CHAPTER I. INTRODUCTION AND AIM OF THE WORK

I.A. GENERAL INTRODUCTION.

Activated carbon is a remarkable, highly adsorbing material with a large number of applications in the remediation of contaminated groundwater [1]. Its properties and uses have been known for centuries, but modern applications involving water and wastewater treatment have expanded the understanding of its nature and potential. Activated carbon is an effective adsorbent primarily due to its extensive porosity and very large available surface area. The chemical nature of the carbon's adsorptive surface is also important but is usually considered much less significant [2]. The specific properties of an activated carbon are the result of both the raw material used to produce it and the activation process, which boosts its adsorbent qualities.

Adsorbents are generally seen as materials of high surface area with developed highly porous structure [3].Traditional adsorbents (e.g. activated carbons, silica gels, clays and aluminous) generally exhibit a high degree of surface and textural heterogeneity, whereas the newer adsorbents(e.g. zeolites, carbon molecular sieves and modified silica) are more uniform. Most adsorbents of technological importance are highly ‘active’. The required large surface is generated either by the production of very small particles or, more usually by the formation of a pore structure [2].

Traditional methods for the production of activated carbons involve two thermal treatment stages (Thermal Activation). These are primary carbonization at 500-700 ^{0}C in which the carbon precursor eliminates non-carbon species and leads to a fixed carbon mass and a rudimentary pore structure . Enhanced porosity results consequent to the second heat treatment (beyond 800 ^{0}C), performed by selective gasification in an atmosphere of oxidizing gases (steam, CO_2, air or mixture of gases). As a measure of the degree of activation, the so-called “burn-off” is usually used, which is the percentage weight decrease of the material during activation, referred to the weight of the original carbonized product [4]. When the burn-off is <50% a micro porous carbon is obtained, when it is >75% a macro porous product results, and between 50 and 75% the product is a mixed structure of micro and meso-porous [10].

Both CO_2 and steam are mild oxidants at 800-950 ^{0}C, and eliminate carbon atoms from the char particle via CO and /or $CO+H_2$ in such a way as to favor the selective burning of the interior of the particle, with the subsequent creation of porosity. It has been shown that, for a given temperature, the reactivity with steam is larger than with carbon dioxide [8,9,11]. In addition to the above mentioned two-step process, a newly developed one-step steam pyrolysis scheme was reported [5-7]. This process saves energy by restricting thermal treatment in one step (at somewhat lower temperature), saves time and promotes carbon yield.

Activated carbon is used in water and wastewater treatment primarily as an adsorbent for the removal of relatively low levels of organic and inorganic contaminants via transfer from the dissolved phase to the solid carbon surface. While its adsorbent nature also makes it useful for the filtration of contaminated air, only its use in water treatment. As a result, they are most effective in the removal of a large variety of organic contaminants, including trihalomethanes, pesticides and herbicides, and polyaromatic hydrocarbons [12]. However, activated carbon may also be used for the removal of trace metals such as cadmium and lead, and it has also been effective in removing some polar organics as well. On the other hand, activated carbons do not effectively remove contaminants of high solubility or inorganic salts like nitrates.

Phenol and phenolic compounds are the major organic compounds of many industrial waste waters[13]. These compounds are present in the waste effluent waters from the coking plants, fertilizer, pharmaceutical, plastics, organic, chemical, steel and petroleum industries, as well as from dye manufacturing. They are considered pollutants because they increase oxygen demand and cause an unpleasant taste in drinkable water supplies. Chlorophenols are produced when phenol-contaminated water is chlorinated in the purification process. These derivatives are very distasteful and potential health hazards, even in the low parts per billion range [14]. In recent years, restriction have been placed on the industry by the various regulatory bodies in order to prevent the discharge of phenolics into receiving water streams. These measures have stimulated the development of dephenolizing processes for the treatment of waste effluent water. Current methods for removing phenolics from wastewater include microbial degradation, adsorption on activated carbon, chemical oxidation (using such agents as ozone, hydrogen peroxide or chlorine dioxide), incineration methods, solvent extraction and irradiation [15-18]. Advanced oxidation processes (AOPs) such as UV/H_2O_2, H_2O_2/O_3, H_2O_2/metals, or UV/O_3, in which highly-oxidative free radicals are generated, have proven to be very effective to oxidize and destroy these compounds during the last few years[19-22]. Under appropriate operating conditions, these organics can be degraded to nontoxic final products such as carbon dioxide and water. Integration with other wastewater treatment operations, (AOPs) may serve either as a tertiary polishing operation, or as an initiation step, wherein recalcitrant pollutants are partially degraded and the decomposition of partially degraded by – products is left to a less expensive technology [23].

The preparation of activated carbons (AC) with selective porosity developments is of interest to attain optimum application depending on the use of the AC, an essentially micro porous material or a wider porosity adsorbent may be necessary [24-25]. The porous texture of an

AC is determined by many factors. Among them the precursor used, activating mechanism, activating gas, preparation conditions and presence of catalysts [24-25], can produce great changes in porosity.

Solano et al.[25], proposed that catalytic species benefit the preparation of AC as they increase the reaction rate and change the porosity distribution the result should that calcium catalyzed carbon activation by CO_2 produces a remarkable development of the mesoporosity. However, the effect was not clear when the reaction was done with steam, probably due to the low steam pressure used [25]. Cannon et al. [26-28], found that calcium catalysis of the steam and CO_2 carbon gasification also causes microspores to widen.

The adsorption capacity of a given AC depends on several factors such as the nature of the adsorbent, the nature of the adsorbate, the solution conditions, etc. The equilibrium capacity of an AC for target compounds is the main factor to be taken into account in the design of full-scale adsorption columns and any decision regarding its economic feasibility [29].The properties of activated carbons are a function of the carbonaceous precursor material and of the preparation conditions used [4], one of which could be the rate of the activation process. Changes in the activation process rates may be obtained by varying the activation temperature, the partial pressure of the activating agent or by use of a catalyst. Although catalytic carbon gasification has been subject of many investigations [30], its application to activated carbon preparation has not been widely analyzed.

The use of calcium as a catalyst of the carbon-CO_2 reaction, was investigated in the preparation of activated carbons. Two different porous carbon precursors were used and the porosity of the activated carbons obtained with and without calcium were compared. It was found that the addition of calcium to the CO_2-carbon activation influences the gasification rate and the adsorption capacity of the resulting activated carbons[31]. It was proposed that catalytic activation may be used to tailor the pore size distribution in a way which is not possible by the usual uncatalyzed activation process. The rapid development of gas adsorption processes in industry has necessitated the parallel development of a fundamental understanding of the mechanisms involved in gas phase adsorption systems[32]. Adsorption occurs when any clean solid surface is exposed to a gas or vapor [33]. The amount adsorbed at the gas/solid interface is dependent on the nature of the molecular interactions, the surface area and porosity of the adsorbent and the experimental conditions. Following the collision of a gas molecule with a solid surface only a limited number of outcomes are possible. The molecule may rebound from the surface or be adsorbed chemically or physically . The molecule interactions, either physical or chemical will lead respectively to chemisorptions or physisorption (specific or non-specific). In gaseous adsorption systems below 200 ^{0}C physical adsorption predominates[34]. Comparison of the energetic of adsorption provides a useful indication of the relative affinity of an adsorbent for different molecules (polar, non-polar, etc.).

