AIN - SHAMS UNIVERSITY

INSTITUTE ENVIRONMENTAL

STUDIES AND RESEARCH

NON - CONVENTIONAL BLEACHING PROCESS OF PAPER PULPS TO REDUCE WATER POLLUTIONS

THESIS

Presented from

SOHIER ABD - ELATY MOHAMED

(B.Sc.)

For M.Sc. Degree

Environmental Studies and Research

SUPERVISED BY

Prof. Dr.

ASHRAF AHMED HAMED

Chemistry Dept.

Faculty of Science

Ain-Shams University

Cairo

Prof.Dr.

OLFAT YASIN MANSOUR

Head of Cellulose and

Paper Dept.

National Research Center

Cairo

1993

ACKNOWLEDGEMENT

The authors wishs to express her gratitude to both Prof. Dr. Ashraf Ahmed Hamed,Prof. of Organic Chemistry, Faculty of Science, Ain Shams University and Prof. Dr. Olfat Mansour, Prof. of Cellulose and Paper Chemistry, Head of Cellulose and Paper Dept. National Research Centre, Cairo, for suggesting the problem supervision in discussion of the results and advice during preparation of this thesis.

The author also wishs to record her deep thanks to Dr. Ibrahim Zaki Selim, Assistant Prof. Physical Chemistry Dept. National Research Centre Cairo, for suggesting the point and plan for this research, fruitful supervision, continuous encouragement, useful discussion and interpretation of the results. Also deeply thanks to him for his continuous help and advice through the development of this work.

Finally, thanks to every body helped me, specially Zakaria Sultan for the facilities and help he provided.

بسم الله الرحمن الرحيم

CONTENTS

Page

CHAPTER I

- Introduction and Review of Literature 1

I.1. Cellulose: Molecular Structure and Properties 1

I.2. Preparation of Celluloses from Lignocelluloses 5

I.2.1. Pulping 5

I.2.2. Bleaching 5

I.2.2.1. Bleachability of Pulp 6

I.2.2.2. Single-Stage Bleaching with Hypochlorite 7

I.2.2.3. Multistage Bleaching 8

I.2.2.4. Number of Stages in Multistage Bleaching 10

I.3. Bleaching with Peroxide 13

I.4. Role of the Water and Solvents in the Bleaching Process 16

I.5. Classification of Organic Solvents 17

I.6. Preparation of Laboratory Hand-Made Paper 18

I.6.1. Beating 18

I.6.2. Sheet Formation and Making 20

I.7. Physical Characterization of Paper 21

I.7.1. Basis weight 21

I.7.2. Tensile Srength 21

I.7.3. Bursting Srength 22

I.7.4. Tearing Resistance 22

I.7.5. Double Folding Endurance 23

I.7.6. Brightness of Paper 23

I.7.7. Opacity of Paper 23

I.7.8. Water Uptake 24

Page

I.8. Industrial Wastes and Pollution 25

I.8.1. Pollution Caused by Industrial Wastes in Alexandria 25

I.8.2. Types of Pulp and Nature of Pollutants Produced 25

I.8.2.1. Bleached and Umbleached Kraft Pulp.. 25

I.8.2.2. Sulphite Pulping 26

I.8.3. Types of Paper Mill Pollutant due to Pulp and Manufactures 26

I.8.3.1. Suspended Solids 27

I.8.3.2. Soluble Organics 28

I.8.4. Aesthetic Pollution 29

I.8.5. Pollution Toxic to Aquatic Life 29

I.9. Aim of the Present Work 37

CHAPTER II

EXPERIMENTAL TECHNIQUE

II.1. Chemical Analysis of Investigated Pulps 39

II.1.1. Determination of Moisture Content 39

II.1.2. Estimation of Lignin 39

II.1.3. Estimation of Alpha Cellulose 40

II.1.4. Estimation of Extractable Hemicellulose.. 41

II.1.5. Estimation of Ash 41

II.1.6. Estimation of the Degree of Polymerization 42

II.1.7. Permenganate Number 44

II.2. Bleaching of Pulp 45

II.2.1. Chlorination 45

II.2.2. Extraction by Soda 46

Page

II.2.3. Hypochlorite Step 46
II.2.4. Chlorite Step 46

II.3. Bleaching with H_2O_2 47
II.4. The Non-conventional Bleaching Process 47

II.4.1. Preparation of Chlorine Bleaching Solutions
II.4.2. Preparation of H_2O_2 Bleaching solutions.... 48

II.5. Physico-chemical Properties of Non-Conventional Bleaching Solutions 49

II.5.1. Density 49
II.5.2. Viscosity 49
II.5.3. Dielectric Constant 49
II.5.4. Molar Volume Contraction 50
II.5.5. Molar Polarization 51
II.5.6. pH Measurements 51

