

APPLICATION OF ELECTRO- TECHNOLOGIES IN THE PROCESSING OF FLAX AND HEMP STEMS

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ABSTRACT

APPLICATION OF ELECTRO- TECHNOLOGIES IN THE PROCESSING OF FLAX AND HEMP STEMS

Plant based natural fibers are extracted from various parts of the plants such as leaf, inner bark and fruit/seed. Basic examples of plant-based fibers are flax, hemp, pineapple, cotton, coconut, oil palm, banana trunk fibers etc. Natural fibers are used as a replacement of synthetic fibers because of their similar physical properties like tensile strength, extensibility, density etc. The production of natural fibers involves various steps, which includes loosening of fibers from the plants, thus increasing the processing cost; but use of natural fiber based products is encouraged due to their degradability and there by reducing environmental pollution. The processing of natural fibers starts with the loosening of fibers after harvesting followed by separation of fibers (decortication). The clean fibers are then subjected to further processing depending on use in various industries like biocomposite industry, paper industry and apparel industry. The objective of this research was to introduce an electro- processing technology to help separate plant based fiber from its stem. Flax (*Linum usitatissimum*) and hemp (*Cannabis sativa*) stems were selected for the research because both flax and hemp are important crops in Canada.

The main objectives of this study were: 1) To develop a novel retting method for the processing of pre- soaked flax and hemp stems by the application of microwave energy to the flax water mixture; 2) To evaluate the efficiency of retting in relation to the changes in compounds present in the fibers such as cellulose, hemicellulose, lignin and pectin through chemical analysis and 3) To develop an effective electro- osmotic dewatering system for the high moisture retted flax and hemp stems using a bench type roller press at various applied voltages.

Prior to conducting studies on the novel retting method using microwave energy, it was essential to perform an initial study on a conventional retting method to quantify retting effects on the physical and structural properties of the fibers for the process optimization. To achieve this goal, experiments were performed at the Institute of Natural fibers, Poznan, Poland on the effect of water- retting on a local variety of flax stems (Modran). The analysis of retted and non- retted flax fibers resulted in a conclusion that retting is the most important step in the processing of flax fibers and it directly affects quality attributes like strength, fineness, and homogeneity. Scanning

Electron microscope images of fibers were also analyzed and the retted fibers showed much cleaner surface when compared to decorticated non- retted fibers.

After the initial analysis of water retted flax stems, a novel retting method was introduced by applying microwave energy and studies were conducted to establish the effect on pre- soaked flax stems. The combined effect of pre- soaking, microwave volumetric heating and the non- thermal effect of microwave energy resulted in retted flax stem. Retting efficiency was observed at various combinations of pre-soaking, microwave treatment times and microwave energy levels. Fried tests, fiber diameter distribution analysis, Near Infrared analysis (NIR) of lignin, hemicellulose and cellulose of the obtained fiber were performed in order to determine the retting efficiency. Colorimetric analysis and tensile strength tests were conducted on the flax fibers to compare the quality of fibers after microwave retting and no significant changes in the physical qualities were observed. From industrial point of view, microwave- assisted retting is acceptable because of the ease of recyclability of the pre-soaked water and comparably shorter duration of the retting process. The microwave- assisted retting was repeated on the hemp stems to investigate the acceptability of this method in hemp varieties. NIR analysis and diameter distribution analysis were performed to study the efficiency of retting. Microwave- assisted retting on hemp was proved to be efficient from the analysis of the compounds (lignin, hemicellulose and cellulose) presented in the fibers and its diameter distribution. Tensile strength and color was subjected to analysis and the results did not show any significant change in the strength and color of hemp fibers with respect to microwave- assisted retting treatments.

After establishing the microwave- assisted retting of flax and hemp stems, the next step was to study the chemical changes occurring in the fibers during microwave assisted retting, and flax stem was selected for the analysis and studies were performed by gravimetric methods. Pre-soaked flax stems were subjected to microwave assisted retting at different power levels (W/g) and the efficiency of microwave assisted retting was studied by the analysis of chemical compounds presented in the retted flax fibers processed from the stems. Response surface statistical design was used for this study with JMP[®] 10 software. Cellulose, hemicellulose, lignin and pectin concentrations and the sugar content in the solution obtained after the treatment were investigated. Cellulose percentage in the fiber was increased significantly with the increase of microwave power at various soaking levels, which proved the release of cellulosic fiber with the application of microwave energy during retting. Hemicellulose, lignin and pectin concentrations

decreased significantly after microwave-assisted retting which explained the degree of retting with the help of microwave energy. This study used the change in chemical composition of the fibers, which was used as a tool to estimate the effectiveness of microwave- assisted retting and the results were used to optimize the process.

A kinetic model was developed on the chemical changes occurred during microwave assisted retting of pre- soaked fibrous stems. The rate of change of compound release from the pre- soaked flax and hemp stem due to microwave- assisted retting was analyzed in terms of its soaking time, microwave energy and the time of retting. The rate of change of composition in the model fitted with the observed values of cellulose, hemicellulose and lignin. The rate coefficient for all the treatments were increasing within the treatment limit, which indicated the increased reaction rate due to microwave energy. The model was developed from the data obtained from flax stems and was validated by using hemp stem processing data.

Fully soaked flax and hemp stems after microwave- assisted retting was collected at very high moisture level and those stems have to be dried to a lower moisture level of around 10% for further decortication to separate the fibers or to 4% for storage. To ease the drying process, an electro- osmotic bench type roller press system was introduced for the dewatering of retted flax and hemp stems. Since the pre- soaked stems are slightly charged, water molecules moved towards the anode when the stems were subjected to electro- osmosis between two electrodes. The applied pressure between two electrodes, the applied voltage and the pre- soaking time of the stems were the factors affecting the electro-osmotic dewatering.

The stems after dewatering were subjected to short term microwave- assisted drying at controlled temperature and then moved to a fiber processing facility where the retted stems were decorticated to biofibers. Effectively retted stems with appropriate electro- technology produces high quality fibers whereas non- retted, under retted and overly retted stems lead to the production of low quality fibers.

RESUME

APPLICATION D'ÉLECTRO-TECHNOLOGIES DANS LA TRANSFORMATION DES TIGES DE LIN ET DE CHANVRE

Les fibres naturelles à base de plantes sont extraites de différentes parties de la plante comme les feuilles, l'écorce interne et les fruits/graines. Des exemples communs de fibres à base de plantes sont le lin, le chanvre, l'ananas, le coton, le noix de coco, feuilles de palmiste, fibres d'écorce de bananier, etc. Les fibres naturelles sont utilisées comme remplacement aux fibres synthétiques dû à leurs propriétés physiques semblables telles que le force de tension, l'élongation, la densité, etc. La production de fibres naturelles exige plusieurs étapes, incluant la séparation des fibres après la récolte, ce qui augmente le coût de production; cependant, l'usage de produits naturels à base de plantes est favorisé dû à leurs propriétés biodégradables, ce qui réduit la pollution environnementale. La transformation des fibres naturelles commence avec le rouissage des fibres, suivi de la séparation des fibres (décortication) et par la suite, les fibres nettoyées sont transformées davantage selon leurs usages industriels, tels que les industries de biocomposites, des pâtes et papiers et du vêtement. L'objectif de la recherche présentée ici était d'introduire un processus d'électro-technologie pour la transformation des fibres provenant de la tige des plantes. Les tiges du lin (*Linum usitatissimum*) et du chanvre (*Cannabis sativa*) furent sélectionnées pour cette recherche parce que le lin et le chanvre sont disponibles au Canada ainsi qu'ailleurs dans le monde.

Les objectifs principaux de cette étude étaient: 1) de développer une nouvelle méthode de rouissage pour la transformation des tiges de lin et de chanvre pré-trempées par l'usage d'énergie micro-ondes sur le mélange de lin et d'eau pour écourter la durée; 2) d'évaluer l'efficacité du rouissage par rapport aux changements des composés présents dans les fibres comme la cellulose, l'hémicellulose, la lignine et la pectine par une analyse chimique; et 3) d'élaborer un système efficace de déshydratation par électro-osmose pour le lin et le chanvre rouis, ayant une haute teneur d'humidité, en utilisant une presse à rouleaux sous différentes pressions appliquées.

Avant d'entamer l'étude sur une nouvelle méthode de rouissage par micro-ondes, il était essentiel de réaliser une étude préliminaire sur une méthode conventionnel de rouissage et sur la manière que le rouissage influence les propriétés physiques et structurales des fibres pour l'optimisation

du procédé. Pour atteindre ce but, une série d'expériences a été menée à L'Institute of Natural Fibers (Poznań, Pologne) sur les effets de rouissage à l'eau sur les tiges d'une variété locale de lin (Modran). Les analyses de fibres de lins rouies et non-rouies ont mené à la conclusion que le rouissage est l'étape la plus importante dans la transformation des fibres de lin et cela affecte directement la qualité des attributs de force, de finesse, et d'homogénéité. Des images de fibres par microscopie d'électronique à balayage furent analysées et la surface des fibres rouies semblait beaucoup plus lisse par rapport à celle des fibres décortiquées non-rouies.

Après l'analyse initiale de rouissage à l'eau de tiges de lin, une nouvelle méthode de rouissage fut élaborée avec l'usage de l'énergie micro-ondes et des études furent menées sur ses effets sur les tiges de lin pré-trempées. L'effet combiné du pré-trempage et du chauffage volumétrique causa un rouissage de la tige de lin. L'efficacité du rouissage fut observée sous diverses combinaisons de pré-trempages, de durées des traitements aux micro-ondes et de niveaux d'énergies. Les tests de Fried utilisés pour analyser la distribution des diamètres des fibres et les analyses par spectroscopie infrarouge (NIR) de la lignine, l'hémicellulose et de la cellulose des fibres obtenues ont permis de déterminer l'efficacité du rouissage. Des analyses colorimétriques et des tests de force de tension furent menés sur des fibres de lin pour comparer la qualité de ces fibres après rouissage par micro-ondes et aucun changement significatifs n'a été observé à ce qui a trait aux qualités physiques. D'un point de vue industriel, le rouissage assisté par micro-ondes est acceptable dû à la facilité de la réutilisation de l'eau utilisée pour le pré-trempage ainsi que la durée relativement courte du procédé. Le rouissage assisté par micro-ondes fut répété avec des tiges de chanvres de différentes variétés pour déterminer l'acceptabilité de cette méthode. Ainsi, des analyses NIR et de la distribution du diamètre des fibres furent aussi conduites pour déterminer l'efficacité du rouissage. Le rouissage assisté par micro-ondes sur le chanvre s'avéra efficace à en juger les résultats des analyses de composés (lignine, hémicellulose et cellulose) présents dans les fibres et la distribution du diamètre. Aucun changements significatifs ne fut observé au niveau de la force de tension et de la couleur des fibres de chanvre.