I.A.1. Physical and chemical adsorption.

Adsorption from solution onto a solid occurs as the result of one of two characteristic properties for a given solvent-solute-solid system, or a combination there of. The primary driving force for adsorption may be a consequence of lyophobic (solvent-disliking) character of the solute relative to the particular solvent, or of a high affinity of the solute for the solid [35-37]. For the majority of systems encountered in water and wastewater treatment practice, adsorption results from the combined action of the two forces. Each of the two primary causes for adsorption can be affected to varying degrees by a number of factors. The degree of solubility of a dissolved substance is by far the most significant factor in determining the intensity of the first of the two driving forces. The degree of solubility can be thought of as the extent of chemical compatibility between a solvent system and a solute [38-39]. The more a substance likes the solvent system- the more hydrophilic in the case of an aqueous solution – the less likely it is to move toward an interface to be adsorbed. Conversely, a hydrophobic – water disliking –substance will more likely be adsorbed from aqueous solution [41]. A large number of organic contaminants, such as sulfonated alkyl benzenes, have a molecular structure comprised of both hydrophilic and hydrophobic groups[42]. In this case ,the hydrophobic part of the molecule tends to be active at the surface and undergo adsorption, whereas the hydrophilic part tents to stay in the solution phase if at all possible. The “solubility – amphoteric” character of the substance results in an orientation of the molecule at the interface, the hydrophobic part adsorbed at the surface, and the hydrophilic part directed toward the solvent phase [40]. The second primary driving force for adsorption results from a specific affinity of the solute for the solid . In this context, it is desirable to distinguish between three principal types of adsorption:

(i) adsorption of the first type falls within the realm of ion-exchange and is often referred to as exchange adsorption . Exchange adsorption is, as the term implies, a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. For two potential ionic adsorbates in like concentration and in the absence of other specific sorption effects, the charge on the ion is the determining factor for exchange adsorption. In a system containing a monovalent ion and a trivalent ion under the stated conditions, the influence of kinetic energy to remain in solution phase is the same for each, but the trivalent ion is attracted much more strongly toward a site of opposite charge on the surface of the adsorbent. For ions of equal charge, the molecular size [hydrated radius] determines order of preference for adsorption, the smaller ion being able to accomplish closer approach to the adsorption site and thus being favored .

(ii) adsorption occurring as a result of van der walls forces is generally termed “physical” adsorption, a term which has come to represent cases in which the adsorbed molecule is not affixed to a specific site at the surface but is, rather, free to undergo translational movement within the interface. Adsorption of this type is sometimes referred to also as “ideal” adsorption:-

(iii) if the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as “chemical” adsorption, “activated” adsorption, or “chemisorption”. Chemically adsorbed molecules are considered not to be free to move on the surface, or within the interface.

Physical adsorption is usually predominant at low temperature, and is characterized by a relatively low energy of adsorption, that is, the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. Chemical adsorption processes exhibit high energies of adsorption, because the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical interaction between the adsorbent and the adsorbate is favored by higher temperature, because chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures. Most adsorption phenomena are combinations of the two forms of adsorption, that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at an interface. Thus it is generally not easy to distinguish between physical and chemical adsorption .

Many adsorption processes involving organic molecules result from specific interactions between identifiable structural elements of the sorbate and the sorbent. These interactions may be designated as “specific adsorptions” as opposed to adsorption which occurs as a result of simple columbic interactions. The adsorptive interactions of aromatic hydroxyl and nitro-substituted compounds with active carbon, may be considered to be specific adsorption processes resulting from the formation of donor-acceptor complexes of the organic molecule with surface carbonyl oxygen groups, with adsorption continuing after these sites are exhausted by complication with the rings of the basal planes of the carbon microcrystallites [43].

I.B.AIM OF THE WORK.

The previous review demonstrates the important role played by activated carbon in a large number of contemporary processes involving purification, separation and recovery. Accordingly, an escalating consumption appears all over the world due to increasing pollution levels as a result of raised human activities and to more stringent environmental measures and public awareness. Due to the lack of suitable resources of coal or coconut shell in several countries it becomes demanding to search for equally feasible raw materials as precursors to activated carbon. Agricultural residues constitute such a source, as they are highly abundant, renewable and accumulating low-cost feed stocks in a large number of countries.

Both Date Pits (DP) and Cotton Stalks (CS) were currently applied as precursor materials and as adsorbents in several water treatment processes. It is worth mentioning that the annual accumulation of both wastes reach about two million tons, and find no economic utilization fields. Agricultural by-products have lost their long traditional and important role as low cost fuel and energy in rural districts. Their regular accumulation raises many environmental problems and nuisance. DP and

CS were chosen due to their granular structure, insolubility in water, chemical stability, high mechanical strength, and their local availability at almost no cost. Natural DP and CS used in this work were obtained from the food industry waste in Egypt and agricultural waste in Mashtul El-Souk –Sharkia – Egypt.

Heavy metals are considered harmful to the environment and belong to one of the most toxic groups of water pollutants. There has been increasing concern and more stringent regulation standards pertaining to the discharge of heavy metals to the aquatic environment, due to their toxicity and detriment to living species including humans. Heavy metals are non-degradable and can accumulate in living tissues, so they must be removed from polluted water. Currently there is increasing interest in removing (Pb^{2+},Cd^{2+} , Fe^{3+}, Mn^{2+} and Sr^{2+}) ions from drinking water due to their supreme toxicity to human health in small concentrations. According to the Egyptian Environmental Affairs Agency (EEAA), Law # 4, 1994, the permitted concentration of Pb^{2+},Cd^{2+} , Fe^{3+}, Mn^{2+} and Sr^{2+} ions in drinking water are 0.05, 0.01, 1.0, 0.50 and 0.05 µg/L, respectively [266]. Long term drinking water containing heavy metals higher than this level can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in humans. Therefore, the elimination of heavy metals from water is important to protect public health.

Nitrogen adsorption technique was applied in order to estimate the surface area and internal porosity, based on different standard procedures. Currently employed probe molecules were tested for determining the uptake of organic species from aqueous medium ; these are methylene blue, congo-red, phenol, p-nitrophenol, in addition to iodine.

The proposed research program is directed to investigate the following aspects:-

1-Preparation of different types of activated carbon from cheapest sources (DP and CS).
2-Characterization of the different adsorbent materials used.
3-Adsorbability of typical heavy metals pollutants to these materials.
4-Studies of the factors affecting the adsorption process.
5-Determination of adsorption isotherms.
6-Applications:- removal of some heavy metals (pb, Cd, Fe, Mn and Sr) from aqueous solution and treatment of underground wastewater.

I.C.REVIEW OF LITERATURE.

