THESIS

ON

# PRODUCTION OF CHARCOALS WITH ION EXCHANGE PROPERTIES

Presented to

The Faculty of Science
Ain Shams University
Cairo

By

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(M.Sc.)

For the Degree of
Doctor of Philosophy in Chemistry

1972

# PRODUCTION OF CHARCOALS WITH ION EXCHANGE PROPERTIES

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# ACKNOWLEDGEMENT.

The author wishes to express her thanks to Prof. Dr. S. K. Tobia head of Chemistry Department for the facilities at his disposal and for his interest in this work .

The author also wishes to express her deepest gratitude to Dr. R. Sh. Mikhail, Prof. of Physical Chemistry, for suggesting the work to be described in this thesis and for his continuous help, criticism and valuable discussions.

The auther is also indepted to Dr. Sh. Nashed Assistant Professor of Physical Chemistry, for his continuous help criticism and valuable discussions.

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# CHAPTER I

## Introduction and object of investigation

### 1.1 Introduction:

The adsorptive properties of carbons were known and studied long before the term "active carbon" was coined. Hence, the early history is covered by the literature on charcoals and various chars, bone, and blood.

When vegetable or animal materials are heated in a limited supply of air, a carbonized or charred decolourizing product known as charcoal is obtained. Charcoals from various sources have different names according to the raw materials used. Charcoals from coal are usually called cokes, another type is graphite, but these two types are not considered as charcoals, though they usually come under the same definition.

The earliest vegetable charcoal used was wood charcoal made by burning or distilling wood in stacks. The destructive distillation of wood was one of the major chemical industries in many countries, the principal products are charcoal, acetic acid, acetone, methyl alcohol, methyl acetone, glycol, furfural, tannins, vanillin, various phenolics, neutral oil and oleoresins.

Wood charcoal has been used as fuel for centuries. Its ability to take up odours has been appreciated for decades, and it was utilized in the form of wood ashes. It has been frequently used to remove unpleasant smells and colouring matter from certain solutions. Besides its use as decolourising materials, charcoal is used as an adsorbent of gases and vapours, in manufacturing of gun powder, and as an ingredient of food for domestic animals.

Almost any waste vegetable substances can be destructively distilled to produce charcoal. Agricultural waste products such as corn husks, corn cobs, corn stalks, baggase, rice hulls, rice stalks, fruit pits and shells and many others are abundant and form a cheep source for charcoal. The choice of any particular agricultural waste for the preparation of charcoal would therefore depend on the availability, the price and the facility of collecting it from farms and factories and the cost of transportation as well as on the value of the by-products accompanying the carbonization process.

Agricultural waste products in Egypt are produced annually at the rate of about nine million tons,(1) only a very small fraction of these amounts is used in industry (e.g. for packing purposes, paper and cardboard manufacture) and in agriculture (e.g. cattle food); but the bulk is used directly as fuel. Thus it is interesting to find means of converting agricultural wastes into valuable products. In particular, in view of the lack of forest wood in Egypt, the use of agricultural waste products in the preparation of good adsorbing carbon is important.

Some work in this direction has been done in this department. Thus the adsorptive and swelling properties of cotton stalks and casuarina, Acacia Arabia and Mulbery was studied by Said$^{(2)}$. Also the adsorption of certain vapours on charcoals prepared from rice husks and rice straws was studied by Razouk and co-workers$^{(3-5)}$. The adsorptive properties of charcoals prepared from corn cobs and date pits were also studied by Razouk <u>et al</u>$^{(6, 7)}$ in an attempt to find out the optimum conditions for preparing charcoals.

In the present investigation the use of local agricultural wastes in producing active charcoal is pushed further. Charcoals obtained by destructive distillation at different temperatures of casuarina and date pit were oxidized in solution with the aim of producing charcoals with ion exchange character. The possibilities of using such charcoals in cation exchange processes as well as in adjusting soil alkalinities have been pointed out by Puri and Mohajan (8). More recently, a number of commercial carbon materials of ion exchange properties have been considered in developing a practicable and economical process for desalting water.(9)

## Surface oxidation of Charcoal: Preparation and Characterization of cation responsive charcoals:

Puri et al (10, 11) pointed out that treatment of activated or outgassed charcoal with oxygen at temperatures (12, 13) varying from 100-600°C, could fix appreciable amounts of oxygen at the charcoal surface. This oxygen comes off on degassing at high temperatures, as carbon dioxide, carbon monoxide and water. The effect of oxygen that comes off as carbon dioxide could alter the surface behaviour and other surface characteristics, such as titrable acidity, catalytic properties, redox potential, water isotherms and immersional heats of wetting (13, 14, 15) In 1959 Puri et al (16) showed that oxidized charcoal covered with a layer of chemisorbed oxygen, when suspended in water or aqueous solutions, behaves very nearly as a reversible hydrogen electrode, the potential ($E_H$) of which varies with the activity ($aH^+$) of hydrogen ions according to the equation

$$E_H = E_0 - RT/FpH.$$

This behaviour is due to the presence of $H_2Co_3$ held at the surface complex in the oxide layer on charcoal. Such materials can stabilize ($E_H$-pH) relation in aqueous solutions. The validity of the equation was verified for charcoal from three different sources by;

(i) Adding measured amounts of base to the charcoal suspension and determining pH value with a glass electrode and the electrode potential ($E_H$) with a platinum electrode.

