Preparation and Characterization of Activated Carbon from Date Pits by Physical Activation in a Fluidized Bed Reactor

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Summary: The preparation of activated carbon from date pits was experimentally investigated by physical activation with a mixture of superheated steam and air in a fluidized bed reactor. The effect of different process parameters like particle size of the precursor, temperature of carbonization, time of activation and operating pressure of the fluidizing medium on different physical, chemical and adsorptive characteristics of the resultant products were studied. It was thereafter established, that granular activated carbon in 25% yield, of moderate activity in liquid phase and lower Ball Pan Hardness No. (BPH No.), than the desired ASTM Standard was obtained from date pits in particle size of 1.00 - 2.00 mm. The other operational variables optimized through this study were operating pressure of 20 psi in 60 minutes of activation time.

Introduction

Activated carbons are unique and versatile adsorbents because of their extensive surface area, microporous structure and high adsorption capacity. This commodity is assuming increasing importance in many economic sectors and concern industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile, in certain biomedical applications and for the removal of organic matter from water and waste water [1,2]. These may be prepared from various carbonaceous substances by any of the two processes developed by Ostrejko [3], namely physical and chemical activation processes. The former is a high temperature process as compared to the latter one, and is mostly used in the preparation of granular activated carbons. Two types of reactors namely static & fluidized bed, and superheated steam, carbon dioxide or other oxidizing gases are used as activating medium in this process. Unlike the process of chemical activation, no hazardous liquid effluents are generated in this process.

These authors have been engaged in systematic R&D work on the development of know-how for the preparation of powdered and granular activated carbons (PAC and GAC), from different indigenous precursors viz. agro wastes, inferior woods, low rank coals and their subsequent characterization [4-7]. In this connection, a study was also undertaken on the preparation of PAC from date pits by the process of chemical activation [8]. Date (Phoenix dactylifera L), is grown in all the four provinces of Pakistan and its annual production is to the tune of 2,34,200 tons. Stone or pit accounts for about 15% by weight of whole date [9]. Henceforth, an approximate amount of 35,000 tons of date pits is available in the country, which has presently no potential use and is merely wasted.

Several studies have been conducted by various investigators for the preparation of PAC and GAC from date pits by the process of chemical activation [8,10,11]. The aim and objective of the present study is to prepare GAC from date pits by the process of physical activation in a fluidized bed reactor. Moreover, different process parameters like particle size of the precursor, temperature of carbonization, fluidization pressure of activating medium, time of activation etc. were also optimized in light of % yield, strength and degree of activity achieved in various products ,obtained under different sets of working conditions.

Results and Discussion

Washed and dried date pits in two particle sizes of 1.00-2.00 mm & 2.00-3.00 mm were used to explore their suitability as an indigenous raw material for preparing *GAC* (granular activated carbon) by the process of physical activation, with a mixture of superheated steam and air, in a locally developed, designed, fabricated and patented fluidized bed reactor [12].

Table-1 presents the proximate chemical analysis of date pits.

It may be seen in Table-1 that hemicellulosic and fibrous portions account for about 75-76 % of

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Table -1: Proximate Chemical Analysis of Date pits

Constituents analyzed	% Found
Moisture	8.00
Oil	8.80
Protein	5.00
Carbohydrates (mainly hemicellulose)	61.00
Fibre	15.70
Ash	0.85

the whole date pit. These constituents mainly contribute towards 30-35 % yield of activated carbon as shown in Table-2, after the successive processes of carbonization and physical activation.

Table-2 depicts various physical and chemical characteristics of various GAC products, obtained under different sets of working conditions, as regards temperature of carbonization (T) and initial particle size of the raw material (D).

A review of Table-2 clearly shows, that sample $D_2 T_2 P_2 t_2$, prepared from date pits of particle size 2.00-3.00 mm (D_2) and higher temperature of carbonization 700-750°C (T_2) showed highest activity in case of all the three adsorbates under study. Henceforth the two parameters —'D_2' and 'T_2'— were selected and utilized in onwards studies. The fluidized bed process has shown better activation with smaller size particles of 1.00 — 2.00 mm, as it assists in more vigorous movement of particles in the fluidized bed, which helps the volatile gases to escape more easily from the particles, thus enhancing the pore development and also the resultant activity (13). This table also shows that yield in either of the case varied between 29-34%. This observation quite well corresponds with another study, which describes that carbonization yield of date pits varies between 26 — 36% [14].