Après avoir établi le processus de rouissage assisté par micro-ondes des tiges de lin et de chanvre, l'étape suivante était d'étudier les changements chimiques dans les fibres durant les traitements par micro-ondes; les tiges de lin furent sélectionnées pour des analyses par méthodes gravimétriques. Des tiges de lin pré-trempées et soumises au rouissage par micro-ondes à différentes intensités (W/g) et l'efficacité fut mesurée en analysant les composés chimiques

présents dans les fibres provenant des tiges. Les concentrations de cellulose, d'hémicellulose, de lignine et de pectine et la teneur en sucre dans la solution obtenue après le traitement furent déterminées. Le pourcentage de cellulose dans les fibres augmenta de façon significative avec l'augmentation de la puissance des micro-ondes avec des temps de trempage variés, ce qui démontra le relâchement de fibres cellulosiques suivant le traitement par micro-ondes. Les concentrations d'hémicellulose, de lignine et de pectine diminuèrent significativement après le rouissage assisté par micro-ondes. Cette étude a utilisé les changements des compositions chimiques des fibres comme outil pour estimer l'efficacité du rouissage assisté par micro-ondes et les résultats furent pris en compte pour optimiser le procédé. Un modèle de cinétique sur les changements chimiques pendant le rouissage assisté par micro-ondes et le pré-trempage des tiges fibreuses fut développé. Le taux de changement des composés relâchés des tiges de lin et de chanvre pré-trempées suite au rouissage assisté par micro-ondes fut analysé en ce qui à trait au temps de trempage, énergie des micro-ondes et du temps de rouissage. Le taux de changement de composition dans le modèle concorda avec les valeurs obtenues pour la cellulose, l'hémicellulose et la lignine. L'augmentation des taux observés a été associée à l'utilisation de l'énergie micro-ondes. Le modèle fut développé à partir des données obtenues des tiges de lin et fut validé en utilisant les données sur les changements chimiques des tiges de chanvre.

Des tiges de lin et de chanvre complètement trempées après rouissage assisté par micro-ondes furent collectées avec une teneur très élevée et ces tiges ont dû être asséchées pour diminuer le taux d'humidité à environ 10% pour une décortication subséquente pour séparer les fibres ou à 4% pour entreposage. Pour faciliter le séchage des tiges de lin et de chanvre, un système électro-osmotique à presse à rouleaux a été développé. Étant donné que les tiges pré-trempées sont légèrement chargées, les molécules d'eau furent retirées lorsque les tiges furent soumises à une électro-osmose entre deux électrodes. La pression appliquée entre les deux électrodes, le voltage appliqué et le temps de pré-trempage des tiges furent des facteurs qui affectèrent le séchage par électro-osmotique. Suite au séchage, les tiges furent soumises à un assèchement de courte durée par micro-ondes à une température contrôlée et furent transportées à des installations de transformation de fibre où les tiges rouies furent décortiquées en des biofibres. Un rouissage adéquat de tiges grâce à une électro-technologie produit des fibres de grande qualité, tandis que des fibres non-rouies, sous-rouies ou sur-rouies produisent des fibres de mauvaise qualité.

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THESIS FORMAT

This thesis is submitted in the format of papers suitable for journal publication. This thesis format has been approved by the Faculty of Graduate and Postdoctoral Studies, McGill University, and follows the conditions outlined in the Guidelines: Concerning Thesis Preparation, which are as follows:

“As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research. The structure for the manuscript-based thesis must conform to the following:

1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis).
2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges between the different papers are mandatory.
3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts.

The thesis must include the following

- (a) A table of contents;
- (b) An abstract in English and French;
- (c) An introduction which clearly states the rationale and objectives of the research;
- (d) A comprehensive review of the literature (in addition to that covered in the introduction to each paper);
- (e) A final conclusion and summary;

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers”.

CONTRIBUTION OF AUTHORS

The following are the manuscripts prepared for publication.

- i. **Nair, G.R.**, Yaylayan, V., Rho, D., and Raghavan, V. (2013) Application of Electro-Technologies in Processing of Flax Fiber. *Fibers (MDPI)*, 2013, 1 – 21-35.
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- iii. **Nair, G.R.**, Yaylayan,V., Rho, D. and Raghavan, V.(2013) Microwave Assisted Retting- A Novel Processing Method. *Biosystems Engineering* 116 (4): 427-435.
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- v. **Nair G.R.**, A. Singh, and Raghavan, V. Microwave- Assisted Degumming of Hemp Stems. (To be submitted).
- vi. **Nair G.R.**, A. Singh, Rho, D., Yaylayan, V and Raghavan. Mathematical Analysis of Compound Release During Microwave- Assisted Retting of Flax Stems (To be submitted).
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The research work reported here was performed and completed by the candidate Gopu Raveendran Nair. He was responsible for the experimental setup, design of experiment, analytical work in the laboratory, data analysis, modeling and preparing the manuscripts and thesis. Professor G. S. Vijaya Raghavan is the thesis supervisor, providing scientific advice and technical supervision. He was also directly associated with editing and reviewing the manuscripts.

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TABLE OF CONTENT

ABSTRACT	ii
RESUME	v
ACKNOWLEDGEMENTS	viii
THESIS FORMAT	ix
CONTRIBUTION OF AUTHORS	xi
LIST OF TABLES	xiii
LIST OF FIGURES	xx
NOMENCLATURE	xxiii
CHAPTER 1. GENERAL INTRODUCTION.....	1
1.1. Problem Statement.....	1
1.2. Hypothesis	2
1.3. Objectives	3
CHAPTER 2. LITERATURE REVIEW	4
2.1. Introduction	4
2.2. Structure of Natural Agricultural Fibers	5
2.3. Retting	6
2.4. Role of Electromagnetic Energy in Retting of Biofibers	8
2.5. Microwave- assisted Retting Process of Flax and Hemp	11
2.6. Retting Efficiency Analysis	12
2.6.1. Fried Test	12
2.6.2. Near Infrared Analysis.....	13
2.6.3. Analysis of Physical Properties	13
2.6.3.1 Tensile Strength	13
2.6.3.2 Color Difference Measurement	14
2.6.3.3 Fiber Diameter Analysis	14
2.7. Mathematical Modeling	15
2.8. Electro- Osmotic Dewatering of Retted Flax and Hemp Stems	16
2.8.1. Double Layer	16
2.8.2. Helmholtz- Smoluchowski Theory	17
2.8.3. Zeta Potential	18
2.8.4. Electro- Osmotic Permeability	18
2.8.5. Design of Electro –Osmotic Dewatering Apparatus	19
2.8.6. Roller Press for Electro-Osmosis	23
2.8.7. Design Parameter for Dewatering of Flax and Hemp Stems	24

2.9. Microwave Drying of Retted Flax and Hemp Stems	25
2.10. Summary	26

CONNECTING TEXT..... 27

CHAPTER 3. COMPARATIVE EVALUATION OF PHYSICAL AND STRUCTURAL PROPERTIES OF WATER RETTED AND NON RETTED FLAX FIBERS 28

3.1. Abstract	28
3.2. Introduction	28
3.3. Experimental Section	30
3.3.1. Flax straw	30
3.3.2. Non- Retted Flax Fiber	30
3.3.3. Water –Retting of Flax Straw	30
3.3.4. Measurement of Impurity	31
3.3.5. Scanning Electron Microscope analysis of fiber structure	31
3.3.6. Weighted Average Length	31
3.3.7. Linear Density	32
3.3.8. Applications of Biofibers	33
3.4. Results and Discussion	33
3.4.1. Impurities	33
3.4.2. SEM Analysis	34
3.4.3. Weighted Average Length	35
3.4.4. Linear Density (Thinness) of the Flax Fibers	36
3.4.5. Tenacity and Elongation	36
3.4.6. Applications of Biofibers	37
3.5. Conclusion	38

CONNECTING TEXT..... 39

CHAPTER 4. MICROWAVE- ASSISTED RETTING- A NOVEL METHOD OF PROCESSING OF FLAX STEMS 40

4.1. Abstract	40
4.2. Introduction	40
4.3. Materials and Methods	42
4.3.1. Flax stems	42
4.3.2. Microwave Apparatus.....	42
4.3.3. Experimental Procedure.....	43
4.3.3.1 Microwave Treatment	43
4.3.3.2 Measurement of Retting Efficiency	44
4.3.3.3 Near Infrared Analysis	44
4.3.3.4 Calorimetric Analysis	45
4.3.3.5 Fiber Diameter Analysis	45
4.3.3.6 Tensile Strength	46

4.3.4. Statistical Analysis	46
4.4. Results and Discussion	46
4.4.1. Microwave Treatment and Retting Efficiency	47
4.4.2. Calorimetric Analysis of Flax Fibers	52
4.4.3. Diameter Distribution of Flax Fibers	52
4.4.4. Analysis of Tensile Strength of Flax fibers	53
4.5. Conclusion	55

CONNECTING TEXT..... 56

CHAPTER 5. APPLICATION OF MICROWAVE ENERGY IN DEGUMMING OF HEMP STEMS 57

5.1. Abstract	57
5.2. Introduction	57
5.3. Materials and Methods	59
5.3.1. Hemp stems	59
5.3.2. Microwave- Assisted Retting Apparatus	59
5.3.3. Experimental Procedure.....	59
5.4. Results and Discussion	59
5.4.1. NIR spectrometer Analysis	59
5.4.2. Calorimetric analysis of Hemp Fibers	63
5.4.3. Diameter Distribution of Hemp Fibers	64
5.4.4. Analysis of Tensile Strength of Hemp fibers	65
5.5. Conclusion	67

CONNECTING TEXT..... 68

CHAPTER 6. ANALYSIS OF CHEMICAL COMPOSITION CHANGES DURING MICROWAVE- ASSISTED RETTING AND OPTIMIZATION OF THE PROCESS 69

6.1. Abstract	69
6.2. Introduction	69
6.3. Materials and Methods	70
6.3.1. Flax stems	71
6.3.2. Microwave Apparatus.....	71
6.3.3. Experimental Procedure.....	72
6.3.3.1 Microwave- Assisted Retting	72
6.3.3.2 Analysis of Compounds	72
6.4. Results and Discussion	73
6.4.1. Cellulose Concentration	73
6.4.2. Hemicellulose Concentration	75
6.4.3. Lignin Concentration.....	77
6.4.4. Pectin Concentration	79
6.4.5. Sugar Content in the Solution	81
6.4.6. Visual Analysis of Flax Fibers	83

6.4.7. Process Optimization	86
6.5. Conclusion	86

CONNECTING TEXT..... 88

CHAPTER 7. MATHEMATICAL ANALYSIS OF COMPOUND RELEASE DURING MICROWAVE-ASSISTED RETTING OF FLAX STEMS 89

7.1. Abstract	89
7.2. Introduction	89
7.3. Materials and Methods	91
7.3.1. Microwave- Assisted Retting	91
7.3.2. Near Infrared (NIR) Analysis	92
7.3.3. Kinetic Model studies	92
7.3.4. Validation of the Model	93
7.4. Results and Discussion	93
7.4.1. Rate of Change of Cellulose Content	93
7.4.1.1 Rate Coefficient	97
7.4.2. Rate of Change of Hemicellulose Content	98
7.4.2.1 Rate Coefficient	102
7.4.3. Rate of Change of Lignin Content	102
7.4.3.1 Rate Coefficient	106
7.4.4. Validation of the Model	106
7.5. Conclusion	108