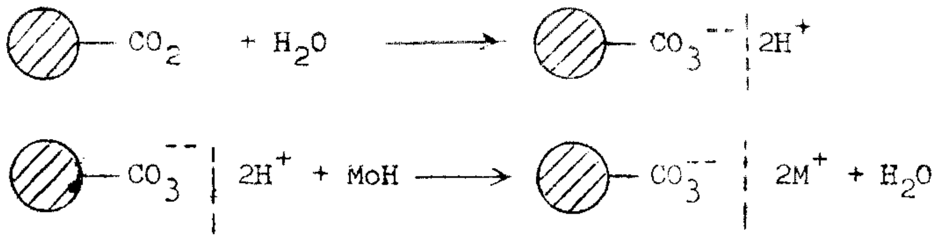
(ii) Making similar determinations with buffer solutions treated with the charcoal at 180°C. The mean $E^o$ was 407 mv. by method (i) and 390 mv. by method (ii) and the mean slope of the curve was 50.2 and 50.7 mv./pH respectively for the two methods.

(iii) Deviation from the theoretical slope of 57.7 mv./pH was attributed to the inaccessibility of some of the surface $H^+$ ion deep within micro-capillary pores of the acidoid charcoal.

Puri <u>et al</u>(17)(1961) prepared two samples of charcoal, one by the carbonization of recrystallized cane sugar (by adding sulphuric acid, followed by exhaustive washings) and the other by burning small pieces of coconut shell electrically at 350° in a limited supply of air. The charcoal samples were well ground to pass through a 100 mesh sieve. Sugar charcoal was free from ash, while the ash content of the coconut shell charcoal was lowered to about 0.24 percent upon extraction with HF acid. They studied the surface reaction of sugar and coconut shell charcoals, before as well as after degassing at 750° and 1200°C, with oxygen and few oxidizing solutions of varying oxidizing potentials at ordinary temperature (e.g. potassium persulphate, potassium bromate, potassium periodate, potassium nitrate and chlorine water). They found that, the base adsorption capacity of original as well as degassed samples increases appreciably on treatment with various oxidizing solutions. Some of the treatments gave highly acidic charcoals with base adsorption capacities of over 1000 m.equiv./100 g. They believe that the various oxidation treatments add an appreciable amount of oxygen to charcoal as carbon dioxide complex which is the cause of the surface acidity of charcoal. It appears highly probable that the treatment of outgassed charcoals with oxidizing solutions results partly in the formation of the usual carbon dioxide complex in which two oxygen atoms are assumed to be attached to a single surface carbon atom, and partly in the formation of a different complex in which oxygen atoms are added up at unsaturated ethylenic double bond sites created on elimination of chemisorbed gases on evacuation. The formation of new complex may be represented tentatively as

where the shaded circle represents the charcoal surface and -c and -c two carbon atoms. Such a complex may evolve carbon dioxide on degassing but may not react with alkalies.

Puri *et al*(18) (1964) prepared sugar and coconut shell charcoals, the two charcoals were evaluated as cation exchangers in batch and column operations, and had a high exchange capacity imparted to them by the existence of chemisorbed layer of carbon dioxide. Hydrogen, sodium, calcium and barium charcoals could be easily prepared. Charcoals with $Na^+$ in exchange position can be used for the removal of $Ca^{+2}$ from solution by cation exchange i.e. for softening hard water by simple column process. The column can be regenerated by leaching with a solution of NaCl. Charcoals with $H^+$ in the exchange position can be used for removing the alkalinity from water and that with $Ca^{+2}$ in the exchange position can be used in raising the calcium status of irrigation water by replacing a part of $Na^+$ by 1/2 $Ca^{+2}$ in the solution. The possibility of using charcoal with $Ba^{+2}$ in the exchange position for removal of sulphate ion has also been indicated . These cation exchange surface reaction imparted to the charcoal surface may be illustrated as follows:



M may be Ca, Na, Ba..... etc.

The metal cation introduced in the surface in the above manner can be exchanged by other common cations as in zeolites, permutites and soil by treatment with suitable electrolytes. The replacing powers of the various cations were found to decrease in order in which they occur in the lyotropic series.(19)

Puri et al.(20) prepared two samples of sugar and coconut shell charcoals. A portion of the charcoal was treated with chlorine water to raise the oxygen content. The total amount of oxygen and hydrogen were evolved as carbon monoxide, carbon dioxide and water on outgassing charcoal at 300, 400, 500, 700 & 1100°C. They studied the effect of nature of the surface of sugar and coconut shell charcoals on the adsorption of ammonia in solution or in the gaseous phase. They found that the surface of the charcoal was altered by outgassing at temperatures between 300-1100°C. The interaction appears to involve two distinct reactions. The first reaction is neutralization and the adsorbed $NH_3$ can be recovered on hydrolysis with hydrochloric