CHAPTER IV SUMMARY AND CONCLUSIONS

The present investigation aimed to the economic utilization of an abundant local agricultural by-product, that is field and secondary plant residues. Amounts of these residues (in Egypt) are estimated to be around 25 million tons annually without their beneficiation in valuable processes. This amount is far in excess of any local use and thus presents an environmental burden with respect to storing and disposal. Potentially good adsorbents, activated carbons, are well recognized to be obtained from such ligno-cellulosic discard materials. Their conversion into good adsorbents would serve two aspects: partial disposal of an environmental burden and production of valuable materials with diverse applications in modern life. These share in helping decontamination programs of potable water and wastewater streams from the hundreds of species pouring from various drain sources: chemical industry, petroleum, nuclear industries, textile and food stuff industries, agricultural drainage, and others. The increasing demand for effective treating materials, instead of their importation at high cost, poses the production of these adsorbents in developing countries based on locally available feedstocks and known-technologies.

An introductory part focused on activated carbon as a well-established, worldwide known adsorbent employed in a large variety of water treatment schemes. Its consumption at high rate (Kg/capita) discriminates between highly developed and less developed countries, which vary between 500 and 20 g/capita. An escalating world consumption of active carbon is observed during the last two decades (≈ 7 % yearly) to reach more than 400,000 tons (the year 2000) per annum.

Two factors contribute in this concern: (1) an increasing worldwide pollution due to increased development and industrialization and (2) increased public awareness, and developed detection tools towards identification of the various contaminants. Ascetic measures poses the control of pollution levels as these (organics and inorganic) have adverse impact on the environment and to life dangers on the life of globe occupants (including inhabitants man).

Some previously reported studies during many decades were concerned with production of activated carbon particularly under chemical treatment with $ZnCl_2$ or thermal activation with steam (two-step) processes. The $ZnCl_2$ process declined since 1970 due to its environmental polluting action and equipment corrosion and interferes in the life cycle. Decontamination programs had become “a must” and not just luxury schemes, as it contribute in reducing the health bills associated with the deteriorating human welfare.

The literature pertaining to activated carbon was postulated to deal essentially with two aspects: source materials and schemes of production. The farmer, precursors, depends on fresh biomass (animal and agricultural biomass) and the latter aspects is physical (or thermal) and chemical activation procedures. Accordingly, a large number of raw materials were investigated and reported in the last decades, and developed schemes were invented. Cotton stalks (CS) or date pits (DP) were chosen as a raw materials for many reasons: because of both are highly abundant renewable by-products, with good mechanical strength, generated in high amounts and of insignificant economic value.

Based on the above mentioned background, the experimental part of this thesis was designed with respect to activation schemes and methods of material characterization. Single-step steam pyrolysis for some types of activated carbons: (1) Single-step steam pyrolysis at 600- 800 ^{0}C, (2) single-step steam pyrolysis at different temperature with accompanying flow of N_2-activation, (3) single-step steam pyrolysis at 700 ^{0}C in presence of catalytic gasifying metal oxides of calcium or iron, (4) single-step steam pyrolysis conditions at 700 ^{0}C with accompanying flow of air-activation. These processes, become favorite specially during the last decade, as they save both energy and time, produce high carbon yields, and good adsorbing carbons are obtained under controlled conditions. Steam pyrolysis was performed in the established temperature range of 600-800 ^{0}C with different holding time.

The third part displayed the results and their discussions. The obtained diverse products were subjected to different schemes of analysis to asses the physico-chemical and adsorptive properties of the different forms of adsorbents. In general, all of the steam-treated precursors exhibit slightly lower apparent and packed density of their corresponding of carbon parent materials. Average apparent density of the CS-series is 0.292 g/cm^3 which is lower by about 24% from the raw precursor, whereas the packed density is 0.528 g/cm^3 higher by about 26% as the raw precursor. On the other hand, for the DP-series of carbons their average apparent density is twice that for the CS-series (i.e. 0.574 g/cm^3), which is also lower by 21% from raw material, their mean packed density is also higher than the CS-carbons (i.e.0.755 g/cm^3) that is around 150 % higher.