II.6. Paper Manufacture 51

II.6.1. Beating and Disintegration 51
II.6.2. Sheet Making 52

II.7. Paper Testing 52

II.7.1 Physical Properties of Paper 53
II.7.1.1. Thickness 53
II.7.1.2. Tensile Strength.................... 53
II.7.1.3. Bursting Strength................... 54
II.7.1.4. Tearing Resistance.................. 55

II.7.2. Optical Property of Paper and its Testing.. 55

II.7.2.1. Brightness 55
II.7.2.2. Opacity 56
II.7.2.3. Tappi Opacity 56
II.7.2.4. Double Folding Endurance 57

Page

CHAPTER III

RESULTS AND DISCUSSION

III.1. Properties of Umbleached Paper Pulp 58
III.2. Properties of the Bleached Pulps by Conventional Methods 60
III.3. Properties of Bleached Pulps Using Different Organic Solvents (Non-conventional Method) 61
III.3.1. Bleaching of Rice Straw Pulp Using the 4-stage Method (Process I) 66
III.3.2. H_2O_2-two stage Bleaching Process of Pulps (Process II) 77
III.3.2.1. For Rice Straw Pulp Bleaching..... 77
III.3.2.2. For Bagasse Pulp Bleaching........ 84
III.4. Preparation and Properties of Paper-Sheets 91
III.4.1. Preparation of Paper-Sheets from Bleached pulps 91
III.4.2. Properties of Paper sheets Prepared from Rice straw Pulps Bleached by 4-multi-stage Method (Process I) 91
III.4.3. Properties of Papers Made from Rice Straw Pulps Bleached by the two-Stages-H_2O_2-Process (Process II).................. 95
III.4.4. Properties of Paper Prepared from Bagasse Pulps Bleached by the Two-Stages-H_2O_2-Process 97
REFERENCES 102
SUMMARY 111
SUMMARY IN ARABIC.

SYNOPSIS

The object of this thesis is the study of bleaching rice straw and bagasse pulps using the conventional and non conventional methods applying the multistage bleaching processes. In the non-conventional method water - organic solvent bleaching mixtures was used to reveal the effect of using solvents to minimize the pollution caused by industrial wastes discharged into the drain. Different types of polutants produced in pulp and paper industry. In bleaching, the pollution parameters to be considered are suspended solids, biodegradable organics and small fibers, color form and materials rotentially toxic to aquatic life. The pollution caused by pulp manufacture especially the bleaching process is due to fiber debris, soluble organics and inorganics. Methanol, ethanol, acetone and dioxane are the organic solvents which used in this work in the first stage of the 4- or 2-multistages processes (process I and process II).

On studying the effect of using water-organic solvent mixtures as bleaching media on contents of bleached rice straw and bagasse pulping, it was found that using 30% methanol, 50% ethanol and 50% acetone in bleaching mixtures applying process (I) produced rice straw pulps suitable for paper making, due to increase in viscosity and decrease in both density and dielectric constant of these media. But on using the non-conventional method by applying process

(II), for bleaching rice straw pulp, it was found that methanol is the most suitable solvent that can be used leading to pulps of suitable properties for paper making. On applying process (II), using the non-conventional method for bleaching bagasse pulp, it was found that using acetone and dioxane in the bleaching mixture lead to pulps of suitable proeprties for paper making.

Moreover, we study the effect of changing the percent and the kind of the solvent on the physical characterization of paper - sheets prepared from pulps produced from the non conventional bleaching method. It was found that using methanol, ethanol, acetone in percent 10%, increased the physical, optical and mechanical properties of the paper prepared from rice straw pulp bleached by the non conventional multistage bleaching processes. But the use of dioxane in the bleaching mixture affected the properties of the pulp and papers prepared thereform in a different ways.

Also, it was found that using process (II) (conventional and non -conventional methods) on bleaching the rice straw pulp, produced papers of high tensile strength and breaking length, so it is preferable than process (I).

It was shown from the properties of paper - sheets prepared from bagasse pulp bleached by the conventional and non - conventional methods (process II) that they are preferable than those prepared from rice straw pulps.

CHAPTER I

Introduction and Review of Literature

CHAPTER I

INTRODUCTION AND REVIEW OF LITERATURE

1.1. Cellulose: Molecular Structure and Properties:

It is interesting to note that after more than a century of scientific investigation numerous findings, controversies and debates, cellulose term in its pure form means different things to different groups. To organic chemists, it means β-D-(1-4) -linked glucopyran. To the technologists, it means an asymptotic entity. often called α -cellulose, which represents the alkali insoluble portion of wood pulp. To the biologists, it means the fine microfibrils of plant cell walls that reach a hgih degree of purity and perfection in a group of green algae, including Valonia. Cladophora and Chaetomorpha. These groups have been concerned not only with the chemical structure of cellulose and its reactions, but also with its inter - related physical morphological and biological properties[1].

