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ACTIVATED CARBON FROM FRUIT PITS
Part I. Effect of Chemical Treatment on the Adsorptive Properties of Carbonized Date Pits

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The effect of chemical treatment on disintegrated pits of date (*Pheonix dactylifera* L.) by zinc chloride and phosphoric acid as compared to simply carbonized date pits on their adsorptive properties have been studied. It has been observed that the fraction of lower particle size, apparently found in the outer layer of the pit, gives a product of balanced micro and macropores, low bulking value and enhanced activity in liquid as well as gas phase by zinc chloride activation. In contrast, the phosphoric acid activation gives a product quite low in activity and available pore space.

Key words: Activated carbon, Date pits, Chemical activation.

Introduction

Agricultural residues are cheap source for the manufacture of activated carbon and inferior woods [1], agrowastes [2,3], fruit pits [4] etc. The two factors which however play a decisive role in selection of an appropriate raw material for the manufacture of activated charcoal are its availability and relatively low cost. Little work has been done on fruit pits for the preparation of activated carbon. However, the work so far has been carried out shows that these carbons may easily be processed in fluidized bed reactors for gas activation [5] due to uniformity in the size and density of each of the pits and may satisfactorily be used in gas masks. Later on, Lopez Gonzalez *et al.* [6] used olive pits for obtaining activated carbon by the process of chemical cum physical activation.

Date (*Pheonix dactylifera* L.) suits well to local environmental conditions and is grown in all the four provinces of Pakistan. The total annual production of dates in Pakistan is about 2,34,200 tons [7]. The stones or pits accounts for about 15% by weight of the whole date [8]. Henceforth an approximate amount of 35,000 tons of date pits is available in the country which is presently being merely wasted. As far as its collection is concerned, it is indeed a problem. However, modern food processing industry which export dates after depitting may be an ideal source for its collection and profitable utilization.

The carbonization of date pits was investigated by Razouk *et al.* [9] with some studies on chemical activation of date meal by zinc chloride for vapour adsorbent carbons. However, no work is known to authors regarding the use of activating agents *viz.* $ZnCl_2$ and H_3PO_4 prior to carbonization of date pits. The present study describes the preparation of activated carbon from date pits by chemical activation process[10]. Their adsorptive characteristics have been evaluated for liquid as well as gas phases.

Experimental

The date pits were first washed free of dirt and inherent pulp portion and dried in an electric oven at 105°. The dried pits were analysed (Table 1) by Standard Method [11]. 100 Grams of the whole date pits were then carbonized (treatment'A') in a stainless steel vessel out of contact with air at a temperature of 850-900° for 4 hrs.

The pits were crushed in pilot plant disintegrator and classified in a standard sieve shaker into three different particle sizes of (#1) 3.36 to 5.59 mm, (#2) 1.68 to 3.36 mm and (#3) 0.30 to 0.80 mm. Two activating agents namely phosphoric acid [12] and zinc chloride [13] have been used for this study. 100 Grams of date pits of each of three particle sizes were treated with one litre of 85% orthophosphoric acid (treatment 'B') and 100 gms of zinc chloride dissolved in 50 ml of 10% HCl (treatment 'C'), dried and carbonized in an inert atmosphere at 650-700° for 4 hrs. The carbonized materials were then refluxed with 10% HCl, filtered and washed with water free of phosphate and chloride ions respectively. The resultant charcoals were dried and stored in airtight bottles for their characterization. The bulk and true density [11] and thereafter pore space per 100 gms [14] of these activated carbon samples were calculated. The percentage yield and ash content of these samples were also determined. Their adsorptive capacities for iodine,

Table 1. Chemical Analysis of Date Pits.

S.No.	Constituents analysed	Amount present %
1.	Moisture	8.00
2.	Oil	8.80
3.	Protein	5.00
4.	Carbohydrates (Mainly hemicellulose)	61.00
5.	Fibre	15.70
6.	Ash	0.85

methylene blue, molasses and carbon tetrachloride were determined [15] to evaluate their activity for liquid and gas phase requirements.