CONNECTING TEXT..... 109

CHAPTER 8. ELECTRO-OSMOTIC DEWATERING OF HIGH MOISTURE FLAX STEM 110

8.1. Abstract	110
8.2. Introduction	110
8.3. Materials and Methods	112
8.3.1. Flax Stems	112
8.3.2. Electro- Osmotic Dewatering Apparatus	112
8.3.3. Experimental Design	112
8.3.4. Electro- Osmotic Permeability	115
8.4. Results and Discussion	116
8.4.1. Water Removal	116
8.4.1.1 Effect of Voltage on Electro- Osmosis	118
8.4.1.2 Effect of Cylinder Pressure on Electro- Osmosis	118
8.4.1.3 Effect of Soaking on Electro- Osmosis	119
8.4.2. Electro- Osmotic Permeability	120
8.5. Conclusion	122

CONNECTING TEXT.....	123
CHAPTER 9. ELECTRO-OSMOTIC DEWATERING OF PRE-SOAKED HEMP STEMS	124
9.1. Abstract	124
9.2. Introduction	124
9.3. Materials and Methods	125
9.3.1. Hemp Stems	125
9.3.2. Electro- Osmotic Dewatering Apparatus	125
9.3.3. Experimental Procedure.....	125
9.4. Results and Discussion	125
9.4.1. Water Removal	126
9.4.1.1 Effect of Voltage on Electro- Osmosis	128
9.4.1.2 Effect of Cylinder Pressure on Electro- Osmosis	130
9.4.1.3 Effect of Soaking on Electro- Osmosis	130
9.4.2. Electro- Osmotic Permeability	131
9.5. Conclusion	133
CHAPTER 10. GENERAL SUMMARY AND CONCLUSION.....	134
CHAPTER 11. CONTRIBUTION TO KNOWLEDGE AND TECHNOLOGICAL INNOVATION	137
CHAPTER 12. RECOMMENDATION FOR FUTURE STUDIES	138
REFERENCES.....	139

LIST OF TABLES

Table 2.1 Chemical compositions of selected natural fibers	6
Table 3.1 Percentage Impurities in fibers	33
Table 3.2 Linear densities of flax fibers	36
Table 3.3 Strength test result comparison of retted and non- retted fibers	36
Table 4.1 Experimental design of microwave- assisted retting of flax	44
Table 4.2 Diameter distributions of flax fibers	54
Table 5.1 Components of hot water treated pre- soaked hemp stems	63
Table 5.2 Diameter distribution of hemp fibers	66
Table 6.1 Central composite design for compound release in various retting treatments of flax stems	84
Table 7.1 Experimental designs for microwave assisted retting of flax stems	91
Table 7.2 Model parameters, R^2 and RMSE values associated with release of cellulose rate at various MW treatment of flax stems	94
Table 7.3 Observed and predicted values of cellulose rate changes with respect to microwave – assisted retting time	95
Table 7.4 Observed and predicted values of hemicellulose rate changes with respect to microwave – assisted retting time	99
Table 7.5 Model parameters, R^2 and RMSE values associated with release of hemicellulose rate at various microwave- assisted treatment of flax	100
Table 7.6 Observed and predicted values of lignin rate changes with respect to microwave – assisted retting time	103

Table 7.7 Model parameters, R^2 and RMSE values associated with release of lignin rate at various microwave- assisted treatment of flax	104
Table 7.8 Model validation using microwave- retted hemp fibers	107
Table 8.1. Experimental design of electro- osmotic dewatering of flax stems and water release due to electro- osmosis	113
Table 9.1 Experimental design of electro- osmotic dewatering of hemp stems and water release due to electro- osmosis	127

LIST OF FIGURES

Figure 2.1 A schematic comparison of stalk cross section of flax and hemp.....	6
Figure 2.2 Scanning electron micrographs of flax stems	7
Figure 2.3 Schematic diagram of a microwave treatment system	12
Figure 2.4 Process of dewatering by electro osmosis dehydration	20
Figure 2.5 Pressurized electro- osmotic dewatering.....	22
Figure 2.6 Roller press electro- osmotic dewatering apparatus.....	23
Figure 3.1 (a)Water retting of flax stems. (b) retted flax stems after 72 hours	31
Figure 3.2 Flax fiber samples prepared for SEM analysis	32
Figure 3.3: Weighted average length of flax fiber	32
Figure 3.4 Cross- sectional view of (a) non retted and (b) retted flax fiber	34
Figure 3.5 Longitudinal SEM view of (a) non- retted and (b) retted fiber	34
Figure 3.6 Percentage of lengths by mass – non-retted flax fiber	35
Figure 3.7 Percentage of lengths by mass – retted flax fiber (long).....	35
Figure 3.8 Percentage of lengths by mass– retted flax fiber (short).....	35
Figure 4.1. Microwave apparatus for retting of flax	43
Figure 4.2.Retting efficiency of various treatments (Fried test).....	47
Figure 4.3 NIR analysis of cellulose content in flax fibers	49
Figure 4.4. NIR analysis of hemicellulose in flax fibers	50
Figure 4.5 NIR analysis of lignin in flax fibers.....	50
Figure 4.6 Colorimetric analyses of flax fibers	52
Figure 4.7 Analysis of tensile strength of flax fiber	53

Figure 5.1 Cellulose content in hemp stems.....	60
Figure 5.2 NIR analysis of hemicellulose in the hemp fiber	61
Figure 5.3 NIR analysis of Lignin in the hemp fiber	63
Figure 5.4 Colorimetric analysis of hemp fibers of various treatments	64
Figure 5.5 Tensile strength of hemp fibers	65
Figure 6.1. Microwave apparatus for retting process	71
Figure 6.2. Cellulose percentage in flax fibers after various treatments	74
Figure 6.3 Response surface curve of cellulose percentage in flax fibers	75
Figure 6.4 Hemicellulose percentages in flax fibers after various treatments.....	76
Figure 6.5 Response surface curve of hemicellulose percentage in flax fibers	77
Figure 6.6 Lignin percentage in flax fibers after various treatments	78
Figure 6.7 Response surface curve of lignin percentage in flax fibers	78
Figure 6.8 Pectin percentage in flax fibers after various treatments	80
Figure 6.9 Response surface curve of pectin percentage in flax fibers	81
Figure 6.10 Sugar release in the solution after various treatments	82
Figure 6.11 Response surface curve of sugar release in flax fibers	82
Figure. 6.12 Optical microscopic images of the flax fibers	85
Figure 7.1 Observed and predicted values of rate of change of cellulose percentage in flax fiber	96
Figure 7.2 Rate coefficient for cellulose release for various treatments	97
Figure 7.3 Observed and predicted values of rate of change of hemicellulose percentage in flax fiber	101
Figure 7.4 Rate coefficient for hemicellulose release for various treatments	102
Figure 7.5 Observed and predicted values of rate of change of lignin percentage in flax fibers	105
Figure 7.6 Rate coefficient for lignin release for various treatments	106

Figure 8.1. Roller press electro- osmotic dewatering apparatus	113
Figure 8.2 Actual versus predicted % of water removed by electro osmosis	116
Figure 8.3 The significance of the % water removed by various electro- osmotic treatments	117
Figure 8.4. Response surface curve of % electro- osmotic water removal with respect to cylinder pressure and voltage	119
Figure 8.5. Response surface curve of % electro- osmotic water removal with respect to soaking and voltage	119
Figure 8.6 Electro- osmotic permeability with respect to various electro- osmotic dewatering of flax stems	121
Figure 8.7 Prediction profile of the treatment for maximum desirability	122
Figure 9.1 Actual versus predicted plot of % of water removed from the hemp stems by electro osmosis	126
Figure 9.2 % Of total water removed by various electro- osmotic treatments on hemp stems	128
Figure 9.3 Response surface curve of % total water removal with respect to cylinder pressure and voltage	129
Figure 9.4 Response surface curve of % electro- osmotic water removal with respect to soaking and voltage	130
Figure 9.5 Electro- osmotic permeability with respect to various electro- osmotic dewatering of flax stems	131
Figure 9.6 Prediction profile of the treatment for maximum desirability	132

NOMENCLATURE

i_e	electrical potential gradient (V/cm)
v_e	electro- osmotic velocity
ΔL	length of capillary between the electrodes (m)
ΔV	electric potential (V)
A	cross sectional area of the fiber (m ²)
A	cross- sectional area (cm ²)
a^*	CIE standard nomination for green/red
ADF	acid detergent fiber
b	constant associated with the dielectric loss factor (dimensionless)
B	fraction of original component present in the biomaterial
b^*	CIE standard nomination for blue/yellow
C	chemical concentration
CTAB	cetyl trimethylammoniumbromide
D	dielectric constant (dimensionless)
D	dielectric loss tangent
EDTA	ethylenediaminetetraacetate
EM	electro- magnetic
$F_{\max}$	maximum force applied (N)
HW	hot water treatment

k	rate constant
k_e	coefficient of electro- osmotic permeability ($\text{cm}^2/\text{V.s}$)
L^*	CIE standard nomination for lightness
M	Total mass of the sludge in the cell
M_w	Mass of water displaced
m_s	mass of the dry sample (kg)
MW	microwave treatment
NDF	neutral detergent fiber
NIR	near infrared spectrometer
q_a	quantity of water removed in m^3/s
R_0	initial resistance of the material to be dewatered (Ω)
RMSE	root means square error
SD_1	initial solid concentration of the sample (%)
SD_2	is the final solid concentration of the sample (%)
SEM	scanning electron microscope
t	time (s)
$\tan \delta$	tangent of loss angle
THC	tetrahydrocannabinol
V	Volume of the sludge
w.b	wet basis moisture content (%)
X	amount of compound present in the biomass (%)
X_i	amount of compound present in the untreated flax stem (%)
ΔE	total color difference

ε'	dielectric constant
ε''	the dielectric loss factor
ε^*	relative permittivity
μ	viscosity (Pa.s)
ζ	zeta potential (mV)
σ_t	tensile strength (Pa) N m ⁻²

CHAPTER 1

GENERAL INTRODUCTION

1.1 Problem Statement

Flax and hemp fibers are used as a replacement for synthetic fibers because of the similarity in the physical properties of flax and hemp stems compared to artificial fibers. The main reasons for the wide acceptance of biofiber from flax and hemp are their biodegradability and environmental friendliness. Potential uses of flax and hemp fibers include biomaterials (inside panel of motor vehicles, building materials), special quality papers (currency, cigarette) and apparels (Akin, 1989; Sharma 1987).

Biofibers are comparably more expensive than synthetic fibers, and the obvious reason is the high cost involved in various processing steps. Stem based fibers are located as bundles inside the cortex of the stems and pectin acts as glue to the fibers located strategically to cement the fiber bundles to the stalk of the plant (Van Sumere, 1992). Fibers are separated from the stems by the process called decortication/ scutching, in which the dried stems are passed through multiple rollers to crush its stems and then the fibers are separated by combing action. Since the fibers are glued together and attached to the stems with strong chemical bonds, fibers contain more coarse fibers with impurities like shives and dust on their surface. To overcome this difficulty, prior treatments are conducted for the loosening of fibers by breaking the strong chemical bonds before decortication, which is called retting.