Table-3 depicts the influence of variables of residence time and operating pressure of fluidizing medium (superheated steam + air), on the adsorptive properties of different GAC products. It shows that, both the variables have quite strong influence on the eventual activity of the end products, specially in their lower range viz. t_1 - t_2 (60 -75 minutes) & P_1 - P_2 (10-15 psi), whereas this effect although present, but quite less prominent in higher range in both the cases. Table-4 presents different physical characteristics like pore space, ball pan hardness No. and surface area of pores correlated with micro (>10A°), meso (> 15 A°), and macroporous (>28 A°) area of the GAC products, calculated from their adsorption data against the three adsorbates [15]. Table 3 also shows that the sample 'D_2 T_2 P_2 t_2', prepared in lesser residence time of 75 minutes, showed optimum

Table-2: Effect of variables of particle size and carbonization temperature on different physical & chemical characteristics of finished products

Sample Code*	Iodine No. (mg/gm)	Methylene Blue No. (mg/gm)	Molasses No. (mg/gm)	Bulk Density (gm/cc)	True Density (gm/cc)	Pore Space (cc/100 gm)	Ash content (%)	Yield (%)
$D_1T_1P_2t_2$	85	27	73	0.5535	0.8415	62	3.5	34.8
$D_1T_2P_2t_2$	239	104	107	0.4302	0.8367	113	4.0	32.1
$D_2T_1P_2t_2$	504	205	119	0.5832	1.4562	102	5.7	31.2
$D_2T_2P_2t_2$	697	252	159	0.6613	1.7428	106	5.9	28.8

*Carbonization Temperature -- T (T_1= 500-550°C. T_2=700-750°C)
Particle Size -- D (D_1=1.00-2.00 mm D_2=2.00-3.00 mm)
Operating Pressure -- P (P_1=10psi, P_2=15psi, P_3=20psi, P_4=25psi)
Residence Time -- t (t_1=60 min. t_2=75min, t_3=90 min. t_4=120min)

Table-3: Effect of variables of residence time and operating pressure on different chemicals characteristics of finished products

Sample Code	Ash Content (%)	Iodine No (mg/gm)	Methylene Blue No. (mg/gm)	Molasses No (mg /gm)
$D_2T_2P_2t_1$	5.7	205	108	68
$D_2T_2P_2t_2$	5.9	697	252	159
$D_2T_2P_2t_3$	6.1	705	270	167
$D_2T_2P_2t_4$	6.3	715	268	181
$D_2T_2t_2P_1$	5.4	350	120	108
$D_2T_2t_2P_2$	5.9	697	252	159
$D_2T_2t_2P_3$	6.3	735	265	166
$D_2T_2t_2P_4$	6.2	755	272	170

Table - 4: Effect of variables of residence time and operating pressure on different physical characteristics of finished products

Sample code	Yield (%)	Bulk Density (gm/cc)	True Density (gm/cc)	Pore Space (cc/100gm)	Ball pan hardness No.	Surface Area of pores >10A° m^2/g	Surface Area of pores > 15A° m^2/g	Surface Area of pores >28A° m^2/g
$D_2T_2P_2t_1$	39.0	0.7217	2.1096	91	83	175	309	33
$D_2T_2P_2t_2$	28.8	0.6613	1.7428	106	74	635	720	77
$D_2T_2P_2t_3$	20.7	0.6533	1.8118	98	65	643	772	80
$D_2T_2P_2t_4$	17.2	0.6411	1.8790	103	53	652	766	87
$D_2T_2t_2P_1$	33.2	0.6815	1.7979	96	79	311	343	52
$D_2T_2t_2P_2$	28.8	0.6613	1.7428	106	74	635	720	77
$D_2T_2t_2P_3$	24.7	0.5263	1.7798	134	71	671	758	80
$D_2T_2t_2P_4$	15.8	0.4945	1.7810	146	66	690	778	82

activity in case of all the three adsorbates. Further increase in time (t_3 &t_4) did not result in any significant increase in the activity. Therefore, this optimum time (t_2) was selected and utilized in following set of experiments designed for the selection of optimum pressure of fluidizing gas, varied in the range of 10,15,20 and 25 psi.