Results and Discussion

The present study describes the preparation, influence of particle size and activating agent on different physical and chemical characteristics of the activated carbon samples prepared from date pits.

Table 1 describes the chemical analysis of date pits collected from a local food packaging industry.

Table 2 describes three different particle size of pits utilized for the preparation of various activated carbon samples. It was initially observed after disintegration of whole date pits and their further classification that particle size #1 and #2 were found to be 60% and 28% respectively whereas the finer particle size #3 was in the range of 10 to 12%. It also shows different physical and chemical characteristics such as bulk and true density with the resultant pore space and also the ash content and percent yield of these samples. For sample 'A', which is simply carbonized unactivated date pits, the bulk density is the highest and true density is the lowest resulting in a negligible pore space. In the case of B_1, B_2 and B_3, samples of different particle sizes activated with phosphoric acid, the bulk density increases by decreasing the particle size and true density is very slightly affected by this variation which results in lowering of pore space. It may further be noted that this decrease in pore space with the decrease in particle size of the raw material is very prominent in B_2 and B_3. In samples activated with zinc chloride (C_1, C_2 and C_3), variation in bulk density of different samples with the decrease in particle size is very marginal but shows a regular pattern. However, it is not the case in true density where the increase is much pronounced in samples C_2 and C_3. This pattern of decrease in bulk and increase in true density of these activated carbons results in gradual increase of their pore space [14]. Furthermore it is observed that a variation in bulk density of the sample markedly affects its resultant pore space as compared to true density where this effect is less pronounced. The ash content of different samples shows a regular pattern of gradual increase with decrease in particle size of the raw material which may be due to the increased ash content in the finer particles of disintegrated date pits (Table 2). The pattern in case of percent yield obtained is closed to that of ash. This enhancement in yield of these activated carbons may be due to the higher ash content in the parent raw material. It may be seen here that variation in ash content of the carbon samples have a pronounced influence on their bulk density. The ash content of samples C_1, C_2 and C_3 is far less than that of B_1, B_2 and B_3. This may be due to the ash reducing action of zinc chloride [16]. Henceforth their actual yield is quite higher than those of the phosphoric acid activated samples.

The tests of iodine, methylene blue, molasses and carbon tetrachloride were performed for evaluating the adsorptive characteristics of these activated carbon samples [17]. First three tests are generally used for empirical characterization of liquid phase activated carbons covering the entire range of smaller molecules imparting taste and odour to large molecules of colour bodies. Iodine, methylene blue and molasses tests empirically correlate with total surface area in pores greater than 10, 15 and 28Å respectively [17]. The carbon tetrachloride activity test which is a good quality control requirement for measuring the total capacity of activated carbon for adsorption of pure organic vapours has also been performed. Figures 1 and 2 depict these adsorptive characteristics of activated carbon samples.

Table 2 also shows the surface area of pores greater than 10 and 28Å in diameter which correspond to their relative activity against iodine and molasses respectively. It may be seen in Table 2 that activity in the case of 'A', an unactivated carbonized sample of date pits is nominal, which is also indicated by its meagre pore space. In phosphoric acid activiated samples B_1, B_2 and B_3, a moderate increase in activity has been observed. However, adsorption of iodine, methylene

Table 2. Different Physical and Chemical Characteristics of Activated Carbons from Date Pits.*

Sample**	Bulk density (Db)	True density (Dt)	Pore space (c.c./100gm)	Surface area of pores>10Å	Surface area of pores >28Å	Ash content (%)	Yield (%)
A	0.9100	1.1790	25	38	166	5.4	25.5
B_1	0.4303	1.5967	170	283	231	5.8	36.3
B_2	0.4950	1.6435	141	278	237	6.8	37.0
B_3	0.7032	1.6144	80	151	219	8.3	38.0
C_1	0.3500	1.5328	220	723	192	1.1	31.3
C_2	0.3495	1.6525	226	735	196	1.4	31.9
C_3	0.3450	2.1441	243	797	287	3.6	38.5