Steam pyrolysis of CS results in low carbon yields depending on the heat treatment temperature and duration. At 600 ^{0}C it ranges between (29.4 and 25.0%), at 700 ^{0}C between (22.3 and 8.2%) and at 800 ^{0}C between (9.1 and 8.3 %). Concurrent N_2-flow slightly affects the carbon yield whereas the metal catalysts exhibit different effects (calcium increases gasification and iron reduces it). Flowing air during steam pyrolysis promotes gasification (as air contains ~20% oxygen) with considerable reduction in the carbon yield. In contrast, DP appears to be more thermally stable under moderate conditions of temperature (600 and 700 ^{0}C) or for short durations up to 1hr of contact. Thus at 600 ^{0}C the attained yields at (½, 1 and 2 hr) are (32, 28 and 26 %), at 700 ^{0}C (26, 25 and 21%), at 800 ^{0}C (21, 16 and 10%) in the same order. Running nitrogen during pyrolysis slightly affects the DP-derived carbons, as well as flowing air. The presence of calcium enhances gasification (lowering yield compared to corresponding CS*S*71) whereas iron reduces gasification (increasing the carbon yield). The permeated inorganic matter, determined as ash, is generally low to moderate (3.1 to 8.8%) under all conditions, except in pure steam at 800 ^{0}C which attains 10.3 to 13.5 % (1 and 2hr, respectively). It is thus evident that, the considered properties, carbon yield and ash content, are governed by the parent precursor nature. CS with original fluffy and soft nature control the carbon yield (under 2hr contact with steam at 800 ^{0}C the raw material is completely burnt whereas DP with a yield of ~10%. Also CS with a high initial ash content around 5% result in steam-activated carbons with ash contents attaining 18.5%. These natural properties of the precursor has been already noticed to be reflected on the apparent and packed density of the carbons derived from both raw materials. Such values are anticipated to affect the adsorption capacity from aqueous solutions.

The types of adsorbents were observed to be obtained; these materials; such property was qualitatively observed from the FTIR spectra and quantitatively by the end group titration methods. The most adsorbents prepared by steam-pyrolyzed carbons of DP show a basic surface (pH = 8-9.7) and CS show a basic character also with surface (pH=9-10) and values of basic sites reaches to approximately 3 mmol/g. It was difficult to detect or differentiate between the acidic or basic groups, as the absorption due to the O─functionalities overlap in the various ranges of the spectra.

Characterization of porosity was achieved by the long established procedure of N_2 adsorption at 77K, in order to estimate the specific surface area and pore volume. Steam pyrolysis of CS at 600 ^{0}C is associated with small successive increase in surface area and pore volume, from (105 to 184 m^2/g), and (0.048 to 0.099 ml/g), respectively. Products obtained at 700 or 800 ^{0}C are characterized by similar and low-developed carbons unaffected by the soaking period at either temperatures. Average surface areas are 208 and 282 m^2/g, and average pore volumes of 0.104 and 0.116 ml/g, respectively. Upon treatment in flowing steam for 2hr at 800^{o}C, CS were completely gasified such that insignificant yield was obtained. Under additional simultaneous flow of nitrogen (i.e. steam or nitrogen) low adsorbing carbons were produced. Added gasifying catalysts did not affect properties of the carbon adsorbents, rather it adversely affected the internal porosity by considerable reduction especially in case of the calcium addition. The only observed relative porosity enhancement appears upon co-flowing of air during thermal treatment at 700 ^{0}C for1hr. In this case both surface area and total pore volume are raised by about 80 % to reach on S_{BET} of 338 m^2/g and V_p of 0.169 ml/g.

Steam pyrolysis of DP at 600 ^{0}C show a gradual porosity development with duration, S_{BET} from 24 to 218 m^2/g and V_p from 0.021 up to 0.097 ml/g. These values are very similar to those for the CS. Only in case of DP no ultramicroporosity (≤ 7.2 Å), is detected, although the mean pore dimensions are the same (~ 10.0Å). Steam activation of DP at 700 ^{0}C becomes more effective where a surface area around 400 m^2/g is attained with a small increase in total pore volume to 0.18 ml/g, and a corresponding narrow pore dimensions around 9.0 Å. Thus, pyrolysis at 700 ^{0}C seems to produce the same gasifying action on DP irrespective of soaking duration at this duration. Generated porosity at this temperature lies within micropores and indicates an increased content in ultramicropores (V_{ou}^{α}) whereas wider pores in mesopore range are unaffected (less than 10%).