A review of Tables-3 & 4 clearly shows that, sample '$D_2T_2t_2P_3$', activated at a pressure of 20 psi showed optimum activity in case of all the three adsorbates. Moreover in this particular case, yield was around *25%* and pore space was 134cc/100 gm. Ball pan hardness No., which is one of the prime characteristic of any GAC sample, is also detailed in Table — 4. It is quite evident from the data therein, that the increase in fluidization time has a more pronounced adverse effect on eventual strength properties of GAC products, as compared to the variable of operating pressure. This effect is rather more clearly demonstrated in Figs 1 and 2, where the slope showing variation of BPH with change in fluidization time is more steeper than that of operating pressure. However, neither of the GAC sample, obtained from date pits, attain the minimum standard hardness of 95% required for GAC [17].

The data on retention of original particle size of the GAC samples, after fluidization under specified conditions, has been depicted in Table-5. The sample selected in respect of optimum activity, yield, pore space and surface area-'D_2 T_2 t_2 P_3' - has original particle size retention of 68.6%, which is quite appropriate.

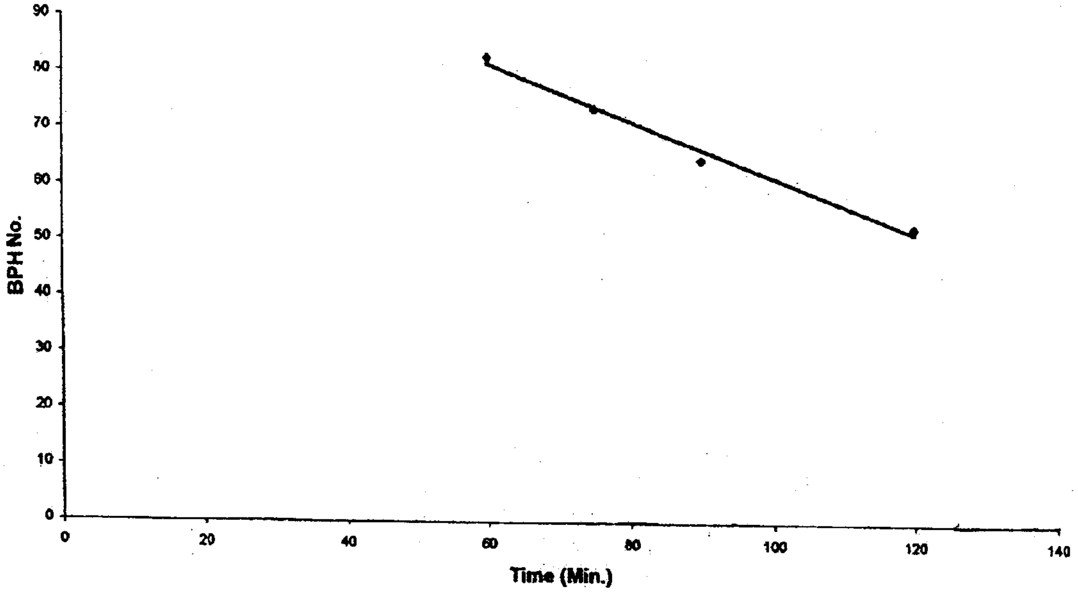

Fig. 1: Variation of BPH No. with Fluidization Time.