The common retting methods adopted for the processing of flax and hemp stems are water retting, dew retting and enzyme retting. Water retting (simply soaking in the water for 1- 2 weeks) is banned in Europe because of the environmental issues related to the pollution caused by this process (Foulk et al, 2001). Dew retting is simply leaving the harvested plant on the field for 2-3 weeks after harvest. Due to the changes in temperature and moisture of the soil plant interface, aerobic microorganisms attack the plant and break those strong pectin bonds, which results in loosening of the fibers from the stems. Anaerobic microorganisms are responsible for the water retting whereas aerobic microorganisms are responsible for dew retting. This process is difficult to control because of its weather dependence. To overcome the adverse effects of traditional retting methods, scientists discovered enzyme retting, which is a relatively newer

method. In enzyme retting, enzymes are introduced to plant stems, which act on the stems to break the strong pectin bonds leading to the loosening of the fibers (Akin, 2005). This method is very expensive compared to other methods because of the non-reusability of the enzymes. These are the current retting methods and the problems related to it. In this scenario, there is a huge potential for the study to discover a less polluting, energy and time saving novel retting method for the processing of biofibers. After retting, the flax and hemp stems are either moved to a storage area or to a decortication facility. At decortication step, the stems are passed through multiple rollers to crush the dry stems for the separation of fibers and then comb/scutch to remove all impurities from the fiber's surface. To perform decortication, the flax and hemp stems have to be dried to a lower moisture level of around 10% (w.b) and for storage, the moisture level should be 4%. The usual drying of retted stems is carried out by hot air method. Removal of water from 100% wet stems using hot air leads to high-energy utilization and because of the non-uniformity of stems; the conventional drying method also is not uniform, which affects the quality of the final product. These problems resulted in formulating studies focussed on introducing a pre-drying/ dewatering technique after retting which reduces the surface water thereby minimize the time and energy required for the drying of the stems.

1.2 Hypothesis

Previous studies were conducted to understand the role of microwave energy in chemical reactions in biomass processing, irradiation etc. From the studies, it was learned that polysaccharides like pectin could decompose at lower temperatures with the application of microwave energy, which threw light on the effect of microwave in biomass processing (Tsubaki and Azuma, 2010). They concluded the release of pectin was the result of application of electromagnetic energy.

The hypothesis of this study is that microwave energy can be applied to flax and hemp stems at lower temperature for the decomposition of pectin bonds to loosen the fibers from the stems. Electro-osmosis can be applied as a pre-treatment for the dewatering of water-stem mixture to reduce the time and energy for further drying of the stems.

1.3 Objectives

The main objectives of the research are to:

- Conduct initial study to investigate the effect of conventional retting on the physical and structural properties of biofibers by performing water retting on flax stems;
- Develop a novel retting method by the application of microwave energy on flax and hemp stems and to compare physical properties with non- retted fibers;
- Analyze the efficiency of retting with respect to change in the chemical composition of retted fiber and to optimize the process with compositional changes;
- Develop a kinetic model for microwave- assisted retting with respect to its rate of change in the components such as lignin, hemicellulose and cellulose.
- Develop an electro- osmotic dewatering system for the retted- soaked flax and hemp stems as a pre- treatment before drying and decortication.

CHAPTER 2

REVIEW OF LITERATURE

2.1. Introduction

Natural agricultural fiber has been used all over the world from ancient times. In the past, plant fiber was used for making clothes, but now it has a wide range of applications from automotive to aerospace industries (Akin et al., 1996; Akin, 2012). Plant fibers are used as a better replacement for synthetic fibers in a wide range of applications. The natural fibers are of different types, which are from plant origin and animal origin (cotton, linen, silk, wool etc.). Our topic of interest is plant fibers, especially fibers from plant stems like flax, hemp etc. Studies show that replacement of synthetic fiber with natural agricultural fiber has increased in the field of biocomposites. Natural fibers are low in density, biodegradable and their market value are dependent on the quality of the final product. But the big disadvantage of natural fibers is that they do not have same consistency in quality as compared to synthetic fibers. This inconsistency is due to variety of reasons such as climate, crop variety, retting process, and processing equipment used for fibers (Thomsen et al., 2006, Foulk et al., 2011). In natural fibers, climatic conditions play an important role in fiber production. Low temperature and high relative humidity during growing season contribute to fineness and length of fiber.

Flax (*Linum usitatissimum* L.) is a plant, which is widely growing in Canada as well as globally and is used in various food and industrial products. The seeds of hemp and flax are used in the food industry for making oil, cattle feed etc. The stem is used for the production of fiber, bio composites, high quality paper and many other industrial applications. Flax plant belongs to the family *Linaceae*. The flax seeds are primarily used in the food industry, while the plant stems are used in fiber production. The stem height of flax plants range from 0.20 m to 1.50 m (Hegi, 1925). Different crop varieties have different cellulose and non-cellulosic contents which are key factors for retting and fiber quality (Sharma, 1988). Flax and hemp fibers are biodegradable, sustainable, renewable, economical, and easily available in Western Canada. Bio fiber for the textile industry, production of bio-composite materials and the paper industry are produced from flax and hemp straw (Atton, 1989). Retting is a very important factor for processing of fiber and

ultimately fiber quality. The flax stems after retting process always contain high amount of water. The drying of retted stem is conducted by hot air drying (Nair et al., 2012). The hot air drying method is very inefficient since the major part of the energy will be wasted in forcing the air through the bale. Other disadvantage of hot air drying is lengthy drying time during the falling rate period. Retting and drying are the two important energy intensive processes, which determine the quality of the fiber. So those processes should be conducted with better precision for getting high quality fibers. This chapter discusses the application of electro- technologies in various steps in the processing of bast fiber from flax and hemp stems.

2.2. Structure of Natural Agricultural Fibers

The knowledge of physical and chemical structure of the plant is important for the design of electro-technology based fiber production system, because those are the major factors affecting the quality of the final product. The structure of a natural fiber is complicated and flax and hemp fibers have a non-uniform semi cylindrical shape where the fiber diameter becomes narrower towards the end. It always comes with 4-10 fibers sticking together in a bundle (Baley, 2002;Akin, 2004) and can be separated individually. Flax and hemp fibers, placed in the bast (i.e., cortex) region of the stem, lie between the protective cuticle/epidermis barrier and the lignified core tissues. Pectin serves as a glue to hold fibers together in bundles and the bundles to non-fiber tissues (Van Sumere 1992). Hemicelluloses, pectin, and lignin act like a matrix where as, cellulose acts like reinforcement to the matrix (Thygesen, 2006). This is the reason why it is difficult to separate a single fiber from a bundle. Section of flax and hemp stem is shown in Figure 2.1. There are compounds in flax and hemp fiber such as wax, minerals, and water-soluble compounds in addition to the main components. Cellulose, hemicellulose, lignin, pectin and ash components in various fibrous plants are shown in Table 2.1 (Rowell et al., 1997;Mohanty et al., 2001). Cellulose is the main component, which contributes strength to the fiber (Akin, 2004). For composite production, fiber with high cellulose content gives more strength to the final product. The study also found that the tensile strength of retted hemp fiber was more than that of un-retted fiber because its cellulose content is high after retting. For the same diameter of fiber, more force is required for the separation of non- retted fiber bundles, which made them weaker compared to retted fibers due to the damage caused during separation (Thygesen, 2006; Uludag et al., 1996).

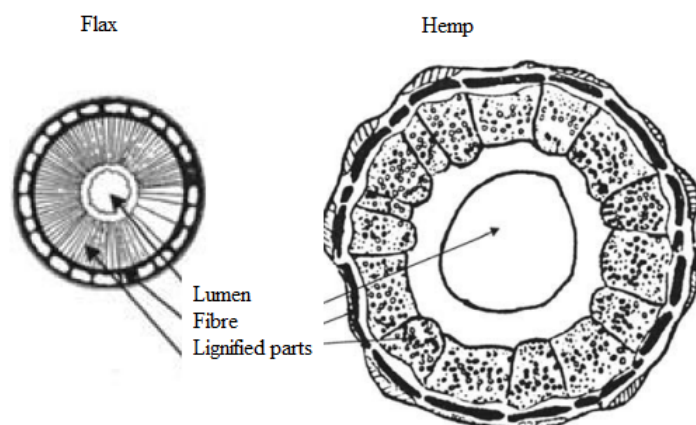


Figure 2.1 A schematic comparison of stalk cross section of flax and hemp (Pallesan, 1996)

Table 2.1 Chemical composition of selected natural fibers (Rowell et al., 1997; Mohanty et al., 2001)

Type of fiber	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Ash (%)
Fiber flax	71	2.2	18.6-- 20.6	2.3	---
Seed flax	43--47	21--23	24--26	---	5
Kenaf	31--57	15--19	21.5--23	---	2--5
Jute	45--71.5	12--26	13.6--21	0.2	0.5--2
Hemp	57--77	3.7--13	14--22.4	0.9	0.8
Ramie	68.6--91	0.6--0.7	5--16.7	1.9	---

2.3 Retting

Production of biofibers from flax and hemp stems includes various steps such as harvesting, retting, decortication, and then those fibers are moved to various industries according to the quality of the fibers. The most important and energy intensive step in the processing of flax and hems stem is retting, which is the separation or loosening of bast fibers from shive

(lignocellulosic core tissues inside the stem) core and other non-fiber fractions, leading to a major problem in flax fiber processing (Van Sumere, 1992; Foulk et al, 2001). Retting should be done very carefully; otherwise the process will end up at either under- retted or over-retted stem's stage. Under-retted flax produces coarser low quality fibers with shive and cuticular fragments, and over-retting results in maximum destruction of cellulose that leads to excessive thinning of fiber (Pallesen, 1996). Structure of flax stem before and after retting is shown in Figure 2.2.

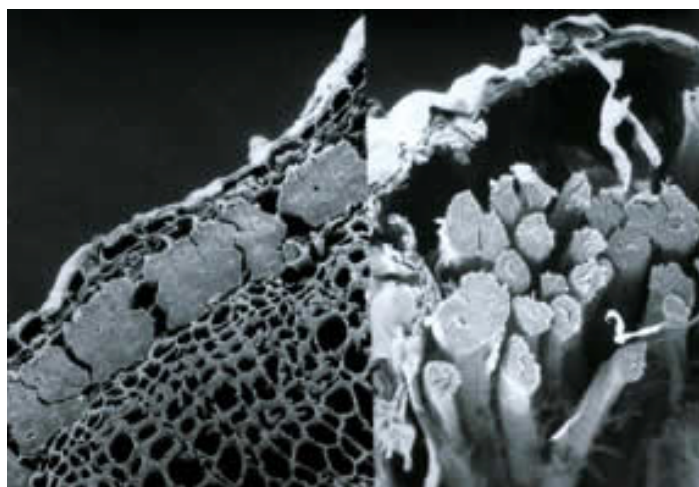


Figure 2.2 Scanning electron micrographs of flax stems. Left: un-retted cross section of stem showing bast fibers in bundles between the cuticle and woody core; right: dew-retted cross section of stem showing separation of fibers and fiber bundles from the non-fiber tissues (Akin, 2005)

Two conventional retting methods, namely water retting and dew retting have been used to extract fibers for textile and other commercial applications. The duration of these processes ranges from 1-2 weeks depending upon the variety of plant. Water retting is achieved by simply soaking the stems in water for 1- 2 weeks (Foulk et al, 2001). Dew retting is by leaving the harvested plant on the field for 2-3 weeks. Due to the changes in temperature and moisture of the soil plant interface, aerobic microorganisms attack plant and break those strong pectin bonds by helping them in loosening of the fibers from the stems. Anaerobic microorganisms are responsible for the water retting whereas aerobic microorganisms are responsible for dew retting. Even though the quality of fiber by water retting is much higher than that of newer methods, this practice has been largely discontinued in Europe because of its high expense and

the pollution and contamination arising from fermentation of the plant material (Akin, 2005).