Cazorla, et al [44] studied the effect of calcium on porosity development during activation of char, from almond shells, in steam and carbon dioxide . Water molecules have a good accessibility to the wider porosity of the carbon material. This explains that uncatalyzed activation in a horizontal furnace and in a fluidized bed reactor do not give important differences in porosity development. On the contrary, the accessibility to the narrow microporosity was difficult, what results in a small development of this range of porosity. The use of calcium in the activation process can be a good procedure to create wider pores than can be achieved during the uncatalyzed carbon gasification. The influence of calcium in porosity development can be explained using the reaction mechanism previously proposed for calcium catalyzed carbon gasification. The effect of calcium on pore size distribution will be strongly dependent on the following factors :(i) the initial porosity of the carbon, as it determines the amount and distribution of calcium species; (ii) the amount of calcium loaded; (iii) the calcium oxide sintering rate, that will be determined by its distribution through the carbon particle and by the atmosphere, and (iv) the rate of gasification . In this studies there was a clear effect of calcium on pore size distribution, it was necessary to attain a good distribution of calcium in the carbon and to have a sufficiently high reactivity.

Hsisheng, et al [45] demonstrated that porous carbons with a very high porosity can be prepared from a bituminous coal with KOH activation. The surface area and the pore volume of the carbons produced can be as high as 3000 m^2/g and $1.5 cm^3/g$ respectively. Investigations of the carbonization conditions have shown that the carbon yield was decreased as function of the carbonization temperature. It was suggested that the decrease in carbon yield can be attributed to volatile evolution as well as to carbon gasification by CO_2 and potassium compounds. The porosity of the resulting carbons increases with the carbonization temperature to a maximum at a temperature of 800 ^oC and then began to decrease with the temperature. Carbon gasification plays an important role in determining the surface characteristics of the carbons. The results also indicated that the porous structures formed from KOH activation are more thermally stable than those from H_3PO_4 or $ZnCl_2$. The optimum chemical ratio of KOH to coal for preparing high porosity carbons was found to be 6 for carbonization performed at 700 ^oC and 4.25 at 800 ^oC . The variation of the surface characteristics with the chemical ratio can mainly be attributed to the interactions between carbon and the oxidizing species such as CO_2 and potassium–containing compounds. Apart from the carbonization temperature and the chemical ratio, the carbonization time also affects the porosity of the carbons.

Tam, et al[46] studied a three–step process involving (i) carbonization, (ii) controlled low temperature air oxidation and (iii) activation (a second carbonization), for producing high surface area activated carbons from macadamia nut shell and coconut shell charcoals. Control of the strongly exothermic oxidation reaction was gained by stepwise heating of the carbon from low (177 ^oC) to high (387 ^oC)

temperatures in flowing air. Activated carbon yields as high as 15 wt % of the dry, raw biomass feedstock, can be achieved when high yield charcoal was used as a substrate for activation by air gasification. This yield was almost double the reported commercial yield for coconut shell activated carbon. This study found that macadamia nut shells were inherently better suited for the production of activated carbon by air oxidation than coconut shells. Two distinct stages were evident during the oxidation (air gasification)step. The first stage involves a rapid increase in the BET surface area with burn off until a value of about 15% was reached. At this burn off the surface area of the carbon reached 600 m^2/g . During the second stage (when the burn off exceeds 15%) the increase in surface area with burn off was much less rapid but it accelerated as the burn off increased . The surface area of the carbons produced in this study reached 1000 m^2/g at a burn off 50-60%.The increase in surface area with burn off during the second stage of the oxygenation step was inversely proportional to the yield of the carbon .

Alya, et al [47] found that a one-step steam pyrolysis in the range (600-700 ^{o}C) for the production of activated carbons from five lignocellulosic materials was feasible. The process was a simple one-step procedure that saves energy and time, performed at moderate temperatures (600-700 ^{o}C), and results in a relatively high carbon yield . Steam serves two functions ; first , it acts as a purging (or carrier) gas that appears to enhance the fast and effective removal of gaseous products and inhibits their cracking causing carbon deposition with pore blocking . Second, it acts as a selective gasification medium, at such moderate temperatures, preventing excessive gasification, and retaining the inherent porosity of the agricultural precursor without consequent widening. Date palm by products, branches, leaves and pits, were demonstrated to be feasible novel feedstocks for the production of good quality carbons.

Treatment of rice husks under the prescribed conditions resulted in a low-grade carbon, and Barbecue charcoal dust, a waste material was upgraded by steam action which raised its adsorption capacity at a low burn off (30-40%). All tested lignocellulosic materials produced microporous activated carbons with limited internal pore volume and narrow porosity.

Girgis, et al [48] also studied the activation with phosphoric acid for the production of activated carbons from lignocellulosic materials. Activation with phosphoric acid offers many recommending advantages :it was one-step process, effective at low temperatures, results in a higher carbon yield, and partial recovery of activant was possible. Its action as activant could be attributed to several effects: (i) its effect as a dehydrating agent, (ii) it inhibits formation of tar and thus enhances formation of char; (iii) it produces chemical and physical changes that modify the degradation process (it weakens the structure, increases elasticity and swelling of the particles); and (iv) upon intense washing of the product an elimination of the deeply situated activant leads to the appearance of the tremendous porosity [49-50]. It was suggested by Laine and Calafat [51] that phosphoric acid forms, in addition, a ‘skin’ of phosphate protecting the internal carbon structure and thus protecting the product form excessive burn off leading to surface area decrease. The notation (50% H_3PO_4 at 500 ^oC) condition was noticed as effective with other carbon precursors (sugar cane bagasse [52], apricot stone shells [53], corn cobs [54], and rice hulls proved also effective with the present carbon obtained from cotton stalks[48] .The amount of phosphoric acid incorporated into the precursors (50% H_3PO_4) seemed to be enough and efficient to attain good impregnation. On the other hand, a temperature of 500 ^0C lies above the pyrolysis temperature of many carbon precursors and seems also effective in carbonization of the lignocellulosic matrix with sufficient devolatilization of the volatile products. Carbons with well developed mesoporosity and high surface area were obtained that seem promising for the adsorption from solution.

Mitchell, et al [55] showed that the production of granular activated carbons (GACs)from selected agricultural by products could be more effective than commercial (GACs) in the adsorption of organic and metal contaminant from water .

Lotfi, et al [56] studied the modified activated carbon for the removal of copper, zinc, chromium, cyanide and some organic chemicals from water and waste water. This phenomenon was used for modifying the carbon surface and therefore enhance its removal capacity for inorganic pollutants. The advantage of fixed–bed modified columns were reducing chemical consumption; eliminating sludge disposal and recycling the ‘cleaned’ wastewater back to the production area. The technique of tetrabutyl ammonium (TBA) and diethyl dithiocarbamate modification optimizes the existing properties of activated carbon giving greater CN^-, Cu^{2+}, Zn^{2+} and Cr^{6+} removal capacity to the plain carbon. The column breakthrough, indicates that tetrabutyl ammonium (TBA) carbon modification, has a cyanide removal capacity of approximately five times that of plain carbon. The sodium diethyl di-thiocarbamate (SDDC)carbon column showed Cu^{2+}, Zn^{2+} and Cr^{6+} removal capacity two to four times higher than that of plain carbon. The removal of these metal ions followed the descending order, $Cu^{2+} > Zn^{2+} > Cr^{6+}$. Two considerations were important with respect to the dynamics of fixed–bed adsorbers using TBA and SDDC modified adsorbent for ions removal, adsorption TBA and SDDC on activated carbon under the influence of the surface hydrophobic character and the exchange of the metal ions with the immobilized functional groups. Firstly, there were certain functional groups on activated carbon such as phenolics, lactonics, carboxylics, hydroxylics and carbonyl groups that could be formed during the activation process. Secondly, there were functional groups on the immobilizing agents that selectively form bonds with the ions. The overall ion removal was a combination adsorption capacity of the plain adsorbent, and the extent of exchange of ions with the immobilizing agent molecules adsorbed on the adsorbent.

