

Evaluation and Modeling of High Surface Area Activated Carbon from Date Frond and Application on Some Pollutants

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ABSTRACT

Activated carbons were prepared through chemical activation of date frond DF, using sodium hydroxide and phosphoric acid as the chemical activating agents. The effect of different parameters, such as particle size, method of mixing, chemical/corn ratio, to choose the suitable conditions for the studying materials was chosen. The activation time and activation temperature, on S_{BET} surface area of the produced activated carbons were discussed. The porosity of the activated carbons was evaluated through nitrogen adsorption. The storage capacity of the activated carbon was evaluated using natural gas. Under the experimental conditions investigated, the optimal conditions for production of high surface area carbons by chemical activation were identified. Products with highly developed porosity were obtained from H_3PO_4 -activation, whereas, micro porous carbons with moderate porosity resulted from NaOH or steam activation schemes. The results were applied on and discussed adsorption of cations and pollutants from aqueous solution.

KEY WORDS: Activated carbons, agricultural waste, chemical activation, adsorption

I. INTRODUCTION

Activated carbons were obtained from date frond, DF by single-step steam pyrolysis or by chemical treatment. DF as a huge solid waste in Egypt is of little or no economic value and highly abundant renewable by-products, with good mechanical strength, and in fact presents a disposal problem. The quantity of DF has been estimated to million tons per year. Products with highly developed porosity were obtained from H_3PO_4 -activation, whereas, microporous carbons with moderate porosity resulted from NaOH treatment or steam activation schemes. Preparative methods for porous carbons are conventionally classified into physical and chemical activation. The latter is carried out in a single heat treatment step in the presence of an added chemical. Phosphoric acid is one of the most commonly used agents for the activation of different precursors, such as coals of different ranks [1,2], viscous rayon fibers [3] and, especially, lignocellulosic feedstocks [4–12]. Recently, H_3PO_4 has been used as chemical activating agent for porous polymers [13,14]. Phosphoric acid activation of lignocellulosic materials is a conventional preparation method for activated carbon [15–18]. In summary, the precursor is impregnated with a solution of phosphoric acid, heat treated up to about 500 °C, and washed with water to extract the excess acid. When peach stones (particle size around 3 mm) are used, it was shown that phosphoric acid penetrates the interior of the particles, reacts with the material and modifies the thermal decomposition [19]. As a result, the carbonization temperature is reduced, the exit of volatile matter is inhibited and the contraction of the particle is lower than in the carbonization of the unimpregnated particle. The consequence is that a relatively low carbonization temperature leads to a high conversion to carbon and to a final product with a well developed porosity, compatible with a relatively high bulk density [19–20]. Activated carbons are widely used in gas purification, solvent recovery, waste water treatment, etc. It is recognized that the pore structure is the most important property of activated carbons for their application in adsorption processes [21]. Activated carbons have a very wide range of pore sizes, from the angstrom Å scale of micropores to the micrometer scale of macropores. They are used in various applications depending on their porous properties. For example, activated carbons with many micropores are used for gas adsorption, mesopores are necessary for the adsorption of large molecules, e.g woods, coconut shell, coal, lignite, peat, and etc. are usually chosen as raw materials for activated carbons. Various carbons differing in porous properties can be obtained by changing the raw materials and/or the preparation conditions, i.e. the carbonization and activation conditions. Many investigations have been performed to explore novel raw

materials (such as waste materials) and to optimize the preparation conditions to obtain activated carbons with the desired porous properties. Optimization of the activation process has been extensively investigated [22,23].