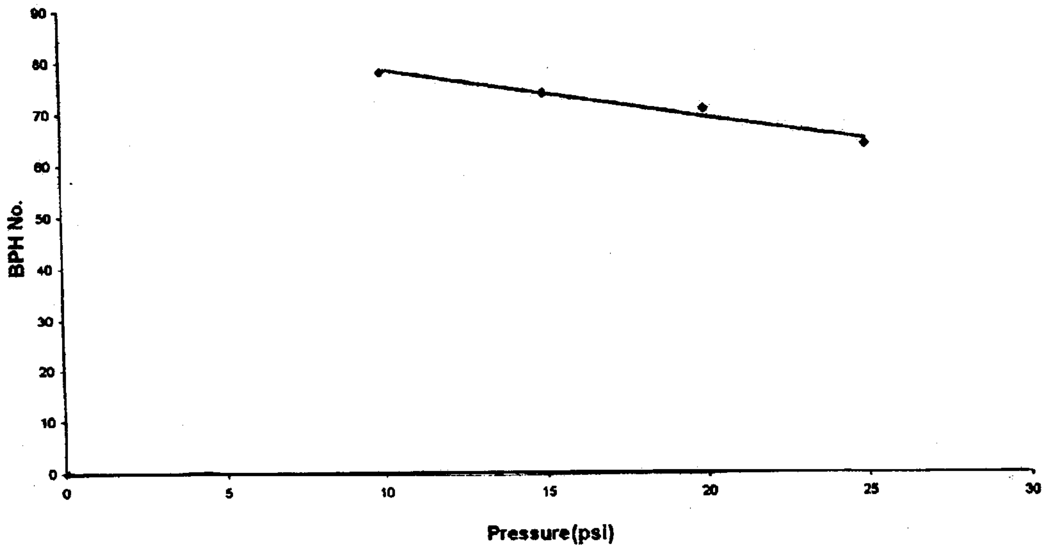

Fig. 2: Variation of BPH No. with Operating Pressure.

Table-5: Effect of residence time and operating pressure on original particle size retention of finished products.

Sample Code	Original particle size retention (%)
$D_2T_2P_2t_1$	80.0
$D_2T_2P_2t_2$	77.8
$D_2T_2P_2t_3$	67.7
$D_2T_2P_2t_4$	56.2
$D_2T_2t_2P_1$	79.2
$D_2T_2t_2P_2$	77.8
$D_2T_2t_2P_3$	68.6
$D_2T_2t_2P_4$	52.1

A comparison of the results of the present study on physical activation with the one performed earlier on chemical activation of date pits [8], reveals that, powdered activated carbon (PAC) samples of higher activity were obtained in case of latter, probably due to better dehydrating action of activating chemicals like zinc chloride and phosphoric acid, which is of course not in case of activating gases like steam, carbon dioxide etc., utilized in the present study.

Experimental

Date pits were collected through the courtesy of a date processing mill after depitting. These were then washed with an stream of water to free them from retaining fruit and then dried in an electrically heated tray drier at 105 — 110°C to constant weight. Washed and dried pits were then disintegrated in a pilot disintegrator and eventually classified to two different particle sizes of 1.00 to 2.00 mm and 2.00 to 3.00 mm on a standard sieve shaker.

A series of experiments were being designed and performed in connection with physical activation of date pits in its two different particle sizes. A semi pilot scale stainless steel fluidized bed reactor, exclusively designed and fabricated in these laboratories, was used in this study [12]. The reactor was provided with a cyclone and placed inside a bricklined furnace. It was heated by two gas fired cup type burners and temperature inside the reactor was monitored by a Ni-Cr thermocouple provided with a gauge, during the course of all these experiments. The operating temperature of the fluidized bed during the period of carbonization was kept in the range of 600-650°C, whereas it was raised to 900-950°C during the period of fluidization. These temperatures have been found to be the most appropriate, commonly practiced in this process [16].

Apart from initial particle size of the precursor, the effect of other process variables, being pursued in this study, were temperature of carbonization, operating pressure of the mixture of superheated steam and air, being used as fluidizing medium [13] and time of activation/residence of the materials, being activated in the fluidized bed. The variables of carbonization temperature, operating pressure and time of activation designed and explored during the course of these experiments, with each particle size of the precursor, were 500-550°C, 700-750°C, 10,15,20 & 25 psi and 60,75,90 & 120 minutes respectively. Experiments with each of the variable were repeated twice including three replicates of each experiment. Replicates were reproducible, and standard deviation was calculated wherever applicable.

Different products (GAC), obtained by physical activation of date pits in the fluidized bed reactor, under different sets of experimental conditions, were then evaluated for their efficacy for adsorption in liquid phase towards adsorbates of different molecular dimensions like iodine, methylene blue and molasses [17,18]. Different physical and chemical parameters of these products like particle size retention, ash content, bulk and true density and ball pan hardness were also determined (19). Moreover, surface area of pores of these samples >10,15 and 28 A°, correlated with the three adsorbates being investigated in liquid phase, were also calculated [15].

Conclusions

It has thereafter been concluded from these studies, that GAC having moderate activity in liquid phase and somewhat lower strength can be prepared from date pits in particle size of 1.00 — 2.00 mm, by physical activation in a fluidized bed reactor, with a mixture of superheated steam and air, at an operating pressure of 20 psi in residence time of 75 minutes.

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