Rodriguez, et al [57] investigated several methods for the characterization of the porous texture (adsorption of vapors and gases, immersion calorimetry) and chemical nature, mainly oxygen surface groups, selective titration and temperature programmed desorption (TPD) of activated carbons. The determination of the volume of micropores was not straightforward since it was a function of the adsorptive selected and the method used to analyze the corresponding adsorption isotherm. With the results obtained in the characterization of a series of activated carbons of gradually increasing porosity by adsorption of several gases and vapors and n-nonane preadsorption , it was found that a simple and convenient evaluation of the microporosity (volume of micropores and heterogeneity of pore size) could be attained by adsorption of N_2 at 77K and CO_2 at 273K. It has also been shown that immersion calorimetry in liquid hydrocarbons with different molecular dimensions was a convenient technique to determine the surface area and micropore size distribution of activated carbons, the results being similar to those obtained by adsorption of the same hydrocarbons (which was a more tedious experimental method).

The determination of the oxygen surface groups of the carbons had been carried out by selective titration and by TPD, and it had been shown that there was a correlation between the amounts of NaOH and $NaHCO_3$ consumed and also between the amount of NaOH consumed and the amount of CO_2 evolved in TPD. These correlations were independent of the oxidizing agent used, thus indicating the difficulty in differentiating the various surface groups, very probably because of the effect not only of the surface grouping itself but also its position in the carbon skeleton. The effect of the texture and chemical nature of activated carbon in adsorption and immersion processes of molecules with different polarity had also been analyzed, and it had been shown that for non-polar molecules (e.g. nitrogen or benzene), the effect was almost nil for both the amount adsorbed and the enthalpy of immersion, but it was very important for polar molecules (especially when the dimensions were small, as for water). The specific interactions of the oxygen surface groups with the adsorbate play a predominant role, although not the only one, and the amount adsorbed or the enthalpy of immersion considerably increase with the amount of surface groups.

Molina, et al [58] studied the effect of gasification by air at (350 ^oC) or CO_2 at (825 ^oC) in the development of micro porosity in activated carbons. The adsorption of nitrogen, benzene, n-butane, iso-butane, 2,2-dimeyhyl butane and iso-octane had been carried out on two series of activated carbons, one prepared by activation of carbonized olive stone in CO_2 at 825 ^oC and another by reacting activated carbon (of the same origin) in air at 350 ^oC. Carbons with low burn off exhibit a molecular sieving effect toward iso-octane (minimum dimension, 0.59 nm). For carbons with medium burn-off, in which molecular sieving was not exhibited (34 to 52% burn off), the characteristic curve was coincident for all adsorbates, but for larger burn off the N_2 data did not fit the characteristic curve. In case of the latter carbons, with wide and heterogeneous microporosity, only the micropore volume deduced from the higher relative pressure branch of the Dubinin-Radushkevich plot or characteristic curve for N_2 at 77K usually in the relative pressure range (0.05 to 0.25) was coincident with that obtained from the hydrocarbons.

Rosa, et al [59] investigated the comparison between chemical, physical and combined activation in terms of porous texture for activation of lignocellulosic materials. The influence of the chemical activating agent: raw material ratio in the preparation of activated carbons from almond shells by chemical activation with $ZnCl_2$ had been studied . The impregnation of almond shells with a constant volume of $ZnCl_2$ aqueous solution, allowing sufficient time for the absorption of the chemical activating agent, was a convenient method to obtain carbons with a well developed microporosity. The gasification of these $ZnCl_2$–activated carbons with CO_2 produces an enhancement of supermicro and mesoporosity with N_2 DR surface area . The comparison of the behavior of carbonized almond shells and $ZnCl_2$-activated carbons in the gasification with CO_2 showed that there was no important difference in reactivity, even though for a given micropore volume the global yields in the chemical activated material were always large.

Krisztina, et al [60] investigated the effect of activation on the surface chemistry of activated carbons prepared from polymer precursors. The activation of the various polymer-based chars, in spite of the similarity of the treatment (temperature, burn off) results in different physical and chemical surface properties .The surface chemistry of these carbons had been characterized by X-ray photoelectron spectroscopy (XPS), adsorption from benzene-methanol binary liquid mixture, and potentiometric acid–base titration. The activation treatment performed with a steam/N_2 mixture at elevated temperature (900 ^oC) not only promotes the relative extension of graphitic regions by removal of noncarbon atoms and part of the amorphous carbon , but also helps on the further development of graphitic regions. It modified the elemental composition, the species of the surface groups and their distribution on the surface . The carbons contain both hydrophobic and hydrophilic sites on their surface already in their carbonized form, but the activated ones showed a more hydrophobic character. The carbons exhibit an amphoteric surface, containing both acidic and basic surface groups. The titration curves show a hysteresis when performed upward and downward. Suspensions of the activated carbons samples exhibit a basic pH. Both the increased hydrophobic property and the basicity can be attributed to extended graphitic regions. Part of the oxygen atoms forming basic functional groups may contribute to basicity as well.

Whitten, et al [61] studied the development and characterization of sorbents produced from Irish sphagnum moss peat. A range of carbon chars was produced from sphagnum moss peat by heating in a furnace with a reduced oxygen atmosphere. A series of heating times and temperatures were selected for the preparation of the chars. Comparative porosity and surface area studies, based on nitrogen sorption isotherms and mercury porosimetry data, were carried out to characterize the chars. Further characterization studies were conducted by electron microscopy techniques. Optimum charring conditions, yielding maximum surface area for N_2 adsorption, were observed at a charring temperature of 800 ^{o}C and charring time 30 minutes. Using the optimum charring conditions, a further series of chars was produced. Prior to charring the raw peat was chemically pre-treated with a range of metal salt solutions of varying percentage concentration. The adsorptive capacity of these chars for N_2 was investigated on the sorptomatic 1900 (Fisons Instruments). The adsorption isotherms were compared to the standard isotherms of Langmuir . Adsorbate uptake was seen to vary with surface area availability, pore volume, pore type and the nature of the adsorbate .