A very pronounced effect of steam pyrolysis on DP appears upon treatment at 800 ^{0}C, and becomes more active with increased duration of contact with steam. Thus, the S_{BET} jumps from 576 to 925 m^2/g and V_p from (0.262 to 0.551 ml/g), although the average pore dimensions are unaffected at 9.0 Å. Data indicate that generated porosity appears particularly in the micropore range with appreciable increase in the mesopore range (≥ 20.0 Å). The ratios of pore volumes (V_{meso}/V_P) and surface area (S_n^{α}/ S_{BET}) is raised from (0.1 to 0.33) and from (0.04 to 0.17), respectively. Particular enhancement in mesoporosity accompanies prolong treatment for 2hr at 800^{0}C, where a large part of the raw DP is gasified leading to a low yield of ~ 10% of activated carbon. This latter value is generally familiar to all steam-activated plant precursors as currently reported, although performed in the conventional two-step scheme. It means that steam pyrolysis of DP carried out at 800 ^{0}C can produce a high quality adsorbing carbon, with an essentially microporous character.

DP-activated carbon under the steam pyrolysis technique seems to be, thus, more amenable and develop a good adsorbing carbon comparable to (and probably better) those derived in the traditional two-step steam-activation schemes. This might save energy, time and probably raw material under the hereby prescribed route of activation. In addition, DP (a hard and compact solid material) seems to need certain severe conditions to obtain the high quality adsorbing carbon (2hr at 800 ^{0}C), as shown previously upon adopting the H_3PO_4-activation route (3hr at 700 ^{0}C, with 50 % H_3PO_4) [146]. Its compact, very low porosity, nature plays a decisive role in deriving good activated carbons by either the present single-step steam activation scheme or the alternative chemical-activation process. It is interesting to notice that the two carbons under consideration (DP*S*81 and DP*S*7½) exhibit identical textural characteristics inspite of the different activation schemes. The main difference is the carbon yields which appear as ~10 and ~40%, for the thermal and chemical procedures, respectively, although the former (present study) does not need any repeated washing thereafter as essentially required by the chemical scheme. On the other hand, CS with their inherited soft and fibrous botanical structure appears to be less amenable to steam-pyrolysis due to its higher gasification rate and to the effect of collapse of the gasified fragile fibers under the superheated steam at high temperature. It is noteworthy to mention that treatment at 800 ^{0}C, for this precursor, for 2hr is accompanied by almost complete loss of raw material.

A concurrent flow of nitrogen, during pyrolysis under steam, appears to be undesirable as the carbons obtained at 700 ^{0}C, are generally of lower porosity. In particular, at 800 ^{0}C the effect of flowing N_2 adversely affect the previously attained porosity in its absence. Running N_2 with steam during pyrolysis seem to dilute pure steam and reduce its oxidizing effect, although this effect becomes lost upon prolonged treatment at 800 ^{0}C for 2hr. Here, the concurrent flowing of N_2/steam results to almost similar carbon product without its presence.

Addition of the catalytic cations of (Ca^{2+} or Fe^{3+}) adversely affects the textural properties of DP*S*71-carbon as it is accompanied by a considerable loss in surface area (S_{BET} from 395 down to 290 and then 217 m^2/g, respectively. Calcium, meanwhile, raises porosity and wideness of pore size, whereas iron reduces considerably total porosity without affecting the very narrow porosity character. Effect of the former cation is confirmed**,** where wider porosity is enhanced (V_o^{α}, and V_{meso}) as well as its parameter of surface area ratio where it is raised ten times (S_n^{α}/ S_{BET} from 0.06 to 0.59). The effect of iron is likewise changed as evident from same .The most effective variable is the concurrent running of air together with steam at 700 ^{0}C for 1hr (DP*S*A71-carbon). This process promotes the total surface area by about 20%, and total pore volume by about 10%. Meanwhile, this is accompanied by generation of porosity in the micropore range with considerable drop in mesoporosity (V_{meso}/ V_P from 15 down to 2 % and S_n^{α}/ S_{BET} from 6 down to 1 %). Under concurrent flowing of air, the generated porosity, thus, appears mostly in the narrow range of pores.

The displayed data present the liquid phase adsorption features of five probe molecules with increasing molecular weights (94, 139, 254, 319 and 696) and molecular sizes (~ 10-20Å) as well as cross-sectional areas (25, 44, 52, 120 and 172 A^2).These widely different solutes include, meanwhile, two categories of widely spread water contaminants, these are the phenolics and dyes. They impart undesirable taste, odor and color in either potable water as well as wastewater streams. Their removal through adsorption onto activated carbon is one of the most practically recommended best available techniques (BAT) especially in low concentrations. Adsorption of the mentioned sorbates illustrate two distinguished different trends. DP-derived carbons present normal uptake of good amounts of the considered pollutants (iodine 110 - 380 mg/g, P = 18-66 mg/g, PNP = 6-94 mg/g, MB =76-275 mg/g, and CR = 35-144 mg/g). These values correspond to accessible surface areas of (0.363 - 0.94, 0.29 -0.55, 0.18-0.73, 0.17-0.81 and 0.17-0.46), respectively. Good adsorbing carbons are thus obtained from DP under the steam scheme of activation, and the degree and extent of porosity plays the basic role in determining the adsorption characteristics.

