure 3 shows a 3D response surface plot of IR and activation temperature on the MB number, whereas Fig. 4 shows response surface plot of activation time and temperature on MB number. At low IR and activation temperature, MB uptake was low, while it increased significantly at higher IR and activation temperature. The highest MB adsorption was observed when both the variables IR and temperature had highest values within the range studied. In addition, it also indicates an optimum IR as the MB was found to decrease at high IR. An increase in MB indicates the increase in suitability of pore size to accommodate the MB molecules. As inferred earlier, an increase in the activation temperature as well as the IR contributes toward decrease in yield which is a potential measure of the increase in porosity either due to creation of new pores or due to enlargement of existing pores. Similar observations on the increase in MB uptake with increase in the activation temperature and IR has been reported Attia et al. (2008) and Tan et al. (2008b) in open literature. Additionally, Fig. 4 shows a significant increase in the MB uptake with increase in the activation time at activation temperatures. Although the statistical analysis indicates activation time to be insignificant due to low changes in the yield, it brings in a significant change in MB adsorption capacity. A combination of high activation temperature and activation time seems to be critical, in generating the structural changes facilitating large adsorption of MB. In general, the MB adsorption not only depends on physical characteristics of porous carbon, but also on its chemical nature. At high activation times, the change (quality and quantity) in functional groups may subsequently affect the adsorption capacity of MB. Generally, at high activation times, an increase in the aromatic content of porous carbon functional groups has been well recorded (Baçaoui et al. 2001; Wang et al. 2005).

Process optimization

The optimum process conditions estimated using optimizer tool in the MINITAB-15 is presented in Table 3, along with the results of repeat runs conducted at the optimized process conditions. The objective functions Y_1 and Y_2 maximized in the experimental conditions region to obtain these optimum conditions. The optimum process conditions were estimated to be an activation temperature of 500 °C, an IR of 3.1 and activation time of 71.4 min., with the resultant BET surface area of porous carbon 846.7 m^2/g and MB of 445.7 mg/g. Taking into consideration the variations involved in experiments as well as the analysis, results are in good agreement with the model prediction, validating the appropriateness of the process optimization exercise. It also confirms the suitability of RSM approach for optimization of process conditions for the preparation of porous carbon. The popular Langmuir and Freundlich adsorption isotherm models were tested, and a maximum monolayer adsorption capacity of the MB was estimated to be 455 mg/g.

Textural characteristics

The structural heterogeneity of porous carbon plays an important role in adsorption processes, and numerous methods have consequently been developed and applied for the characterization of this property. The present work utilized nitrogen adsorption isotherm and scanning electron microscopy (SEM) to characterize the samples. The adsorption–desorption isotherms of N_2 at -196 K for sample prepared at optimum process conditions along with the sample corresponding to maximum adsorption capacity are shown in Fig. 5.

A sharp increase in the amount of nitrogen adsorbed at relative low pressure of 0.1 indicates the micropore filling. A typical Type-I isotherm will exhibit a sharp increase until an P/P_0 of 0.1, beyond which remains constant, which are characteristic of a microporous carbon. Figure 5 shows a sharp increase in the amount adsorbed even beyond P/P_0 of 0.1, with the desorption isotherm showing the presence of hysteresis loops at relative pressure in excess of 0.4, which are characteristic of Type-IV isotherm, which additionally substantiates the highly mesoporous nature of the sample. A steep increase in the slope at high relative pressure ($P/P_0 > 0.8$–1) can be attributed to the development of wider pores and possibly due to capillary condensation in the mesopores (Prahas et al. 2008). It has been reported that porous carbons prepared at high impregnation ratio and activation temperature possess characteristic of Type-IV isotherm, which indicates the presence of micropores along with large amounts of mesopores (Baquero et al. 2003).

The structural heterogeneity of porous material is generally characterized in terms of the pore size distribution. The pore size distribution is closely related to both kinetic and equilibrium properties of porous material and perhaps is the most important aspect for characterizing the structural heterogeneity of porous materials. The surface morphology of porous carbon corresponding to the optimized conditions is shown in Fig. 6. The SEM micrograph

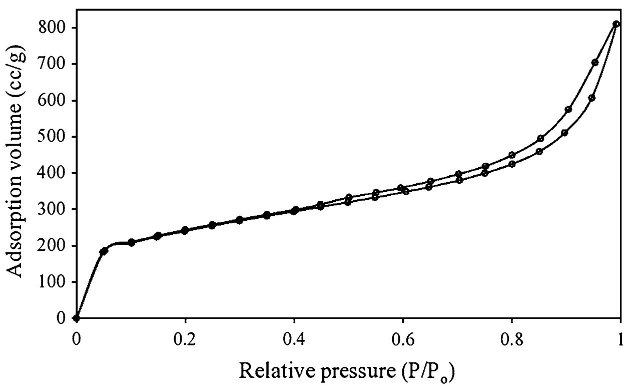

Fig. 5 Nitrogen adsorption isotherm of the activated carbon

Table 3 Model validation

X_1	X_2	X_3	BET surface area (m^2/g)		% Error	MB number (mg/g)		% Error
			Predicted	Experimental		Predicted	Experimental	
500 °C	3.1	71.4 min	846.7	830	2.0	445.7	450	1.0

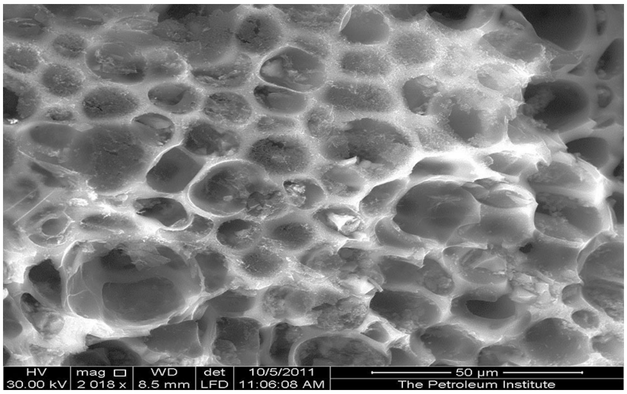

Fig. 6 SEM for activated carbon

confirms the presence of large sized and non-uniform formation of pores, but clearly indicating the presence of large number of pores on the surface.

Conclusion

The following are the key findings in the process optimization of porous carbon process from date pits:

- The process optimization was performed using RSM adopting a Box-Behnken design, for maximizing the BET surface area and MB number. The optimized experimental conditions were identified to be an activation temperature of 500 °C, IR of 3.1 and activation time of 71.4 min, with the resultant porous carbon having BET surface area of 846.7 and MB adsorption capacity of 445.7 mg/g. Such low activation temperature coupled with low activation time and high yield render this process conditions highly desirable for commercial exploitation.
- The nitrogen adsorption isotherm indicates a Type-IV isotherm, with the presence of hysteresis loops at relative pressure in excess of 0.4.
- The monolayer adsorption of MB using the Langmuir adsorption isotherm was estimated to be 345 mg/g for optimized process condition, while the maximum MB adsorption capacity of 470 mg/g, corresponds to the porous carbon with highest of BET surface area.
- The increase in MB uptake with decrease in temperature indicates the adsorption process to be exothermic. Freundlich isotherm was found to match the experimental data as compared to the Langmuir isotherm, owing to the heterogeneous porous nature of the porous carbon.

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