Daifullah, et al [62] evaluated the impact of surface characteristics of activated carbon on adsorption of benzene, toluene, ethyl benzene and p-xylene (BTEX). Activated carbons with highly-developed porosity were obtained from different low-cost waste lignocelluosic materials by impregnation with H_3PO_4 followed by thermal treatment at 500 ^oC. High surface area with high total pore volume products resulted with wide distribution of porosity within micro-mesopore ranges. Three carbon precursors proved the best recommended to respond to this treatment i.e. these were peach stones (PS), almond shells (ALS) and cotton stalks (CS). Olive stones (OS) and date pits (DP) showed relatively lower feasibility which, added to (CS), present highly promising novel raw materials under suggested activation route. Subsequent air treatment of one carbon resulted in considerable destruction of its previous porosity as noticed from surface area and internal volume . Phosphoric acid activation results in the incorporation of appreciable amounts of P_2O_5 and high content of oxygen functional groups, essentially of carboxylic acidity. Increasing surface acidity increases the polarity of the surface and reduces adsorption of the hydrophobic BTEX, in spite of their highly developed porosity by the six-carbons . Adsorption was hampered due to the hydration of these groups, resulting in water clusters on the outside surface and blocking pore entrances thus reducing the surface area available for adsorption. Also, the oxygen-containing functional groups reduced adsorptive capacity by localizing free electrons of the carbon basal planes. The presence of surface acidic phosphate oxides contaminants might also reduce the BTEX uptake. All these factors were simultaneously responsible for the low uptake of BTEX by the six-carbons. Relatively higher uptake of BTEX by a commercial activated carbon was postulated to be due to the basic nature of the carbon surface (pH 7.8) and the absence of phosphorus oxides. The adsorption of BTEX on this carbon may imply electron donor-acceptor mechanism in which oxygen–atoms of the carbonyl group act as electron-donors and the aromatic ring of the adsorbate acts as electron acceptor.

Beck, et al [63] investigated the characterization of surface oxides on carbon and their influence on dynamic adsorption. The aim of this work was to gain a better fundamental understanding of the nature of surface oxide sites present on carbon surfaces, and their role in the adsorption process. A systematic series of active surfaces with different degrees of surface oxidation had been prepared for two model carbons using a number of controlled oxidation techniques. X-ray photoelectron spectroscopy (XPS) analysis gave quantitative and qualitative information regarding the nature of the surface functional groups introduced from the oxidation techniques. An increase in surface oxygen functional groups resulted in a significant decrease in the adsorption performance, for a non-polar adsorbate, of the carbons under humid conditions. Spatial location, strength of interaction, and availability of surface oxygen groups to adsorbate molecules may have also played a part in determining the dynamic adsorption performance of the carbon .

Fumiaki, et al [64] studied the fractal model for adsorption on activated carbon surfaces. Adsorption of organic compounds in aqueous media onto an activated carbon surface usually follows the empirically derived Freundlich equation $W=KC^{1/n}$, where W is the mass of the adsorbed solute, C is the equilibrium solute concentration, and K and n are fitting constants. To analyze this equation, they proposed a simple geometrical model for adsorption of organic compounds. Activated carbon surface was irregular, and the irregularity was similar at any magnification. Because of the self-similarity in raggedness at various resolutions, adsorption of a bulky organic molecule sequesters several neighboring sites from binding. Based on this model, a generalized equation was derived that encompasses the Langmuir and Freundlich equations. The Freundlich equation was shown to be a special case of the expanded Langmuir equation. The parameter n in the Freundlich equation was related to the number of binding sites wasted by the adsorbate binding; hence, it was related to the size of the adsorbate molecule. The experimental result that n was larger than unity supports the above model. The main force for the carbon surface adsorption was the tendency of the adsorbate molecule to be excluded from the aqueous phase . The larger the hydrophobic molecule, the greater the tendency to be excluded from the aqueous phase becomes. For this reason, n was related to the adsorbate affinity. The parameter K was related to the size of the adsorbing space, i.e. the binding capacity, and also to the adsorbate affinity .

Daifullah, et al [65] investigated the extent of utilization of the full surface area of Bone Charcoal (BC) for removal of some organic pollutants which were commonly found in wastewater streams. The adsorbent was a by-product obtained from Pakin Co., Egypt. In this concern, adsorption isotherms of 2-chlorophenol, m-,p-cresol, 4-nitrophenol, 2,4-dichlorophenol and 2-nitrophenol from aqueous solutions by (BC) had been evaluated. The data conform to both Langmuir and Freundlich adsorption isotherms. Also, possible treatment of industrial wastewater by (BC) was assessed. Assessment of the treatment process was in terms of measuring the total Organic Carbon (TOC) before and after treatment as a measure for organic contaminants. The water sample treated was obtained from an Egyptian Company for preparing and dyeing of Wools, Mostorod. It was found that, treatment of wastewater in batch systems using (BC) coupled with uv-irradiation in the presence of H_2O_2 was promising.

Girgis, et al [66] evaluated the steam-activated carbons produced from date pits and their adsorption capacity. Dried ,crushed date pits were subjected to treatment with steam to get activated carbons. A 500 ^oC char was gasified at 850 ^oC in a stream of H_2O /N_2 increasing durations to obtain activated carbons at burn off values of 12 up to 73% . A recently developed one step steam pyrolysis technique was also applied by heating at 600 or 700 ^oC in presence of pure steam. The products were characterized by adsorption of N_2 at 77 K and adsorption of phenol, iodine and methylene blue from aqueous solution. Conventional two step steam activation resulted in carbons with developed porosity. Carbons with medium burn off record the highest texture development which was followed thereafter by a collapse in the internal porosity. Single step steam pyrolysis leads to essentially microporous carbons with enhanced porosity as a function of treatment temperature. All prepared carbons show high pH values indicating surface basicity that increases with degree of burn off . The uptake of phenol, iodine and methylene blue was promoted by increased gasification .

Atia, et al [67] estimated the effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal. A comparison of the textural characteristics of the activated carbons (AC) with the adsorption data obtained showed that the adsorption capacity of phenol was higher in carbons of a basic nature, regardless of textural characteristics. It was found that retention of some organic compounds was less on acidic carbons than in basic nature carbons, even when their equivalent surface area was much more developed. This suggests that there were two different aspects to be considered in the process of adsorption : the kinetic, which was closely related to the macropore and mesopore volume of the AC, and the process of adsorption itself, which might be related with the surface chemistry of the carbons , rather than textural properties .

Vander, et al [68] studied the application of nanofiltration for removal of pesticides, nitrate and hardness from ground water. The drinking water industry faces a growing number of difficulties in the treatment of ground water for drinking water production. Ground water sources were frequently contaminated with pesticides; nitrate concentrations were increased and were close to or above the legal standard of 50 mg/l. Moreover , partial removal of hardness was desirable for reasons of comfort. In the first part of this work, the removal of four pesticides (atrazine, simazine, diuron and isoproturon), the removal of hardness and the removal of nitrates with the membranes was experimentally studied. The results of this study proved that treatment of ground water with nanofilteration allows to produce drinking water with outstanding quality at an operating cost that was not excessive. It showed that the pesticide rejections were satisfactory ; hardness was also very efficiently removed, whereas only a small fraction of nitrate was removed for most membranes.