Enzyme assisted retting is a relatively new process which is considered to be the replacement for the conventional retting methods. Enzyme assisted retting is performed by introducing enzymes like pectinases to the plant stem surface which disintegrate pectin and hemicellulose which then separate fiber from the non-fiber tissues (Akin et al, 2004). The duration of this process ranges from 8 hours to 24 hours. Non-reusability of enzymes is a main concern, which affects the cost effectiveness of the process. Type of retting and duration and bacterial species used in retting are responsible for quality of bast fiber in terms of strength and fineness.

The conventional field- or dew retting has several shortcomings and various uncontrollable factors, which can affect the final quality of the fiber, although the bulk of available fiber has been treated in this way. There are several studies conducted for the retting of flax and hemp stems by using methods other than water retting and dew retting like steam explosion retting (violent boiling of water with stems into steam which initiates separation of fibers), enzyme retting etc. (Foulk et al, 2001, Adamsen, 2002, Adamsen, 2002b; Kessler et al., 1998). ECCO Gleittechnik GmbH (Seeshaupt, Germany) has developed an ultrasound-retting process to separate the bast fibers from the rough plant straw, which are neither subjected to dew nor to water retting. The process separates the fibers from the woody components to a degree sufficient for textile and non-textile applications.

2.4 Role of Electromagnetic Energy in Retting of Biofibers

The fibers are attached together as well as to the outer skin and bark by strong chemical bonds (pectin bond). Usual retting methods allow the degradation of pectin bonds and wax due to the action of microorganisms and enzymes. But this process is lengthy and it is not economical. From the literature, it is reported that the energy of electromagnetic waves are much less than that of the strong covalent bonds with which the fibers are attached. Microwave generator at 2450 MHz frequency produces 1J/mol whereas the energy required to break a C-H bond is 413 kJ/mol (Nuchter et al., 2003). Hence it is clearly stated that microwave energy is insufficient to break strong bonds, which bind the fibers close together to the stem. But at the same time, there are many researchers who proved the effect of microwave in chemical reactions like biomass processing; irradiation etc. and non-thermal effect of microwave played an important role in the reactions. (Galema, 1997; Sridar, 1998; Steel et al., 2002). Microwave energy was widely used

for the decomposition of pectin at lower temperature in various chemical reactions (Tsubaki and Azuma, 2010). Studies are conducted on the effect of microwave in unfolding proteins. George et al. (2008) compared the effects of microwave exposure, ambient heating and a combination of both on citrate synthase unfolding by measuring its binding to the chaperone α -crystalline. The results show with a high level of confidence that unfolding occurs at significantly lower temperatures whenever microwave heating is used. This supports the hypothesis that microwaves have a non-thermal effect on protein conformation that could take the form of a direct interaction of the electromagnetic field with the protein for its water of hydration (George et al., 2008). When electromagnetic energy is applied to any material, it generates heat energy volumetrically due to its nature of converting electromagnetic energy into mechanical energy. Transfer of energy and dissipation of energy as heat is due to dipole rotation.

Sato et al. (1996), conducted studies on microwave irradiation at constant temperature to define the existence of non-thermal effect of microwave, because there was a claim that the irradiation happened only due to temperature produced by microwave. During his experiments, no cell death was observed at 35° C, whereas at 45, 47 and 50° C, the death rates of *Escherichia coli* exposed to microwave irradiation were higher than those obtained in conventional heat sterilization at the same temperature. The microwaves either caused ions to accelerate and collide with other molecules or caused dipoles to rotate and line up rapidly with alternating (2450 million times/s) electric field resulting in a change in secondary and tertiary structure of proteins of microorganisms. The most commonly used electromagnetic energy for post harvest processing such as drying, pasteurization and extraction is microwave, but this review section is focussing more on microwave as an energy source for retting of natural fiber plants. Banik et al. (2003), conducted studies on the bio effect of microwave irradiation and concluded that microwave effects were established in all the areas from microbial cells to animals and human system and they revealed that microwave could athermally induce different physiological effects. The thermal effect of microwave is explained by Maxwell's equation (Oliviera and Franca, 2002). The dielectric properties of the materials are the main property parameters of the Maxwell's equations, and therefore significantly influence the efficiency of electromagnetic (EM) energy coupled into the materials, EM field distribution, and conversion of EM energy into thermal energy within those materials. From engineering point of view, dielectric property is the most important property associated with microwave heating. The dielectric properties of a

material are described by the complex relative permittivity (ϵ^* relative to that of free space) in the following relationship:

$$\epsilon^* = \epsilon' - j \epsilon'' \quad (2.1)$$

where $j = \sqrt{-1}$.

The real part ϵ' is the dielectric constant that reflects the ability of the material to store electric energy when in an electromagnetic field; the imaginary part ϵ'' is the dielectric loss factor that influences the conversion of electromagnetic energy into thermal energy. The ratio of the real and imaginary parts of permittivity represents another important parameter tangent of loss angle ($\tan \delta = \epsilon'' / \epsilon'$), which along with dielectric constant determines the attenuation of microwave power in heating. When the water soaked stem is subjected to electromagnetic heating, the thermal and non-thermal effects enhance the retting (Nuchter et al., 2004). Fundamental knowledge of the structural and chemical characteristics of fibrous plants is important for designing a strategy by using microwave to produce fibers with specific properties required for industrial applications. Calcium levels are especially high in the protective barrier of the flax stem and likely help stabilize pectin and thereby plant tissues in that location.

The aim of applying microwave or any electromagnetic energy is to release the fibers from the plants by breaking these bonds, especially pectin bonds. First we consider the non-thermal effect of microwave in retting of biofibers. Some researchers worked on the effect of microwave on the degradation of biomass, which explained the non-thermal effect of microwave in biomass treatment to denature the strong chemical bonds. Tsubaki and Azuma in 2011, conducted studies on microwave- assisted irradiation of biomass, especially on rice straw, bamboo and other fiber rich plants. According to their study, delignification was accelerated above 180°C corresponding to release of hemicelluloses, supporting splitting of bonds between lignin and carbohydrates. However, glass transition temperature of lignin (130-200°C) is usually lower than that of cellulose (230-250°C) and close to hemicellulose (160-200°C) under dry state. Glass transition temperatures of lignin and hemicelluloses unlike cellulose lowered with increase in moisture content. Therefore heating biomass in water close to the glass transition temperature of cellulose and extraction with solvents having various range of polarity is a strategy for refinery of biomass. This explained the role of soaking as a pre treatment before retting using electromagnetic energy. Water is used in microwave assisted retting, because water is a readily

available and environment friendly solvent for microwave assisted treatment (Tsubaki and Azuma, 2011). Non-thermal effects of microwave in breaking of composites are already proven and the same non- thermal effect can be used for the release of fiber from the plants by breaking the binding forces. Temperature of retting process should be kept to a minimum to avoid the damage of fiber due to high temperature (Nair et al., 2011). But for the pectin and hemicelluloses to breakdown to release the fiber, temperature and microwave both plays a role. So microwave energy along with a high temperature of 90-95° C to 20 minutes is suitable for the retting method. High temperature of more than 120 ° C and longer duration leads to bioconversion of biomass into energy (Budarin et al., 2010). Chemical compositions of fibers from plant stem origin (flax, hemp, ramie etc.) show similarities that results in the structural similarities (Mohanty et al., 2000). In this review, flax plant is taken as an example and the application of electro- technologies on the various steps of processing of flax plant is explained.

2.5. Microwave- assisted Retting Process of Flax and Hemp

The microwave system for the retting process is shown in the Figure 2.3. The flax stems were harvested using combine harvester and they were collected as bales and stored without doing any treatment and those are subjected to microwave- assisted retting process. The first step is pre- treating of the flax and hemp stems by soaking them in the water. The soaking time has to be varied from 12 to 36 hours. This has to be optimized by conducting the lab tests. Glass transition temperatures of compounds are reduced due to soaking with water and hence at lower temperature, compounds decomposed, which helps the breaking of bonds that held those fiber bundles to the stem at lower temperatures (Tsubaki and Azuma, 2011). The power of microwave is another main factor of concern while doing microwave assisted retting. The maximum temperature attained by the flax straw will be determined by the energy applied to the flax samples. The microwave power of 100 W is applied to the flax straw- water mixture of 50 g, which has the initial power of 2 W/g. The microwave treatment time should be less because; the pre- treatment with water itself initiates the process and microwave energy adding up to the speed of decomposition of stronger covalent bonds.

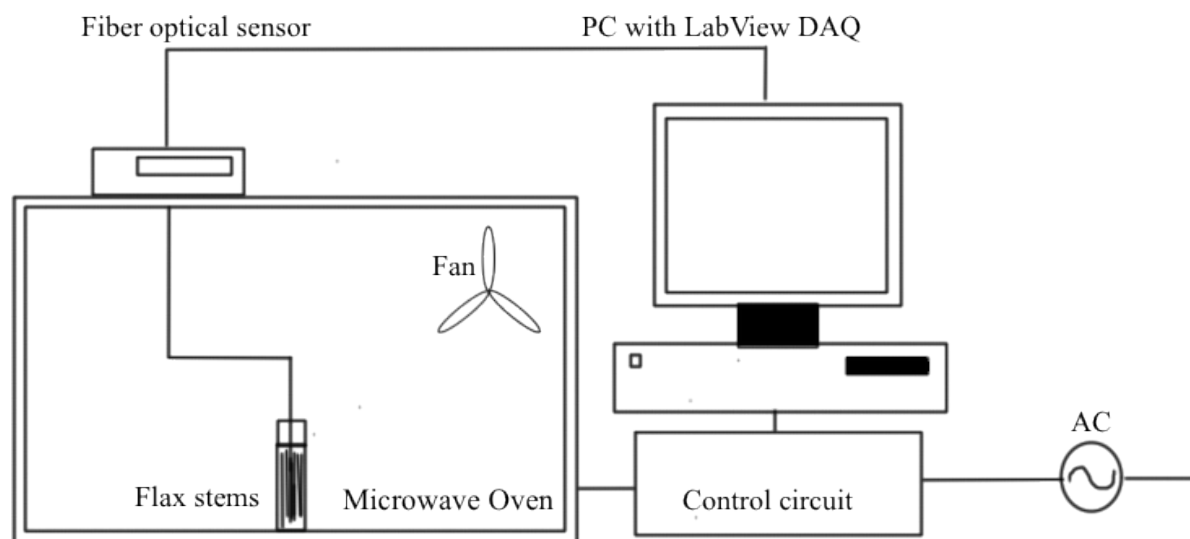


Figure 2.3 Schematic diagram of a microwave treatment system (Nair et al. 2011).