II. EXPERIMENTAL

2.1. Adsorbents.

All series of activated carbons in these papers were prepared from the same precursor. Eight activated carbons were obtained from air-dried and crushed the date frond, DF. Carbons (I and II) were prepared by subjecting the agricultural waste to direct steam pyrolysis at 700 °C one or two hour hold. The raw material was inserted into a stainless steel tube fitted with an internal wire diaphragm and held in a vertical position to dispose of the formed tarry matter. Heating of the pyrolysis tube was started to attain 350 °C for 35 min. then pure steam is admitted from top of the tube using a steam generator. After reaching 700 °C (100-120min), the heated mass was left for 1 or 2 h at either temperature. The cooled activated carbon was weighed to determine burn-off and stored in tight glass containers. Carbons (III-V) were obtained by mixing 60 g of the crushed raw material with 30 g of NaOH solid (wt/wt)g, left overnight, then heat-treated slowly up to holding temperatures of 700, 750, and 800°C. Then the cooled product was thoroughly washed by distilled water till the pH value up to 7.5, and finally dried at 110 °C. Carbons (VI-IX) were prepared by impregnating of the precursor with H₃PO₄ (50 vol.%) followed by thermal treatment at 400, 450, 500 °C for two hours. The cooled activated mass was subjected to through washing with distilled water, so as get rid of extra acid and to attain pH values ≥ 6.5 in the washing solution, and finally dried at 110 °C. The weight loss was determined and referred to the original weight of precursor and denoted as "global burn-off" (GBO). Burn-off % = (weight of the raw material – weight of final product)/ weight of the raw material x= 100.

2.2. Characterization of activated carbons.

This was achieved by the standard adsorption of N₂ at 77k, using a sorpatometer of the type NOVA 1000e (Quantachrome). In spite of limitations of the BET method, in case of activated carbon, it has been and will continue to be used for microporous adsorbents owing to its simplicity and reasonable [7]. Accordingly, the adsorption isotherms were analyzed to get various porous parameters: By applying the BET-equation to determine the S_{BET} surface area, total pore volume (V_p), from amount of nitrogen held at P/P⁰ =0.95, and average pore dimension (radius) from R=2V_p/S_{BET} was evaluated. Other porous characteristics were estimated from the t-plots constructed by plotting volume of gas adsorbed (V_a) versus t-values of adsorption on non-porous standard carbon as reported by Selles-Perez and Martin-Martinez [18]. The obtained α s-values were transformed into t-values by multiplication with 1.52 x 3.54 (Å) as suggested by the same authors. The following porosity characteristics were calculated as follows: total surface area (S_t) from slope of early straight line to zero, non-microporous surface area (S_n) from slope of the late straight portion, ultra micropore volume (V_{0u}) from early intercept of the base straight portion, and super micropore volume (V_{os}) from the late intercept of the base straight portion with V-axis.

2.3. Adsorption capacity from the liquid phase.

Laboratory experiments were performed to evaluate the relative amenability of some water polluted with organic pollutants e.g phenol P and methylene blue MB dye by the prepared activated carbon.

$$\% \text{ Removal} = [C_0 - C_e / C_0] \times 100$$

Where C₀ is the initial concentration of the solute (mg/L), and C_e is the residual equilibrium concentration of the solute (mg/L).

III. RESULTS AND DISCUSSION

3.1. Chemical activation with NaOH

The effects of NaOH on carbonization of carbonaceous materials have been studied by several authors. Thus, studying the formation of active carbons from DF after their reaction with NaOH in the temperature range 700–800°C, indicated that the oxygen of the alkali can remove cross-linking and stabilizing carbon atoms in crystallites. Na metal obtained at reaction temperatures may intercalate and force apart the separate lamellae of the crystallite. Removal of sodium salts, by washing, and carbon atoms from the internal volume of the carbon, by activation reaction, create the microporosity of the activated in the new structure. This mechanism is indicated that high temperature and high NaOH/carbon ratio produced large pores in the carbon structure, due to the presence of Na₂O, derived from NaOH, expanded the carbon atomic layers. When the temperature exceeded 700°C, a considerable amount of Na was formed by the reduction of Na₂O with carbon. Since the inner carbon atoms were consumed, pores were formed in the structure. S_{BET} surface area, total pore volume, radius and pH of the activated carbons obtained by the NaOH treatment are shown in Tables 1 and 2. Carbonization of DF samples that treated by NaOH at 700-800°C to obtain slightly decrease in the surface area of the carbon. But with regard to this blank sample, the chemical activation of DF samples with H₃PO₄ at 400-500 °C brought

about a very large increase in the surface area and pore volumes, even for the lowest NaOH/time and temperature. An increase in this ratio brought about an increase in all textural parameters. As a consequence of the NaOH chemical activation, there was an increase in the micropores, mesopores and a decrease in the diameter. The pH of the activated carbons obtained indicates that they are slightly acidic or almost neutral. It is noteworthy the surface characteristics of activated carbon DF samples, with very high S_{BET} surface area and very large values of micro and macropore volumes.