Hsieh, et al [69] investigated the adsorption of phenol , iodine and tannic acid onto activated carbon fabrics in aqueous solutions. The carbon fabrics were made of polyacrylonitrile with different extents of activation in steam. The increasing extent of activation was accompanied by increasing carbon porosity as well as liquid phase adsorption capacity. Langmuir and Dubinin-Radushkevich (D-R) models were employed to analyze the equilibrium adsorption data. The fractional filling of carbon micropores and the mean free energy for adsorption were estimated according to these modules . It was suggested on basis of this work that the mesopore fraction of the fabrics, the extent of carbon activation, and the adsorbate size were important as well as competitive factors determining the adsorption capacity. Both the equilibrium constant and free energy for adsorption increase with the mesopore fraction, indicating that the mesopores promote the adsorption onto high energy sites ,whereas the fraction filling micropores decreased with the extent of carbon activation and the size of the adsorbates .

Chern, et al [70] evaluated the adsorption of p-nitrophenol onto activated carbon. The adsorption isotherm of p-nitrophenol onto granular activated carbon in 25 ^oC aqueous solution was experimentally determined by batch tests. Both the Freundlich and the Redlich-Peterson models were found to fit the adsorption isotherm data well. A series of column tests were performed to determine the breakthrough curves with varying bed depths (3-6 cm) and water flow rates (21.6-86.4 cm^3/h). The constant-pattern wave approach had been used to develop explicit equations for the breakthrough curves of the fixed-bed adsorption processes with the Langmuir and the Freundlich adsorption isotherms, respectively. The explicit form consists of two parameters one could be directly read from the experimental breakthrough curves and the other could be obtained from the slope at the half time. The experimental half times were very close to those predicted by the self-sharpening wave approach and were proportional to the bed-depth to flow-rate ratio. Four column test runs for p-nitro phenol removal were performed and the results showed that the experimental and predicted breakthrough curves were in good agreement. The experimentally determined overall volumetric mass-transfer coefficients in the liquid phase were less than those predicted by the correlation. Solid-phase mass-transfer resistance had some impact on the overall adsorption rate. A simple equation was proposed to correlate the overall volumetric mass-transfer coefficients in the liquid phase as a function of the water flow rate successfully. The Toth model was used to fit the adsorption isotherm data at varying solution temperatures and pHs satisfactorily.

Juang and Teng [71] evaluated the adsorption isotherm of phenolic compounds from aqueous solutions onto activated carbon fibers . Equilibrium studies for the adsorption of eight phenolic compounds from aqueous solutions onto activated carbon fiber had been carried out in the concentration range 40-500 mg/l at 303 K. The following results were obtained . High adsorption capacities (about 2.0 m mol/g) were generally obtained for the chlorinated phenols compared to the methyl-substituted ones (about 1.8 m mol/g). For two-parameter equations, the Langmuir equation gives the poorest overall fit. The Freundlich equation yields a somewhat better fit but still deviates considerably from experimental data at lower liquid concentrations. For three parameter isotherm equations, the normalized percent deviation obtained using the Redlich-Peterson equation (1.4 –7.0 %) was nearly the same as that obtained using the Toth equation (0.3 –9.6 %) .

Namasivayam, and Kavita [72] estimated the removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. The adsorption of Congo Red by coir pith carbons was carried out by varying the parameters such as agitation time , dye concentration, adsorbent dose, pH and temperature. The study showed that the coir pith carbon is an effective adsorbent for the removal of Congo Red from aqueous solution. Adsorption followed the Langmuir and Freundlich isotherms. Complete removal of the dye can be achieved using an appropriate dosage of the active carbon and pH for waste waters. The results would be useful for the prediction and designing of wastewater treatment plants for the removal of dye. Since the raw material coir pith was freely available in large quantitative wastes in coir industries the treatment method seems to be economical.

Bandosz, et al [73] investigated the surface acidic groups on activated carbons .The effect of oxidation with nitric acid on activated carbons from different origins has been studied by inverse gas chromatography at infinite dilution, Boehm titration, and mass titration to determine the point of zero charge (PZC) of carbons. The effect of oxidation was to generate acidic groups, and this became more pronounced as the temperature of oxidation was increased. The three methods used for estimating the chemical characteristics of a series of carbon surfaces were very useful for determining their degree of oxidation. However, estimating the PZC by mass titration appears to be less sensitive for highly oxidized carbons. The Boehm titration method was not limited to this constraint but was sensitive only to different centers when in aqueous solutions. The method of estimating the acidity by inverse gas chromatography was very useful in the case of carbons. It provides, with high sensitivity, a measure of specific interaction sites that act as adsorption centers in anhydrous environments . The fact that the specific interaction parameters derived from this method also correlates with Boehm titration results makes the chromatographic method equally useful for characterization of activated carbon surface chemistry in aqueous solutions.

Adib, et al [74] studied the relationship between H_2S removal capacity and surface properties of un impregnated activated carbons. The H_2S breakthrough capacity was measured on two series of activated carbons of a coconut shell and a bituminous coal origins. To broaden the spectrum of surface features the samples were oxidized using nitric acid or ammonium persulfate under conditions chosen to preserve their pore structures. Then the carbons were characterized using Boehm titration, potentiometric titration, thermal analysis, temperature programmed desorption, sorption of nitrogen, and sorption of water. It was found that the choice of unimpregnated carbon for application as H_2S adsorbent should be made based on parameters of its acidity such as number of acidic groups, pH of surface, amount of oxygen groups, or weight loss associated to decomposition of surface oxygen species . The results obtained from the analysis of six unimpregnated carbon samples suggest that there are certain threshold values of these quantities which when exceeded, have a dramatic effect on the H_2S breakthrough capacity.

Contescu, et al [75] evaluated the surface acidity of carbons characterized by continuous pK_a distribution and Boehm titration. The surface acidity of several activated carbons was evaluated using the Boehm and potentiometric titration methods. Experimental conditions (particle size, rate of titration) were varied and several procedures to collect raw data for proton binding isotherms (slow continuous addition of titrant , incremental addition conditioned by a pH stability criterion and batch experiments) were compared. When a specific application was required (such as selective ion exchange), it might be advantageous to use a continuous and more detailed picture of acidic functionalities rather than the condensed inventory based on a global classification scheme. The aim of this work to demonstrate that the method for characterization using the distribution function of surface acidity was available, independent method that provides a comprehensive and detailed description of acid base chemistry that occurs in carbon aqueous electrolyte suspensions. The results demonstrated that when experimental precautions were taken the information retrieved by analysis of potentiometer titration curves overlaps quantitatively with Boehm titration, a better agreement was obtained for the fully automatic titration .

Bagreev, et al [76] studied the sorption of hydrogen sulfide on activated carbons. The conditions of the experiment were dry and anaerobic. The results presented in this study showed that under dry anaerobic conditions the thermodynamics of hydrogen sulfide sorption on activated carbons at temperatures lower than 200 ^oC did not depend on surface chemistry, pH, or the presence of specific oxygenated groups. It strongly depends on the degree of sorbent micro porosity. The obtained high values of hydrogen sulfide heat of adsorption suggest that small pores were very active in this process. The results indicated that the heat of adsorption of hydrogen sulfide could be predicted from its dependence on the structural parameters of the carbon surface obtained from the sorption of nitrogen .