2.6 Retting Efficiency Analysis

After microwave- assisted retting, retting efficiency is to be analyzed for optimization of retting process. The following tests are usually conducted for the analysis.

2.6.1 Fried test

Retting efficiency of flax stems are measured by Fried test. Four flax stems are taken in a test tube, and 8 ml of boiled water add into it. Then the closed test tube is vortexed for 10 seconds. After that, the test tube is shaken hard vertically for 4 times. Then the test tube is opened and retting efficiency is measured. Retting efficiency is measured on a scale of 0-3. After Fried test, if no fiber peeled off from the stem, the value is 0, at the same time if all the fiber peels off, the reading is 3 (Van Sumere, 1992; Henriksson et al., 1997; Akin, 2013). Rognes et al., introduced modified fried test in 2000. According to Rognes, 10 ml boiling water is added in a test tube with four incubated flax straws. The test tube is vortexed at full speed for exactly 10 seconds. After vortexing, the test tube is shaken manually four times in vertical direction. The flax stem samples are then taken out and visually graded on a scale from 0–6 in terms of its retting efficiency. When no fiber is released from the stem, it is graded as ‘0’; ‘1’ means bast fibers are separated from 0 to 10 mm of the 10 cm long straw; ‘2’ means, fibers are released from 10 to 25 mm; ‘3’ 25–50 mm; ‘4’ 50–75 mm; ‘5’ means, fibers are separated from more than 75 mm of the straw, but remained attached at some point and ‘6’ is when all fibers are completely detached from the stem (Zhang et al., 2000).

2.6.2 Near infrared (NIR) Analysis

The retting can be analyzed in terms of the changes in the chemical composition of cellulose, hemicellulose and lignin. In a properly retted flax and hemp fiber, cellulose content is higher compared to non- retted fibers (Sharma et al., 1999). Kelley et al., in 2004 conducted studies on the rapid analysis of chemical composition of fiber by using NIR spectrometry. The visible spectra of 500–2400 nm were used for the analysis. A DC light source was used to illuminate the fiber samples and the reflected NIR signal was collected with a fiber optic probe. The samples were filled in a 2.5 cm diameter cup. Thirty individual scans were performed and two spectra were taken from each sample. The reflectance spectra were converted to absorbance spectra and subjected to multivariate analysis. Barton et al., in 2003 conducted study on the NIR analysis of the retted flax stems to find out its fiber content. According to them, the conventional method of measuring the fiber content of flax is time-consuming and difficult, and the results obtained have immense effect on the technique used. In this study, fiber content of flax stems was measured rapidly and objectively by near-infrared spectroscopy (NIRS) using whole pieces of stem in a large cell, in reflectance mode. Compared to the conventional method, the standard error of performance of the NIRS method was between 0.96 and 1.45% (dry matter basis), depending on the model and data processing used.

2.6.3 Analysis of Physical Properties

Tensile strength, color difference and fiber diameter distribution are the physical properties analyzed for the assessment of the retting efficiency of flax and hemp fibers

2.6.3.1 Tensile Strength

Measurement of tensile properties of fibers are important for its further processing such as biocomposites, apparels etc. In microwave- assisted retting, measurement of tensile properties of the fibers before and after the process is essential in order to analyze if there is any significant difference in its tensile properties due to the application of microwave energy. Tensile strength of biofiber can be measured by pulling both the end of the fiber samples by a tensile strength testing machine (ASTM D3822-07). The procedure for the tensile strength test is as follows: The desired length of the fiber was 75 mm, with a gauge length of 50 mm. The fiber is fixed on a 50 mm × 10 mm sheet of paper with epoxy glue, so as to maintain the fiber in a straight and extended position. The flax fiber attached to the paper was mounted on the tensile test machine,

the top end being attached to the testing machine with the help of a high-grip clip and the other end being connected to the chuck at the bottom. After mounting on the machine, the edges of the paper were carefully cut away and force applied in tension until the fiber broke into two. The force and displacement were recorded on an attached computer (Yuan et al., 2001; Nair et al., 2011).

2.6.3.2 Color Difference Measurement

The usual color of flax and hemp fibers is cream to light brown depending on the variety and its processing techniques involved. The color of the fibers can be modified by process like bleaching. But it is advisable to have minimum changes in the color of the fiber due to treatments like heating and other heat involved treatments. But changes in the color of flax fibers after microwave assisted retting with respect to non-retted samples is compared to find if there is any significant change in its color with microwave- assisted retting. Color is assessed within the CIE 1976 L*, a*, b* color space (CIE, 2007) using a tristimulus colorimeter (Minolta Co. Ltd., Japan). Color values are expressed as L* (whiteness or brightness/darkness), a* (redness/greenness) and b* (yellowness/blueness).

The procedure of color difference measurement is as follows: twenty millimeter thick flax fiber samples are placed on a table, and the L*, a*, b* values measured by pressing the measuring head on the top of the samples. Three replicates of each sample are measured. Color difference values of ΔL^* , Δa^* and Δb^* were calculated by subtracting the respective standard color values from the measured values for each set of retted experimental samples (Nair et al., 2012).

The total color difference ΔE is measured as (Minolta, 1991):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2.2)$$

2.6.3.3 Fiber Diameter Analysis

The cross sectional shape of a single flax fiber is almost an irregular polygon but it is represented as almost circular for its characterization in terms of its diameter (Grishanov et al., 2006; Bourmaud et al. 2013). Diameter of the fiber has to be analysed to understand the effectiveness of retting. An effective retting gives maximum percentage of fine fibers than coarse fibers (Foulk et al., 2011). The diameter distribution of the fiber is conducted as per ASTM Standard D7025 by using fibershape version 5.2 image analysing software. Fiber

portions are taken randomly from the fiber bundle and those fibers were spread on a glass slide and inserted into a Nikon scanner. The image showed by the scanner was analysed by a computer connected to the scanner with the help of software named Fibershape Version 5.2.

2.7 Mathematical Modeling

Microwave- assisted retting results in the loosening of fiber from the stems. The process leads to the compositional changes of chemical compounds like cellulose, hemicellulose and lignin in the plant stem, which enables the release of the fiber. The effectiveness of retting can be assessed by the changes in the percentage of these compounds during retting process. A kinetic model can be developed for the prediction of the changes in percentage of cellulose, hemicellulose and lignin at various soaking of flax and hemp stems, microwave power levels and treatment times. Mathematical models were developed for the prediction of lignocellulosic conversion of biomass, which helped the scientists in the optimization of the parameters in order to increase the efficiency of the bioconversion process (Jacobsen and Wyman 2000). The first kinetic model to predict changes in cellulose content was developed by Saeman, in 1945 (Saeman et al., 1945). Based on their theory, scientists developed simple kinetic model for xylan removal during dilute acid pre- treatments of corn stover, timbers and switch grass (Jacobsen and Wyman 2000, Yat et al., 2008, Lu et al., 2009).

The above-mentioned kinetic models are based on a first- order equation of reaction rate on the biomass component. The rate of the reaction is expressed below:

$$\frac{-dB}{dt} = kB \quad (2.3)$$

Where $\frac{dB}{dt}$ is the rate of change of composition, k is the rate constant and B is the fraction of original component present in the biomaterial. According to the theory, rate constant k is dependent on temperature and acid concentration (Jacobsen and Wyman 2000). The existing kinetic models are useful for predicting the changes of compounds like cellulose and hemicellulose during dilute acid pre- treatment under various conditions. But further modifications were required to make these models more reliable and efficient by taking the effect of the interactions among compounds like lignin and carbohydrates into consideration. The model studies of delignification during alkaline pre-treatment need further deep investigations on carbohydrate losses of lignocellulosic materials. As a result, Dang and Nguyen

(2006, 2007) developed an universal kinetic model to predict the compositional changes of lignin and carbohydrates for a variety of treatment conditions taking heterogeneous mass transport into consideration (Dang and Nguyen 2006, Dang and Nguyen 2007). The model is as shown below:

$$\frac{-dB}{dt} = knt^{(n-1)}.C^b.B \quad (2.4)$$

where B is the amount of component (lignin, cellulose or xylose) in the biomaterial, k and n are constants dependent on various factors associated with the nature of the material. C is the chemical concentration. Keshwani and Cheng in 2010 developed a new model for alkali pretreatment of switch grass by replacing C with D , which is dielectric loss tangent of the solvent used for the treatment (Keshwani and Cheng 2010, Xu et al., 2011).

2.8. Electro- Osmotic Dewatering of Retted Flax and Hemp Stems

The microwave assisted retting is done and the resultant stem is of high moisture content. For further processing of fiber, the stems are to be dried completely. The drying of the retted straws is an important step in the extraction of fibers. This is usually a lengthy process if done by air-drying, and requires much energy for controlled heat drying since the quality of the fibers must be maintained. The energy required for pressing-induced dewatering is many times smaller than that required for heat induced water removal. For example, only 7 kJ/kg is needed to expel water at an average pressure of 7kPa versus roughly 2320 kJ/kg for heat-induced water removal (Schwartzberg et al., 1977). A two- step process is proposed. The first step is to dewater the retted straw using a method based on electro-osmosis. (Lightfoot and Raghavan, 1994; Orsat et al., 1999). Electro-osmotic dewatering removed the bulk of free water from the kelp in a rapid and energy efficient manner. This procedure will be used for the design of a novel electro-osmotic dewatering system for the retted straws and fibers. The study is to design a lab scale electro- osmotic dewatering system for the initial dewatering of the flax stem followed by microwave drying for shorter duration to reduce the moisture content of the flax stems to a final dried product.

2.8.1. Double Layer

Electro- osmotic dewatering is possible because of the presence of a double layer at the liquid-solid interphase. The surface charge on the particle and the corresponding counter-ion charge in

the solution are together known as a double layer in electro- osmotic system. Under the influence of an electric field, the cations on the material surfaces starts migrating towards the cathode due to the electrical attraction. The movement of this boundary layer of cation drags the cathode by electrical attraction. Thus there is a transport of water from the anode to cathode, which is known as electro-osmosis. Electro-osmosis is based on electrically induced flow, which is due to the presence of double layer at the biomaterial- water interface. The concept of double layer theory is the basis of understanding the principle of electrokinetic phenomena. Due to the negative charge of the sample, the cations with + charge in the solution are attracted to the flax stems surface by electrostatic attraction in order to balance the surface charge. This combined system of surface charge on the sample and the corresponding counter ion charge in the solution is known as double layer.