3.2. Porous properties of the prepared activated carbons

3.2.1. N₂ adsorption isotherms

Table.2. shows examples of N₂ adsorption isotherms at 77 K on the prepared activated carbons. The amount of N₂ adsorbed on each group of carbons increases with global burn off as expected and suggest the formation of mesopores.

3.2.2. Chemical activation with H₃PO₄

As in table.1.it is obvious that in the phosphoric acid activation method, temperatures around 400-500°C produce the maximum development of porosity, even though the carbonization of the material can be incomplete, because the effect of H₃PO₄ is to produce chemical changes and structural alterations at temperatures lower than in the thermal treatment without impregnation. Phosphoric acid functions in two ways. As an acidic catalyst in promoting bond cleavage reactions and formation of crosslinks; and by being able to combine with organic species to form phosphate linkages, such as phosphate and polyphosphate esters, that can serve to connect and crosslink biopolymer fragments. Thus, phosphoric acid appears to be able to function in two ways (i) as an acid catalyst in promoting bond cleavage reactions and the formation of cross-links via processes such as cyclization and condensation and (ii) by combining with organic species to form phosphate linkages, such as phosphate and polyphosphate esters, that serve to connect and to cross-link biopolymer fragments. This can be tested by removing (leaching) the phosphoric acid for example from a 250 °C product, and then heating to 300 °C (to be compared with no leaching).

3.3. Nitrogen isotherms and analysis by BET and α_s -methods

Nitrogen adsorption isotherm is a standard tool for the characterization of porous materials especially porous carbonaceous adsorbents. The adsorption isotherm can be made to yield valuable information about the surface area and the pore structure of the adsorbent, heat of adsorption and so on. The definition of pore size originally proposed by Dubinin and now adopted by IUPAC as follows: micropores width less than 2 nm; mesopores width from 2 to 50 nm and the macropore width greater than 50 nm. Micropores can be subdivided into ultramicropores (less than 0.7 nm) and supermicropores (from 0.7 nm to 2 nm) . The nitrogen adsorption isotherms obtained for different activated carbon samples are shown in Figs.(1-6). Isotherms have been observed for different activated charcoal DF, in the most cases there is a more gradual approach to a rather ill defined plateau located at higher p/p° . The appearance of hysteresis loops in the nitrogen isotherms of samples shown in the Figs. (1-3) indicate the existence of some mesoporosity.

The hysteresis loop of H4 is indicative of slit-shaped pore, where the adsorption and desorption branches are parallel. The type I isotherm character associated with H4 type hysteresis is of course indicative of microporosity. The type H4 (E) hysteresis loop according to de Boer, is produced by tubular pores which contain a narrow constriction or closed pores of the ink bottle type. In almost all the samples 70% of the pore volume is filled below $p/p^\circ = 50$, indicate these samples are highly microporous. After the sharp movements up to p/p° of 0.1 the isotherm slowly bends showing smaller increment in adsorption. After a p/p° of 0.2 the adsorption becomes further smaller but still continuing the adsorption process almost up to the saturation vapor pressure. Analysis of this process in the light of Kelvin equation shows the presence of pores of almost all diameters even though to different extent in most of the samples. These pores vary from thin micropore to probably broader micropore even if they are present, and are wide open so that the evaporation takes place at the same p/p° as in the adsorption process. From Figs (1-3), It is observed that the adsorption in microporous carbons to be taking place in two steps, a micropore filling step and a mesopore filling condensation step. The BET-plots for microporous carbons were found to be linear in different ranges of relative pressure and the S_{BET} surface area was found to increase with increase in the relative pressure range. They observed that the S_{BET} surface area determined from the pressure range 0.1–0.3 was significantly overestimated because of the quasi-capillary condensation. Meanwhile this range (0.1–0.3) was found to be the best range of validity of the BET-equation for non-porous carbons compared with the α_s -values. They have recommended that the relative pressure range of 0.01–0.05 for S_{BET} surface area determination of microporous carbons. In the current study the linearity between the points in the above range well extends up to a relative pressure of 0.2 and hence the