Rivera, et al [77] studied the bioadsorption of (Pb^{2+}, Cd^{2+}, and Cr^{6+}) onto activated carbon from aqueous solutions. They found that the presence of bacteria influenced the adsorption of heavy metals. This was because of the adsorption of the bacteria on the carbon, which was also enhanced in the presence of (Pb^{2+} or Cd^{2+}). This could be explained by the divalent cation bridging theory. The adsorption of bacteria onto activated carbon modified its porous texture and surface charge density. Thus the increase in negative charge density of the carbon surface favors the adsorption of metallic cations such as (Pb^{2+} and Cd^{2+}), when bacteria were present in solution. In contrast, there was a reduction in the amount of Cr^{6+} adsorbed by the carbon when bacteria were present due to the anionic character of the Cr^{6+} species present. The presence of electrolytes in the solution alongside the bacteria slightly reduces the effectiveness of the carbon columns compared with the adsorption in the presence of bacteria without electrolytes, probably as a result of the competition between Pb_{aq}^{2+} and the cations for the adsorption sites. Moreover, the presence of divalent cations reduces the adsorption of Pb_{aq}^{2+} to a greater extent than does monovalent cations, which is in agreement with the divalent cation bridging theory.

Savova, et al [78] evaluated the influence of the texture and surface properties of the activated carbon obtained from biomass products on the adsorption of Mn^{2+} ions from aqueous solution. The pore structure and chemical properties of the carbon surface undergo significant changes during activation and oxidation treatment. The adsorption of the manganese ions is predominantly site specific and depends on the concentration of surface oxides. This determines the higher adsorption capacity of the oxidized carbon for Mn^{2+} ions in comparison with the carbon activated with water vapor.

The synthesis of activated carbons from mixtures of biomass products was designed to maximize the development of various surface acidic functional groups through the alteration of the composition of the mixtures as well as by attachment of different oxygen groups to the surface during the oxidation and activation treatment. The investigation indicated a suitable approach for obtaining carbon adsorbents with maximum capacity for removal of Mn^{2+} ions from aqueous solutions:

∗ favorable precursor—a raw material containing oxygen in its structure;

∗ ratio of the mixture components—mixture containing substances susceptible to polycondensation and polymerization processes;

∗ surface modification—oxidation with a strong oxidant
(oxidation with air at 400 ^{0}C).

Li, et al [79] measured the competitive adsorption of Pb^{2+},Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon by carbon nanotubes CNTs was studied, the two kinds of experimental data sets showed that the adsorption affinity of (Pb^{2+}, Cu^{2+} and Cd^{2+}) by CNTs followed the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The competitive adsorption capacities of the three metal ions increased with increasing pH and CNT dosage and decreased with increasing ionic strength. Although HNO_3 oxidized CNTs show higher adsorption capacities for heavy metal ions compared with other adsorbents and would find many uses in environmental protection applications, their high cost currently limits their practical use.

Li, et al [80] investigated the adsorption of Cd^{2+} from aqueous solution by surface oxidized CNTs. The specific surface area and pore specific volume of CNTs increase after oxidation with H_2O_2 , $KMnO_4$ and

HNO_3. Their particle sizes decreased due to the fracture at where defects existed. With deepening of the oxidation degree, the isoelectric point (IEP = pH value for zeta potential = 0) shifts to the lower pH value and functional groups on the surfaces of CNTs increase correspondingly. The results of pH and CNT dosage effect on the Cd^{2+} adsorption showed that the increase of Cd^{2+} adsorption capacity for $KMnO_4$ oxidized CNTs was greater than that of the as-grown, H_2O_2 and HNO_3 oxidized CNTs. The manganese deposition on the $KMnO_4$ oxidized surfaces surely contributed to the Cd^{2+} adsorption, to a yet-unquantified extent.

Kononova, et al [81] evaluated the adsorption of (Zn^{2+}, Cu^{2+}, Fe^{3+}) onto carbon adsorbents from manganese sulfate solutions. Sorption of Zn^{2+}, Cu^{2+}, Fe^{3+}/Fe^{2+} on carbon adsorbents under static (batch) and dynamic (columns) conditions from model and industrial $MnSO_4$ solutions had been studied. The industrial solutions were obtained by reducing acidic leaching of manganese and pyrite concentrates. The initial manganese concentration was 35 mmol/ l and concentration of Zn^{2+}, Cu^{2+} and Fe^{3+} ions was 0.2 mmol/ L. It was found out that a complete separation of Mn^{2+} and Me^{2+} (Fe^{3+}) ions was possible under dynamic conditions. As a result purified $MnSO_4$ solutions were obtained which can be applied in MnO_2 electro evolution processes.

Faur, et al [82] studied the removal of (Cu^{2+}, Ni^{2+} and Pb^{2+}) metal ions from aqueous solution by adsorption onto activated carbon cloths. This study had investigated metal ions adsorption onto recent adsorbents, activated carbon cloths. These adsorbents seem to be efficacious to remove metal pollution from water, with monocomponent equilibrium adsorption capacities ranging from 0.080 to 0.175 m mol g^{-1} for (Cu^{2+}, Ni^{2+} and Pb^{2+}). These values were larger than those obtained with an usual granular activated carbon, and were dependent on both activated carbon properties (specific surface area, micropore volume, acidic groups content) and metal ions characteristics (ionic radius, electro negativity). The amphoteric character of activated carbon cloth (ACC) allowed to conclude to an ion-exchange mechanism between metal cations and acidic surface groups of ACC. The adsorption competition between both metal ions was related to monocomponent kinetic rates, a faster adsorption velocity involving a quicker saturation of adsorption sites. Relating to adsorption competition between metal ions and organic matter (benzoic acid), it was strongly dependent on pH conditions. When benzoic acid was under benzoate form ($pH > pK_a$), some ligands were formed between metal cations and benzoate ions which induced an increase of metal ions adsorption capacities because of the high removal of benzoic acid by ACC.

Ricordel, et al [83] showed the removal of heavy metals by adsorption onto peanut husks carbon (PHC). They found that the peanut husks carbon was an effective adsorbent for the removal of (Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+})from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals, as the adsorbent was derived from an agricultural waste by-product and its capacity was much superior to the commercial activated carbon. The adsorption was highly dependent on particle size distribution and on metal PHC ratio. Various kinetic models were used to describe the adsorption process. The kinetic model according to the reaction rate equation was found to be the most in agreement with this system. Since the removal of heavy metals by carbon could be a combination of factors such as adsorption, hydrogen bonding, precipitation and physical removal of insoluble metal complexes, further investigations to study the effect of the other operating conditions were necessary. At present, experiments were conducted in this way. All the peanut husks carbon (PHC) characteristics determined, together with the adsorption assays will play an important role in the future understanding of the adsorption processes of metals from aqueous solutions.

Daifullah, et al [84] studied the purification of wet phosphoric acid from ferric ions using modified activated carbon (rice husk). The results show that the natural rice husk (NRH) could be used as an adsorbent for the effective removal of Fe^{3+} from crude phosphoric acid. Quantitative removal of Fe^{3+} as inorganic impurities from crude phosphoric acid confirms the validity of results obtained in the batch mode studies. In dynamic mode, the NRH could be regenerated and recycled at least three times without affecting the sorption capacity for Fe^{3+} ions. Application of the developed rice husk adsorbent for purification of wet phosphoric acid was considered to be economical.