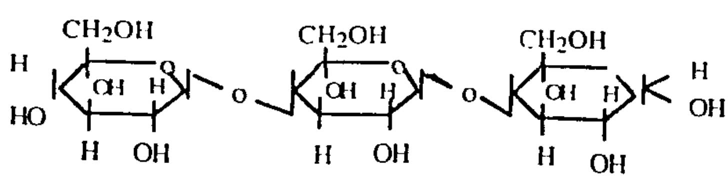
Cellulose was first isolated and recognized as a distinct chemical substance in the 1830 by the French agricultural chemist Anselme Payen Payen concluded more or less correctly, that cellulose and starch were isomeric substances because both have the same carbon and hydrogen content and when subjected to hydrolysis, both yielded

D-glucose[1]. Therefore cellulose pertains to the class of carbohydrates. It contains 44.4 per cent of carbon, 6.2 per cent of hydrogen and 49.4 per cent of oxygen[2]. The precise empirical formula of cellulose was established as $(C_6H_{10}O_5)$. Results from earlier studies on acetylation and nitration had indicated that cellulose has three free hydroxyl groups per $(C_6H_{10}O_5)$ unit[1].

The free hydroxyl groups in cellulose were located at the 2,3 and 6 positions and that the 1,4 and 5 positions were linked by chemical bonds.

In the cellulose moelcule, the D-glucose anhydrides of the B-form are interconnected by the glucosidic linkage 1,4 characterized by the following atomic structure[2].

Cellulose is a linear polysaccharide consisting of anhydro-D- glucopyranose units linked between the 1- and 4-position of adjacent sugar units by aB linkage as shown below[1].



Cellulose Structure .

Based on molecular mechanics calculations of the chain moduli, the cellulose form has 2 intramolecular hydrogen bonds paralled to the glycosidic linkage, and it is unstable in polar solvents because of unfavorable interaction of the t,g conformation (g = gauche, t = trans) of each hydroxymethyl group with the solvent[3].

In the determination of the average molecular weight of cellulose, the usual methods for polymers have been used including osmometry, light scattering measurements, ultracentrifugation , gel permeation and viscometric determinations. The degree of polymerization of cellulose, which is polydispersed, seems to vary with its source and method of isolation.

The alcoholic groups in the cellulose molecule undergoes alcoholic reactions, such as esterification, oxidation and alcoholate formation. In addition, there are also some carboxyl groups which are few in numbers. So, cellulose acts as a monobasic acid. The concentration of carboxyl group is highest in the outer layer of cell walls decreases linearly near the lumen (near too). Cellulose used for chemical reactions is obtained from different raw materials such as wood, cotton staple fibers, sugar can, bagasse and straw.

Pulping processes are of three principal types, mechanical, chemical and semimechanical. The mechanical pulping involves the reduction of the raw material to the fibrous state by mechanical means, generally by grinding the raw material to a pulp. The yield of pulp by this process is about 95%, but the pulp is of low purity and there is a considerable fiber damage. Chemical processes involve the cooking of the raw material with chemicals which selectively remove lignin and other impurities, whereby individual fibers are isolated and partially purified. The yield is much lower than in mechanical pulping, but the pulp is of higher purity, and of little fiber damage. There are three major chemical processes of commercial importance, namely, the soda, sulfate, and sulfite pulping[4]. A modification of soda pulping employing an anthraquinone additive and hence called soda-AQ pulping has been developed and is being put into commercial practice. The advantages are reported to be improved pulp yield and strength especially tear index, for specific softwoods. Semimechanical pulping involves features of both chemical and mechanical pulping. This consists of an initial heat or chemical treatment for softening the raw material, followed by mechanical reduction to the fibrous state[4].

The thermomechanical pulping process (TMP) and the refiner mechanical pulping process (RMP) employ chips rather than the bolts of wood requried in stone groundwood, which is a distinct advantage in supply and handling. They produce groundwood-type pulps capable of replacing or extending chemical pulps[5]. The manufacture of chemical mechanical and/or chemical thermomechanical wood pulp are manufactured by treating lignocellulosic materials with aqueous alcoholic SO_2 solution, heating at 50-170°, recovering the alcohol and unreacted SO_2 and then defibering. Less energy is used than in a method involving pretreatment with Na_2SO_3. Also, pinewood chips in aqueous methanol (MeOH) at 120° were treated with SO_2, the MeOH and untreated SO_2 were recovered and the chips were defibered[6].

1.2. <u>Preparation of celluloses from lignocelluloses</u> :

Lignocelluloses are the raw materials containing cellulose, hemicellulose and lignin. To produce pure cellulose, the following processes are :

1.2.1. <u>Pulping</u> :

Pulping process is the reduction of the lignocelluloses into the fibrous state. It consists of cooking the lignocellulosic raw materials in suitable chemicals using a digester under controlled conditions of temperature, pressure, time and liquor composition or reducing the raw material to the fibrous state by mechanical or semimechanical means.

1.2.2. <u>Bleaching</u> :

The purpose of bleaching is the production of a white pulp of stable color obtained at reasonable cost