evaluation of S_{BET} surface area made in the range 0.005–0.20 bears equal validity as those obtained in the BET analysis of Kaneko et al. The deviation of the BET-plot from linearity becomes clearly remarkable from the relative pressure value of 0.2. The S_{BET} surface area of different activated carbon samples obtained from BET-analysis along with corresponding monolayer capacity V_m values are given in Table 1. The a_s -plots of the activated carbon samples under study are shown in the Fig.2 (a1,b1&c1). According to them if the right reference data, i.e. the data from a reference material having the same value as that of the test material, is not used the straight line extended from the lower p/p^0 values cuts the y -axis (volume adsorbed axis) for a positive or a negative value of the adsorbed volume. The micropore volume for all the activated carbon were calculated and tabulated in Table1. The pore size distribution curves have been constructed based on dividing the pore system into a number of fixed groups of pores, each characterized by a narrow range of pore sizes. The pore size distribution curve for selected activated carbon samples are shown in Fig. 6(e–j). It can be seen from the distribution curve that in the case of oxidized samples, there was decrease in pore volume in lower diameter though the pores at higher diameters have not been affected much, as a result of oxidation, the oxygen groups essentially fixed at the entrance of the micropores and inside the wider micropores, which increases nitrogen constriction to the pores. The micropore volume calculated from the summation of volumes of individual groups of pores V_{ot} is given in Table1.

As comparison of micropore volume values obtained by different methods with the V_m value from BET-method show that the latter value is the smallest among all the samples. This indicate the completion of monolayer coverage on the surface of carbon before all the micropore are completely filled. Among the micropore volume values, the one obtained from a_s -method has highest magnitude. These results clearly indicate that the surface chemical nature as well as surface texture of the activated carbon were changed considerably after oxidization with different oxidizing agent. Thus, the most important difference between the activation mechanism with NaOH and H_3PO_4 is that, whereas the first mechanism remove and avoid the crosslinking, stabilizing the carbon atoms in crystallites, the second mechanism involves an excessive crosslinking by both acid catalysis and through the phosphate linkages. The activated samples, A1,A2,A3,A4,A5,A6,A7,A8,A9) (where DF is date frond , S is physical treatment by single step steam pyrolysis, H is symbol of phosphoric acid, Na is symbol of NaOH, the first number is indicated to thermal treatment multiplication in 100 and the second is the duration time per hour), are A1, A2, A3, A4, A5, A6, A7, A8 and A9 respectively).Treatment with NaOH and H_3PO_4 brought about, with regard to the samples, a large decrease in the ash content and an increase in the carbon content, which increased from sample A1-A3, A4-A5 and from A6-A9. The N and O content gradually decreased with the increase in the temperature and duration time in NaOH/sample. High ash content in carbons is undesirable because mechanical strength and adsorptive capacity are reduced. The high ash content of these carbons can be due to several reasons such as: (i) The inorganic constituent of the raw material can combine with phosphoric acid giving insoluble phosphates, which furthermore, can be trapped inside the carbon matrix due to the crosslinking that produces the treatment with H_3PO_4 and (ii) phosphate and polyphosphate species are incorporated to the carbon matrix, through C–O–P bonds, connecting and crosslinking different organic species. The lowest ash content of sample A4 can be due to [19] steam inhibited the formation of condensed phosphates and eliminated the phosphate groups previously attached to the carbon. Characteristics of activated carbons obtained from phosphoric acid activation are shown in Tables 1 and 2. The activated carbons obtained by this method had an ash content that depended on the atmosphere of the treatment. Thus, the treatment of DF, yielded different ash content depending on the activated method, which in this case, was similar to that of the blank samples. Furthermore, the ash content of these activated carbons was much higher than those prepared from the NaOH method. S_{BET} surface areas Table1, of the blanks,(A4 – A6), were much higher than those of the corresponding activated carbons (A7–A9). Therefore, the H_3PO_4 activation increased the S_{BET} surface area of the samples, although in much higher extent than the activation with NaOH. S_{BET} Surface area of the activated carbons obtained seems to depend on their ash content, with higher ash content the lower S_{BET} surface area. All samples had very low mesopore and macropore volumes and a somewhat higher micropore volume. All these surface characteristics make that the particle density of these samples be higher than in the case of the NaOH treatment.