*Ash content of uncarbonized D.P. of different particle sizes (mm); Size # 1 (3.36-5.95) = 0.55%; Size # 2 (1.68-3.36) = 0.68%; Size # 3 (0.30-0.80) = 2.7%

** A = Untreated; B = H_3PO_4 treated; C = $ZnCl_2$ treated.

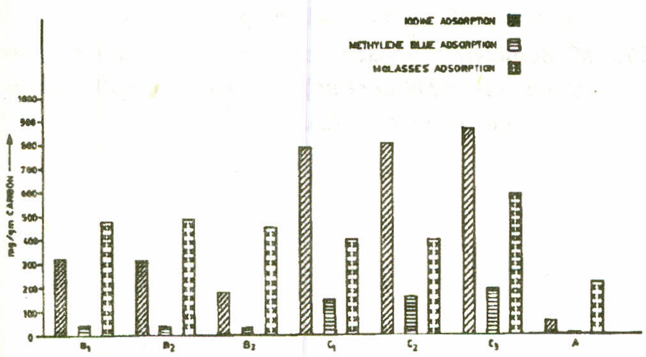

Fig. 1. Adsorption characteristic of activated carbons from date pits. A=Unactivated sample B=H_3PO_4 Act. samples, C=$ZnCl_2$ Act. samples.

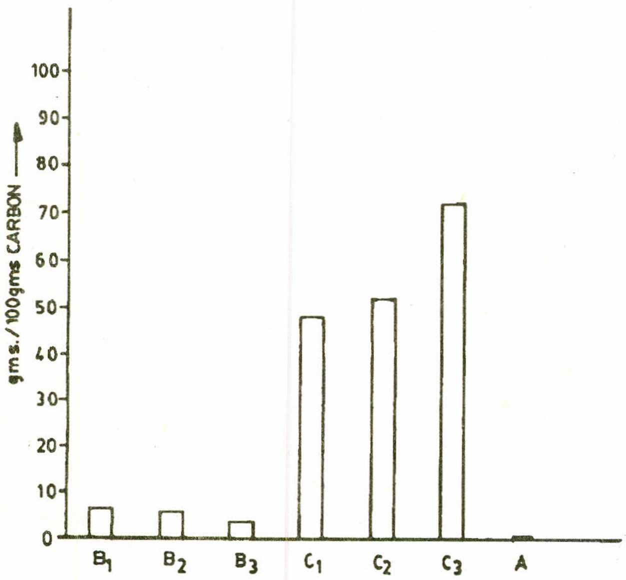

Fig. 2. Adsorption of CCl_4 on activted carbons from date pits.

blue and carbon tetrachloride is generally low and further decreases with the decrease in particle size of the raw material. These samples however perform comparatively better in case of molasses decolorization.

In samples C_1, C_2 and C_3, zinc chloride activated carbons, the activity in all the cases show a prominent enhancement as compared to phosphoric acid activated samples and gradually increases with decrease in the particle size. This overall increase in activity is very pronounced in sample C_3 compared to C_1 and C_2, further confirmed by its increased pore space with the surface area of pores greater than 10 and 28Å, which generally correspond to their micro and macroporous structure [17]. This great increase in activity of C_3 compared to B_3 may be due to solvent action of the former on cellulose [14] which is the major constituent of the outer layer of pits as fine particles (0.30 to 0.80mm) of fibrous nature (10 to 12% as mentioned earlier). In contrast, the inner part (corresponding to 85 to 90% of the whole pit), mainly composed of oil and hemicellulose is not equally sensitive to zinc chloride action and results in somewhat lower activity. It is quite well known that more than 90% of the surface area available for adsorption in active carbons is usually in micropores [15] and for a carbon to be effective, a balance between surface area of micro and macro pores is generally desirable. It may be seen in Table 2 that due to this balance, he samples C_1 to C_3 are found to be far more active than B_1 to B_3.

Conclusion

Date pits, a waste of food packaging industry in its lower particle size is an appropriate raw material for preparing activated carbon of balanced surface are suitable for liquid and gas phase purification by zinc chloride activation method. However, in the case of phosphoric acid activation, a product of much lower activity and higher bulking value is obtained.

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