2.8.2 Helmholtz-Smoluchowski (HS) Theory

Helmholtz (1879) provided a mathematical model for analysis of electro- osmosis in which a single capillary was observed and in 1921, Smoluchowski came up with a modified version of Helmholtz theory. According to HS theory, the electro- osmotic flow of a fluid of certain velocity and dielectric constant through a surface- charged porous medium of zeta potential ξ , under an electric gradient. The electro- osmotic velocity can be derived based on the balance of the electrical and frictional forces between water and the wall of capillary, which is:

$$v_e = \frac{\varepsilon \xi \Delta V}{\mu \Delta L} \quad (2.5)$$

Where v_e is the electro- osmotic velocity, ξ is the zeta potential, ε is the dielectric constant of pore fluid, μ is the viscosity, ΔV is the electric potential and ΔL is the length of capillary between the electrodes.

Electro- osmotic flow mechanism can be explained as a function of the permeability of the medium. So the quantity of water moved in unit time through a single capillary of area a ; by electro- osmosis, q_n is,

$$q_n = \frac{n \varepsilon \xi \Delta V}{\mu \Delta L} \quad (2.6)$$

Considering a prism of saturated porous medium mass with a base area A in contact with the electrodes and length, L , instead of a capillary, the electro- osmotic flow, Q_e , becomes;

$$Q_e = \frac{n\varepsilon\xi\Delta V}{\mu\Delta L}A \quad (2.7)$$

Where n is the porosity of the biomass, which is a dimensionless function (Page and Page, 2002).

The definition of electro-osmosis is as follows:

"At the solid-liquid interface opposite charges are oriented in such a manner that either negative or positive ions are adsorbed on the wall of the capillary while ions of opposite charge remain in the liquid forming an adjacent and parallel layer. If such a capillary is placed into an electric field, the ions contained in the inner layer, which forms part of the liquid phase, will move towards the electrode of opposite sign and drag along the free water enclosed by this moving boundary film". Electro- osmotic mechanism can be explained by Helmholtz-Smoluchowski theory (Casagrande, 1952).

2.8.3. Zeta-Potential

When particles move with a liquid under the effect of an applied field, a plane of shear is formed around the sample. The electrical potential difference between the plane of shear and the bulk solution is called zeta potential (ξ). According to the Helmholtz- Smoluchowshi theory, the electro- osmotic flow rate is directly proportional to the zeta potential. For a biomass, zeta potential is directly proportional to electro osmotic water removal (Chen, Mujumdar et al. 1996). The main factors effecting zeta potential are ion concentration, pH of the fluid and the sludge conductivity. If the ion concentration is too high, the zeta potential is reduced so that the electro- osmotic flow rate decreases (Lockhart 1992). The electro- osmotic flow could be modified by the addition of ionic solutions (Orsat, Raghavan et al. 1999). Changes in pH cause a change in the zeta potential which in turn affects the rate of change of electro- osmotic water removal (Rabie, Mujumdar et al. 1994). An increase in electrical conductivity of biomass reduces the zeta potential at the surface of the solid phase of the biomass (Gazbar, Abadie et al. 1994).

2.8.4. Electro- Osmotic Permeability

The electro- osmotic flow of water through a porous medium, Q_e (cm^3/s) could be presented in the form of Darcy's equation for water flow:

$$Q_e = k_e i_e A \quad (2.8)$$

Where $k_e = \frac{\mu}{D\xi n}$ and is the coefficient of electro- osmotic permeability (cm^2/Vs), and

$i_e = \frac{\Delta V}{\Delta L}$ and is the electrical potential gradient (V/cm), A is the cross- sectional area (cm^2), D is the dimensionless dielectric constant.

The electro-osmotic permeability, k_e depends mainly on, the pore area and is independent of the size of the individual pores, whereas hydraulic permeability is very strongly influenced by the actual pore size (Casagrande 1949). The electro-osmotic permeability is not a constant. This is because the application of an electric field not only generates electro-osmotic flow, but also the associated electrochemical reactions. Over time, these reactions directly change the zeta potential, and inspection of the Helmholtz-Smoluchowski equation will result in a change in electro-osmotic permeability.

2.8.5 Design of Electro- Osmotic Dewatering Apparatus

The mechanism of electro-osmotic dewatering is as shown in Figure 2.4. Electro-osmotic dewatering (EOD) is performed by applying an external electric field under direct current (DC) condition to a semisolid material placed between two electrodes. In the process of EOD for a bed of semisolid material of which the initial water content is uniform throughout the bed, EOD proceeds downwards and the water content in part of the material near the upper electrode opposite to the drainage surface is locally reduced, resulting in an increase of electrical contact resistance between the upper electrode and the material being dewatered (Yoshida and Yukawa 1991; Yoshida and Yukawa 1992; Yoshida 1993). The movement of water is due to an electric double layer, which forms as a result of the polarization of the molecules at the solid-liquid interface. A small electric potential, defined as the zeta potential is formed between the solid and liquid layers. The addition of the various ionic solutions can modify the magnitude of the zeta potential thus modifying the electro-osmotic effect. Most separation technologies are based on a single driving force, such as: molecular size for membrane filtration; density of particles for gravitational separation; ionic mobility of colloidal particles for electrophoresis; and pressure diffusion for centrifugation.

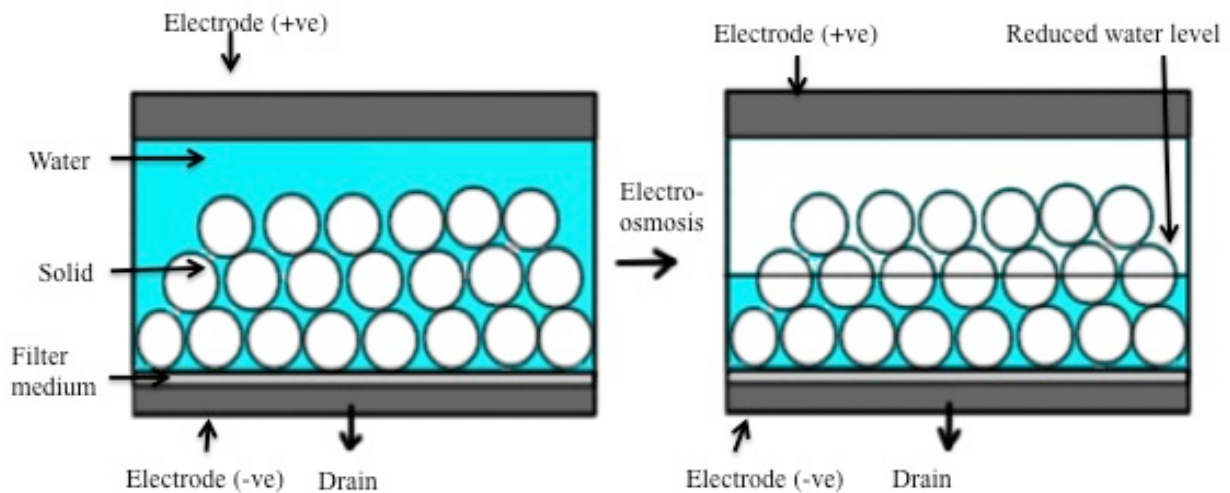


Figure 2.4 Process of dewatering by electro osmosis dehydration. (Mujumdar and Yoshida, 2008)

An improved approach to separation is to exploit two or more driving forces in a single step to increase dewatering efficiency (Orsat et al., 1996; Orsat et al., 1999; Lockhart, 1992). Lightfoot and Raghavan (1994) conducted studies on electrical expression of seaweed and they concluded that electro-osmosis improved expression significantly. Currents of 72.4, 146.9 and 219 A/m² were used to perform electro-osmotic dewatering at pressures of 7.46, 34.6 and 104 kPa above atmospheric pressure. The energy costs for producing dried kelp meal were observed to be significantly lower when dewatering precedes thermal drying. Electro-osmosis was found to be capable of significant energy savings over expression if dewatering followed by drying to produce the final product. For applying EOD practically to various kinds of materials, it is important to increase the dewatering rate, and to decrease the final water content and the electric power consumption for water removal to a maximum level (Rampacek, 1966). From these points of view, various applications of electric field, which are different from continuous DC condition, have been attempted to improve the performance of EOD. In order to reduce the negative effect for dewatering, which is characteristic of EOD, such as the increase of electrical contact resistance, many investigations have been carried out for better and higher performance of EOD. The mechanism of EOD is different from that of such widely used dewatering processes as mechanical methods using fluid pressure, compressive and centrifugal forces. EOD has some advantages compared with mechanical dewatering methods, and it can be more

effective for solid–liquid mixtures consisting of colloidal particles and gelatinous and biological materials that are not successfully dewatered by mechanical methods. In this context we have to discuss about the main factors to be considered for the design of electro – osmotic dewatering system for flax and hemp.

The main factors are,

1. The quantity of stems to be dewatered.
2. Zeta potential of the stem- water mixture (The electric potential between the solid and liquid components, which is a function of the geometry, the pH, and the ion concentration of the substance)
3. The pressure applied (combination of pressure and electro- osmosis is proved to be more economical than electro- osmosis alone (Heath et al., 1984).
4. Type of membrane used.

The conceptual design of the electro- osmotic dewatering system is as follows (Fig 2.5):

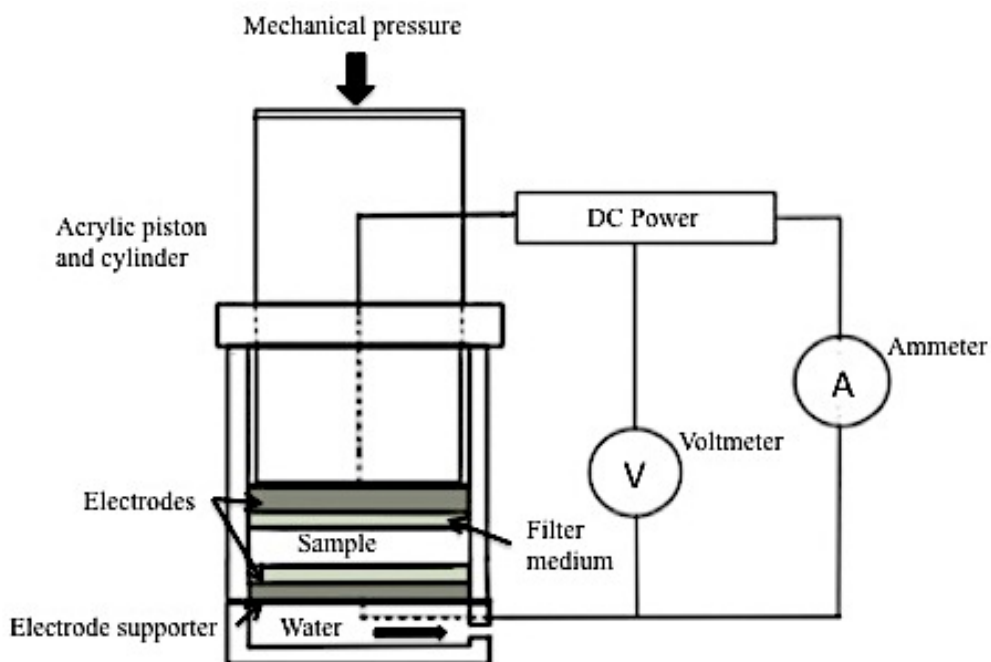


Figure 2.5 Pressurized electro- osmotic dewatering (Mujumdar and Yoshida, 2008)

For the design of electro osmotic dewatering of flax and hemp stems, treatment time is one of the most important factors to be considered and it is to be derived in terms of initial and final

solid concentrations (Yoshida and Yukawa, 1988; Mitchell, 1991). In an electro-osmotic cell, the volume of the sample in the cell V , is expressed as the product of cross sectional area of the cell and the thickness of the sample:

$$V = A L \quad (2.9)$$

where A is the cross sectional are of the sample and L is the thickness of the sample.