3.4. Effect of burn off on porous properties

As shown in Table 1, the porous properties of the prepared activated carbons vary from 60 to 1100 m^2/g for the S_{BET} surface area, from 0.005 to 0.3 ml/g for the micropore volume, and from 0.05 to 0.59 ml/g for the mesopore volume. Some of these activated carbons have a S_{BET} surface area more than, 1000 m^2/g and mainly contain micropores. It is noteworthy that the mesopore volume of (A5-A6), series carbons of groups are quite large. Although the porous properties of (A7-A9), series carbons of all groups are quite similar, the properties of the carbons become different with an increase in burn off. Micropore volume and mesopore

volume are plotted as a function of burn off in Table 2. It is confirmed that all groups of carbons have similar micropore volumes Fig.2(a1). On the contrary, it can be seen that the development of mesopores of (A4-A6), group carbons is much larger than that of group (A7-A9) with a burn off of more than 12.5% Table 2.

3.5. Pore size distributions

Mesopore size distributions calculated by the BET-method are shown in Table 1. It is clear that the distributions of group (A4-A6), differ greatly from those of groups (A7-A9). In group (A4-A6), mesopores are formed in the region narrower than pore radii of 2 nm and the region wider than pore radii of 9 nm as burn off increases Table 2 and Fig.(3). In groups (A4-A6), the development of mesopores is remarkable in the region 3–10 nm, and mesopores are also formed in the region narrower than pore radii of 2 nm and the

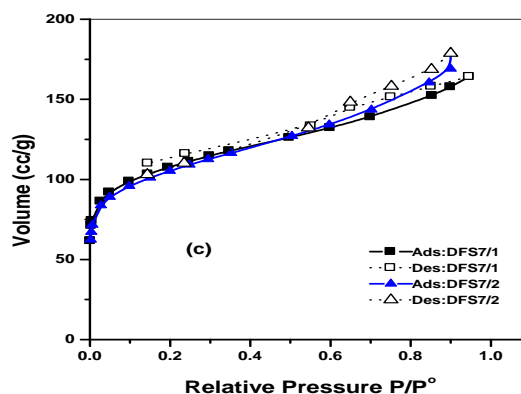
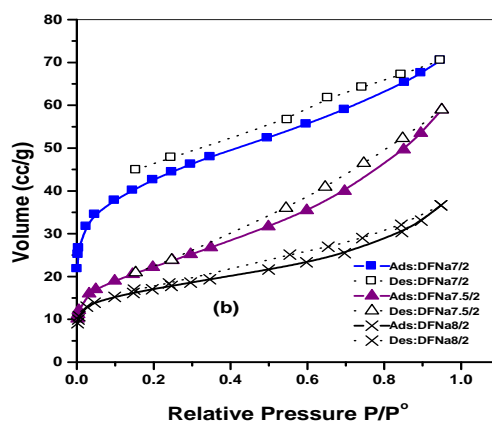
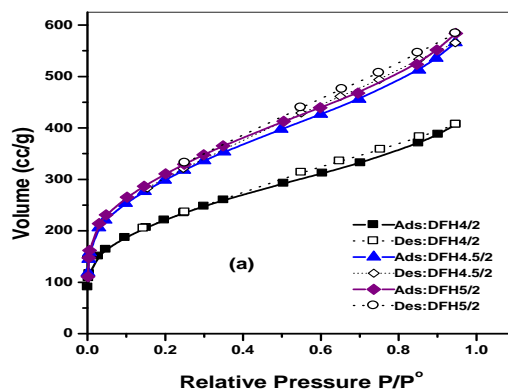


Fig (1):The adsorption isotherms of N₂ at 77K for different activated carbons ACs obtained from DF, where (a) is A4,A5, A6, (b): A7,A8, A9 and (c): A1,A3.