Petrov, et al. [85] investigated the adsorption of (Zn^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+}) ions onto oxidized anthracite. The results presented here and their analysis indicate that the oxidized anthracite shows an ability to adsorb Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} from aqueous solution with increasing capacity in the order $Cd^{2+} < Zn^{2+} < Pb^{2+} < Cu^{2+}$. The pH of the initial solution exerts influence on the adsorption of metallic ions which is negligible at low pH value. The adsorption of metallic ions increases considerably in the range of pH (3-4). Thermo oxidation treatment with air at 400°C leads to considerable enhancement of the quantity of oxygen-containing groups on the anthracite surface. These groups of acidic character and variable chemical nature have different dissociation strengths in aqueous suspension. The presence of all ions in the solution in equal quantities decreases the adsorption of each of them. Apart from the fact that a selective adsorption of the metal ions is observed, the ones preferentially adsorbed completely prevent the adsorption of other ions.

Reed, et al [86] determined the effect of pH, empty bed contact time (EBCT) and hydraulic loading rate (HLR) on Pb^{2+} removal by a granular activated carbon(GAC).They found that the column performance improved dramatically after regenerating an exhausted column that was originally packed with virgin carbon with a simple acid-base rinsing procedure. The acid rinse of the lead-loaded carbon caused lead desorption/dissolution, whereas the base rinse increased the column pH before the next treatment cycle (lead removal increases with increasing pH). Regeneration efficiencies were less than 100%, but column performances after regeneration were not adversely affected. Based on these results it was hypothesized that the size of the activated carbon contactor for a wastewater containing both an organic contaminant and lead would be based on organic removal , whereas the regeneration schedule would be controlled by lead . The effect of HLR on column performance was minimal for 1mg/L lead whereas at 10mg/L lead , column performance was slightly better at the higher HLR. The carbon usage rate (CUR) were high, especially for 10mg/L lead, compared with those observed organic adsorbates. The use of GAC columns for lead removal appears to be most feasible for influent lead concentrations ≤ 1 mg/l.

Shekinah, et al [87] studied the adsorption of Pb^{2+} from aqueous solution by activated carbon prepared from Eichhornia. The results showed that the activated carbon prepared from the aquatic plant (weed) Eichhornia crassipes is efficient in the adsorption of Pb^{2+} ions from aqueous solution. In batch mode studies, the adsorption was dependent on solution pH, initial concentration and carbon dosage. Adsorption of Pb^{2+} ions onto activated Eichhornia carbon (AEC)followed both Langmuir and Freundlich isotherm models. Kinetic data would be useful for the fabrication and designing of wastewater treatment plants. Removal of

Pb^{2+} from radiator-manufacturing industry wastewater confirms the validity of results obtained in batch mode studies. As the plant Eichhornia crassipes is a menacing weed, using it as a carbon source can be viewed as a weed control strategy. Moreover, it is an inexpensive source and therefore may have the advantage of economic viability.

Reed, et al [88] calculated the dynamic (or fixed bed) removal of (Pb^{2+} and Cd^{2+})from aqueous waste streams by using granular activated carbon (GAC) columns. Column pH and influent characteristics appear to be the critical parameters influencing GAC column performance. The sudden increase in the column effluent lead concentration corresponded noticeably with a decrease in the effluent pH. Acetic acid at 0.001M decreased column performance compared with the lead only experiments but large amounts of lead were still removed from solution. It is hypothesized that acetic acid reacted with the carbon associated OH^- (on the surface and in the pore liquid), which produced a more rapid decrease in column pH and a subsequent decrease in lead removal. The presence of EDTA adversely affected column performance most likely because of solution complexation. Wastewaters containing strong complexing agents will either have to undergo pretreatment prior to entering the GAC column or an activated carbon that adsorbs the organic-metal complexes will have to be identified. Column performance was not adversely affected by the regeneration procedure. When the regeneration step was used on virgin carbon, a dramatic improvement in column performance was observed. This was attributed to an increase in OH^- available for surface and pore liquid precipitation as well as an increase in the number of surface sites available for adsorption. The use of the regeneration procedure as a pretreatment step for virgin carbon is recommended. Given the encouraging performance of the GAC columns in treating several lead wastewaters and the relative ease of column regeneration, the use of GAC columns to treat metal-bearing waste streams should be considered.

Biniak, et al [89] investigated the adsorption of Fe^{3+} ions from aqueous solution using a commercially available modified activated carbon. The activated carbon was deashed and then subjected to three different modification procedures: high-temperature treatment under vacuum, in ammonia atmosphere as well as oxidation with conc. nitric acid. The chemical character of the modified carbons was determined by various spectra (FTIR, XPS) and adsorption methods. The effect of pH of the external solution on the isotherms of iron ions adsorption was investigated. Results showed that the presence of both oxygen and nitrogen containing surface functionalites significantly increased the adsorption capacity for Fe^{3+}.

Buczek, et al [90] studied the differentiation of adsorption capacity towards selected heavy metal ions (Fe^{3+}, Co^{2+}, Cu^{2+}) throughout oxidized activated carbon granules. They found that in case of the oxidized carbon the appropriate powdered and core samples were obtained by the method in which the successive layers are removed from the granules by abrasion in a spouted bed. In all carbon samples total oxygen contents, as well as surface of the functional oxygen groups were determined. Additionally the surface chemical structure of the samples was determined by FTIR spectroscopy. The excess adsorption isotherms of the selected cations (Fe^{3+}, CO^{2+} and Cu^{2+}) on the obtained samples were determined 25 ^{o}C. Adsorption took place from aqueous solution with different pHs of corresponding nitrates.

Saleem, et al [91] investigated the selective adsorption of cerium on activated carbon charcoal, from aqueous electrolyte solutions, as function of shaking time, pH, concentration of adsorbate and temperature. The adsorption obeyed Freundlich and Langmuir isotherms. The influence of different cations and anions on cerium adsorption has been also examined. The adsorption of other metal ions on activated charcoal has been studied under specified conditions to check its selectivity for cerium adsorption. Consequently cerium was selectively removed from a mixture containing (Ce, Ba, Sr, Ru, Cs, Cr, Nd, Pr and In). About 99% of the adsorbed cerium on activated charcoal can be recovered with 3M HNO_3 solution. A wavelength dispersive X-ray fluorescence spectrometer was used for measuring the cerium concentration. The adsorption of cerium on various solids is important from the points of view of purification, environmental, and radioactive waste disposal.

Periasamy, et al [92] studied the process development for removal and recovery of Cd^{2+} from wastewater by a low-cost adsorbent prepared from peanut hulls (PHC). They found that peanut hulls carbon is an effective adsorbent for removal and recovery of Cd^{2+} ions from aqueous solutions. Its adsorption capacity is much superior to commercial activated carbon. It would be useful for the economic treatment of wastewater containing Cd^{2+} ions, as the adsorbent is derived from an agricultural waste by-product, namely peanut hulls (PHC).