Cotton stalks-derived carbons exhibit an anomalous behavior of adsorption which is suggested to be mixed with absorption within and between the assumed swelled fibrous, soft and fluffy carbon matrix. The amounts uptaken by the CS-carbons range between (iodine = 219- 310 mg/g, P = 11 -39 mg/g, PNP = 44 - 220 mg/g, MB =70 -248 mg/g and CR =119-248 mg/g) with unreasonably high accessible fractions of surface area. This abnormality was discussed in light of the assumed “swelling” phenomenon under the hydraulic effect of the aqueous media. The thermally derived carbons seem to be collapsed with shrinkage under heat effect, and they might be swelled in the water dissolved solutes. Surface areas determined for selected carbons by adsorption of CO_2 proved the existence of narrow microporosity not estimated by the normal BET-N_2 adsorption. However, this cannot account for the anomaly except for the uptake of iodine with size around 10Å. Nevertheless, cotton stalks-developed carbons may be considered as good adsorbents for the removal of various solutes, irrespective of the mechanism of uptake from aqueous medium.

In general, the best adsorbents observed here are those prepared at higher temperatures (800 ^{0}C), long durations (2hr), in absence of N_2-flow, and in presence of air flow. These factors are associated with better development in porosity available to the accommodation of the contaminant molecules.

In the fourth part, the selected samples were evaluated according to their efficiency and capacity in the removal of some target cations (Pb^{2+}, Cd^{2+}, Fe^{3+}, Mn^{2+}, and Sr^{2+}) using DP or CS-carbons of environmental concern. Different parameters (pH, temperature, initial metals concentration, carbon doses, shaking time, contact time and interfering ions) were studied. %R of (Pb^{2+}, Cd^{2+}, Fe^{3+} and Sr^{2+}) ions from aqueous solution by (DP*S*71-Ca*, DP*S*71-Fe*, and DP*S*81) activated carbons can be noted that more than (80, 90, 40 and 77 %) respectively in the first contact time (150, 120, 220 and 90 min.). Concurrently removal of these cations from aqueous medium are affected by the presence of other ions e.g. (Ca^{2+}, Na^{+}, NO_3^{-}, CO_3^{-}, SO_4^{-}) and masking agents e.g.(oxalic acid and EDTA) in solution. Uptake values are decreased with increasing the concentration of these ions in solution.

Selected samples were evaluated as to their efficiency and capacity in the removal of some ions (Pb^{2+}, Fe^{3+}, Mn^{2+}, and Sr^{2+}) from underground water pollutants in some governorates e.g.(EL-Sharkia, EL-Qaliobya, El-Giza, El–Bherra and EL-Dkahlya) of Egypt. In this concern, complete removal of contaminating metal ions was achieved in various ground water under investigations. Thus the permissible levels were obtained.

Conclusion:-

Cotton stalks and date pits were demonstrated to be feasible raw materials for the production of valuable adsorbents. Many categories of adsorbents were derived from the raw biomass: : (i) activated carbons by steam pyrolysis, (ii) activated carbons by single-step steam pyrolysis conditions at different temperature with accompanying flow of N_2-activation, (iii) activated carbons by steam pyrolysis technique at 700 ^{0}C was performed in presence of catalytic gasifying metal oxides of calcium or iron, (iv) activated carbons by single-step steam pyrolysis conditions at 700 ^{0}C with accompanying flow of air-activation. Adsorbents of varying physico-chemical properties were thus obtained: low and high density, low and high ash content, low, moderate and high developed porosity, and good to high adsorbing capacity.

Contaminating species of the organic (phenol, p-nitrophenol, congo red and methylene blue) and inorganic types (Pb^{2+}, Cd^{2+}, Fe^{3+}, Mn^{2+}, and Sr^{2+}) were removed from aqueous medium. At a very low rate of adsorbents, (10-390 µg/L), complete removal for the contaminating metal ions from underground water was achieved. The permeated high ash, although reduces the apparent surface area and pore volume of some adsorbents, due to positively shares in some of the various adsorption processes achieved from the aqueous phase.