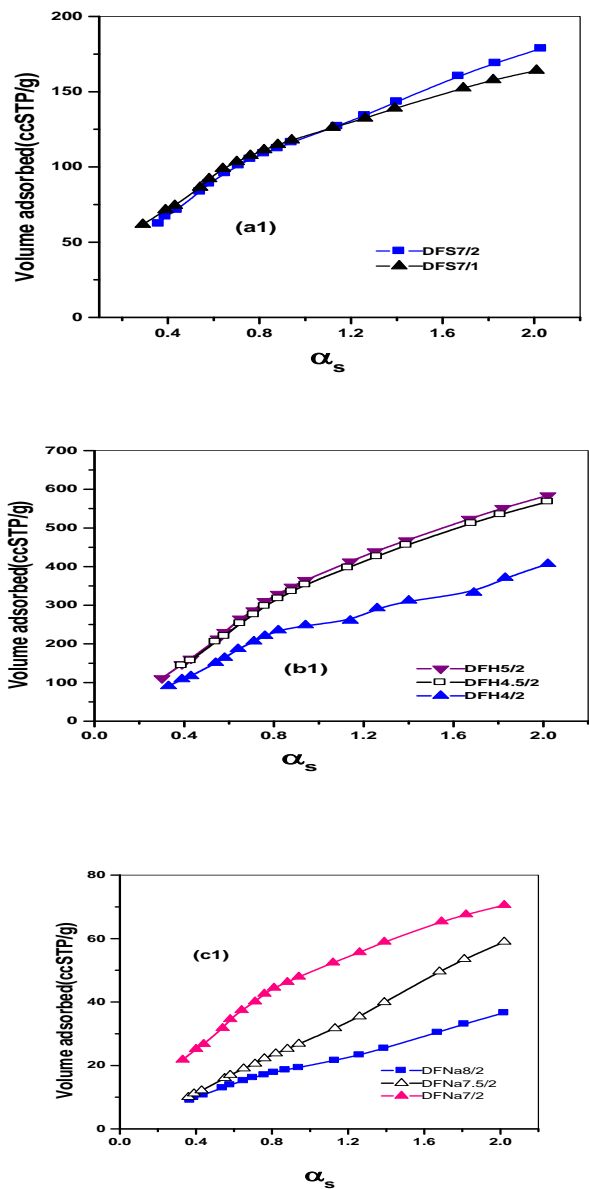


Fig.(2): The α_s -plots for the different ACs obtained from DF, where (a1) is A1,A3, (b): A4,A5, A6 and (c1): A7,A8, A9

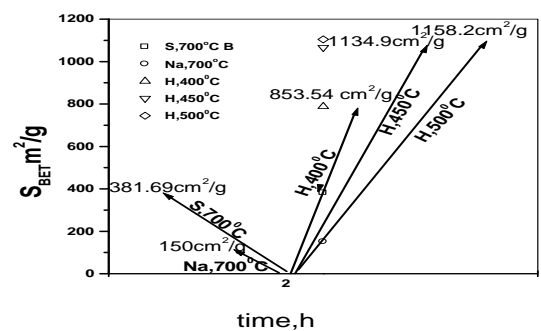


Fig.(3):Vector representation for the effect of chemical activation by H_3PO_4 and NaOH and physical activation by single step steam pyrolysis on S_{BET} of DF.

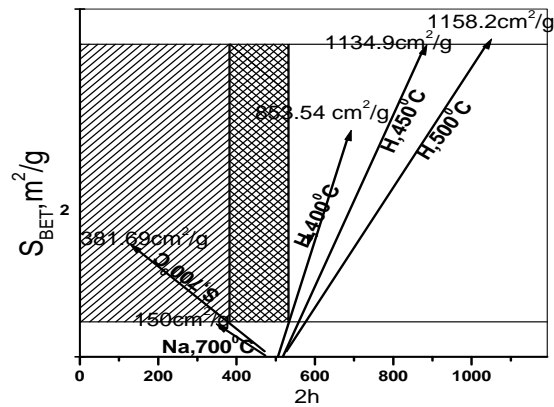


Fig.(4):Optimization of S_{BET} of DF for the effect of chemical activation by H_3PO_4 , NaOH and physical activation by single step steam pyrolysis for 2 h.

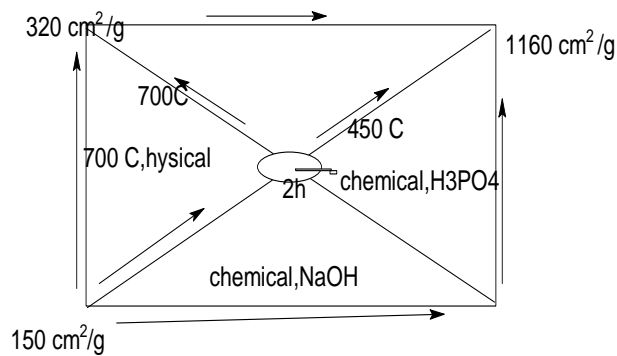


Fig.(5):Modeling of paths between chemical activation by H_3PO_4 , NaOH and physical activation to obtain S_{BET}

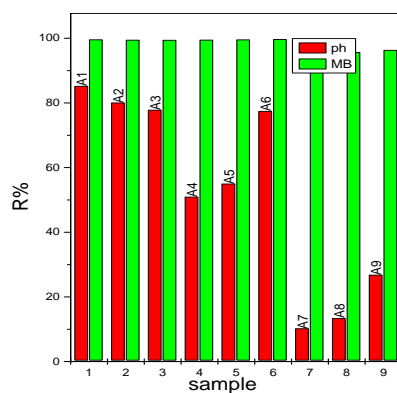


Fig.6.Effect of activated carbons obtained by chemical and physical activation on sorption of phenol(pH) and methylene blue(MB)

Table 1. Surface characteristics of activated carbons obtained by chemical and physical activation

Groups Type of ACs(DF)	Temp °C	S _{BET} m ² /g	S _t ^a m ² /g	S _n ^a m ² /g	V _P ml/g	V _{meso} ml/g	V _{ou} mL/g	V _{ot} ml/g	V _{os} ml/g
A1	700	392.54	299.83	124.0	0.254	0.134	0.046	0.120	0.134
A2	700	385.11	302.55	134.88	0.266	0.158	0.042	0.102	0.094
A3	700	381.69	304.14	166.1	0.276	0.182	0.038	0.094	0.056
A4	400	788.07	853.54	407.2	0.629	0.465	0.008	0.164	0.164
A5	400	1066.02	1134.9	542.9	0.875	0.588	0.002	0.287	0.287
A6	500	1104.65	1158.2	547.6	0.903	0.599	0.001	0.304	0.304
A7	700	150.53	135.83	57.57	0.109	0.062	0.009	0.047	0.038
A8	750	78.21	95.78	82.70	0.091	0.091	0.006	0.066	0.037
A9	800	60.66	55.77	46.15	0.057	0.052	0.003	0.005	0.002

Table 2. Characteristics of activated carbons obtained by chemical and physical activation

Type of ACs(DF)	Temp °C	Ti me, h	pH	Yield %	%R phenol	%R MB	r (Å)	burn- off %
A1	700	1	7.5	19.67	85.25	99.63	12.94	80.33
A2	700	1.5	7.45	19.45	80.11	99.51	13.47	81.52
A3	700	2	7.4	18.33	77.87	99.49	14.46	81.67
A4	400	2	6.6	41.10	50.98	99.53	15.96	58.93
A5	400	2	6.5	40.40	55.02	99.60	16.42	59.60
A6	500	2	6.7	31.33	77.48	99.71	16.35	68.67
A7	700	2	7.5	9.77	10.23	94.81	14.5	90.23
A8	750	2	7.5	5.96	13.41	95.68	23.27	94.03
A9	800	2	7.5	5.46	26.81	96.33	18.79	94.53

Application

The activated samples was applied for adsorption of phenol and MB and it is found that uptake of MB was in range (94-99%), while the uptake of phenol was in range (10-85%).

Modeling.

The surface area of DF-carbons were obtained by different methods of activation, i.e. chemical activation (by H₃PO₄ or NaOH) or physical activation (i.e. single step steam pyrolysis) as in Figs. (3,4 & 5).

IV. CONCLUSIONS

The results of this study showed that DF can be successfully converted into activated carbon with specific surface properties. It was found that the amount of H₃PO₄ used for chemical activation controls, the characteristics of the carbons including surface area, micro and mesoporosity, and pore size distributions. Detailed surface analyses using different mathematical models suggested that: (1) H₃PO₄ at 450 °C required to obtain micropore and mesopore carbons, (2) a theoretical approach can provide complete information about the surface structure of the produced activated carbons; (3) highly activated carbons with an extended pore size distribution, the a_s-method estimates total micropore volume (volumes used for both primary and secondary filling processes).

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