The density of the sample is expressed as,

$$\rho_s = \frac{M}{V} \quad (2.10)$$

where ρ_s is the density of the sample, M is the total mass of the sludge in the cell and V is the volume of the sludge in the cell.

Substituting Equation 2.9 into Equation 2.10, the total mass of the sample is,

$$M = \rho_s A L \quad (2.11)$$

Before the treatment, solid concentration of the samples is

$$SD_1 = \frac{m_s}{M} \quad (2.12)$$

Where SD_1 is the initial solid concentration of the sample and m_s is the mass of the dry sample. After the electro osmotic dewatering, the solid concentration is,

$$SD_2 = \frac{m_s}{(M - M_w)} \quad (2.13)$$

Where SD_2 is the final solid concentration of the sample and M_w is the mass of water collected to reduce the solid concentration from SD_1 to SD_2 .

Substituting Equation 2.12 into 2.13, therefore,

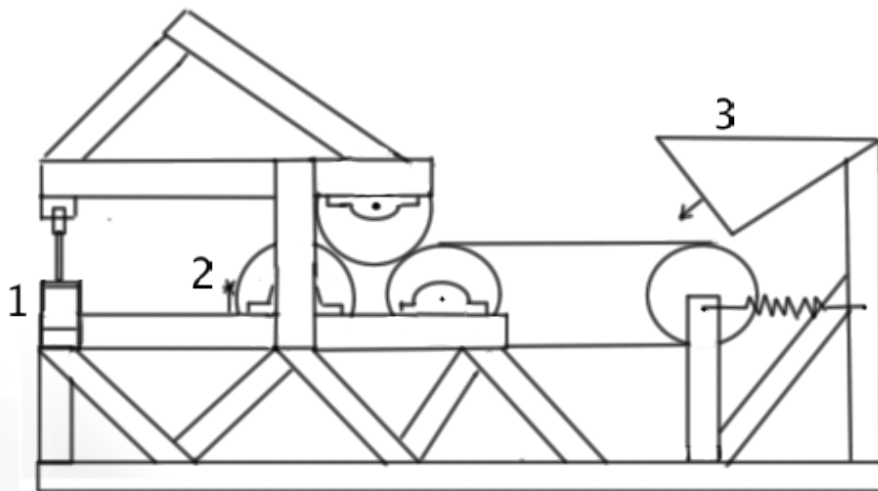
$$SD_2 = \frac{M \times SD_1}{(M - M_w)} \quad (2.14)$$

$$M_w = \frac{(SD_2 - SD_1)M}{SD_2} \quad (2.15)$$

2.8.6 Roller Press for Electro-Osmosis

Roller press electro-osmotic apparatus is another method of dewatering with the help of multiple rollers which acts as electrodes (Figure 2.6). The material to be dewatered passes through the rollers and due to the combined action of the electrodes, roller pressure, roller speed and the voltage. Orsat et al., in 1999 conducted experiments on the effect of chemical pre-treatments in electro-osmotic dewatering using a bench scale electro- osmotic roller press. The studies on chemical pre-treatment on roller press apparatus proved that the potential of combined electro-osmotic press dewatering as a pre-drying process to reduce moisture content with an energy saving when compared to thermal drying alone.

According to Orsat et al. (1999), the addition of electro-osmosis increased the energy requirement in comparison to press dewatering in a significant manner, but at the same time the dewatering efficiency was also increased significantly, which proved the effect of electro-osmosis in dewatering with bench type roller press apparatus. Kondoh et al. in 1990 conducted a successful study of a combined electric and mechanical dewatering. They incorporated electrical field as an addition to a pressure dehydrator, the water content of activated sludge was reduced to 50- 60% when compared to 75-85% achieved with mechanical force, which proved the efficiency of the combination of mechanical force and electro- osmosis.



1. Hydraulic cylinder, 2. Rotating scraper, 3. Feeding chute

Figure 2.6 Roller press electro- osmotic dewatering apparatus (Orsat et al., 1999)

2.8.7 Design Parameters for Dewatering of Flax and Hemp Stems

The design parameters for the electro- osmotic dewatering of flax and hems stems (Grundl and Michalski, 1996) are as follows.

Sample Thickness

From Equation 2.6, it is clearly seen that treatment time (t) is directly proportional to square of the sample thickness (L).

$$t \propto L^2 \quad (2.16)$$

Applied Current

From Equation 2.6, the treatment time (t) is inversely proportional to the current (I)

$$t \propto \frac{1}{I} \quad (2.17)$$

Power Supply

The resistance of dewatering system is minimum when the dewatering starts ($R_0 = \frac{V_0}{I}$). During the dewatering process, the voltage from the power supply needs to be increased with the time of treatment in order to maintain the constant current as resistance increases with time due to electro chemical reaction and desiccation at the anode.

Applied Pressure

When pressure is applied to the highly watered stem sample, a stress is developed on the water in the void spaces as well as in the samples. The increase in pressure causes the void space water to drain off. But from equation 2.8, the electro osmotic flow is independent of pressure (Vijh and Novak, 1997). In practice, the electro osmotic dewatering process can be enhanced by the application of pressure, which produces a significant overall improvement of volume of water obtained.

Type of electrodes

The main criterion in the selection of electrodes is that they must be sufficiently electrically conductive. Besides that, the rate of electrochemical reaction taking place at the electrodes has also to be considered in the selection of electrode material. This is because the surface electrical

resistivity of the electrode increases when electrochemical reaction occurs and high surface electrical resistivity results in a shorter time over which constant current could be maintained. Therefore, an electrode material with a low rate of electrochemical reaction should be selected in the electro osmotic dewatering process as this not only provides a longer time over which constant current could be maintained, but also saves electrical energy due to high surface resistance (Kit, 2006). Dewatering could be conducted to reduce the moisture content to a minimum level. The dewatered stem has to be subjected to microwave drying at controlled temperature for drying it completely.

2.9 Microwave- Drying of Retted Flax and Hemp Stems

The flax and hemp stems after dewatering have to be stored at lower moisture content (10 % (w.b) or below before decortication which, depends on the duration of storage. Nair et al, in 2012, conducted studies on microwave drying of high moisture flax stems to final moisture content of 9% wet basis and compared the results with hot air drying. Flax straw was cut into 0.15 m lengths. The middle part of the plant stem was chosen for the experiment to ensure uniformity in carrying out drying tests. Flax straw samples (25 g) were placed in a jar full of water for 48 hours at room temperature to ensure fully wet conditions. The wetted samples (68-70% w.b.) had their surface water removed using a manually operated centrifugal rotator (salad spinner). The samples were then weighed, and transferred to the microwave apparatus. The microwave drying was done at a temperature of 40°C, 60°C or 80°C. The drying was conducted in an intermittent microwave supply system. The temperature of the drying was almost constant throughout the experiment. The apparatus was adjusted in such a way that, it switched off the microwave generator automatically when the temperature increased beyond the set point and microwave power switched on when the temperature of the product decreased below the set point. The maximum variation was $\pm 3^{\circ}\text{C}$ (Nair, et al., 2012). The drying was conducted till it reached the final moisture content of 9 % (wet basis). Three replicates of each test were done. Flax straw with same initial moisture content were dried by using hot air of 40°C, 60°C or 80°C and the results were compared. At the drying temperatures of 40°C, 60°C and 80°C microwave convective drying took 30.8%, 54.8% and 48.5 % less time, respectively, than hot air drying. Among the microwave- convective drying conditions tested, drying at 80°C method proved to be the most suitable in terms of drying time. Color change and tensile strength were compared and there was no significant difference in the color change and tensile strength between

microwave and hot air dried flax stem samples. Dried flax stem is suitable for the final step of fiber separation, mostly by passing through a mechanical separator to separate fiber and shives.

2.10 Summary

The role of electro-technologies in the processing of fibrous plants from retting till the final step of fiber production is discussed. Microwave and radio frequency are the possible electro-magnetic energies to be used for the fibrous plant retting. The microwave effect makes the retting less energy intensive and less time consuming when compared to other retting methods like water retting, enzyme retting etc. Electro- magnetic energy accelerates the process of release of cellulose by breaking the matrix of binder materials like pectin, lignin wax etc. (Keshwani and Cheng, 2010). Electro- osmosis is a quick method for dewatering of high moisture fibrous plant after retting. Electro- osmosis followed by microwave drying is also a post retting process, which saves a large amount of energy when compared to time taken by hot air drying. The uniformity of drying and rapidity of the process are assured in the above process.

CONNECTING TEXT

Based on the review reported in the previous chapter, retting was found to be the most significant step in the processing of natural fiber. Before going further in to the development of a novel retting method by the application of electro magnetic energy in processing of natural fiber, it is important to evaluate the effect of the conventional water retting and to compare the physical properties of the fiber obtained after retting. To achieve the initial goal, studies on water retting of flax stems were conducted at the Institute of Natural Fiber and Medicinal Plant (INFMP), Poznan, Poland as the part of my summer internship. In the next chapter, flax stems are chosen for the water retting experiments. The retted stems are decorticated to separate the fiber and then the physical properties like tenacity, elongation and its visual analysis are analyzed and the results are compared with non- retted fibers.

CHAPTER 3

COMPARATIVE EVALUATION OF PHYSICAL AND STRUCTURAL PROPERTIES OF WATER RETTED AND NON- RETTED FLAX FIBERS

3.1 Abstract

Flax stems of Modran variety were subjected to water retting under laboratory conditions and their physical properties were compared with non- retted fibers. Physical properties including percentage of impurities, weighted average length, linear density, tenacity and elongation were analyzed and the results were compared. The analysis of retted and non- retted flax fibers showed that retting is the most important step in the processing of flax fibers and it directly affects quality attributes like strength, fineness, and homogeneity. Scanning electron microscope images of fibers were also analyzed and the retted fibers showed much cleaner surface when compared to decorticated non- retted fibers.

3.2 Introduction

Flax (*Linum usitatissimum*) is a fibrous plant and an important commercial crop grown all over the world. Flax plant is mainly grown for its seeds, which are used for various applications from food, cosmetic production to paint mixing (Van Sumere and Sharma, 1991). Flax stem contains natural fibers, which could be used in various applications like production of biocomposites, apparels, high quality papers etc. (Atton, 1989). Flax fibers are comparatively expensive and of high quality when compared to other fibers, which is due to the difficulty of it's processing. Natural fibers including flax fibers are low in density, cheap, and biodegradable. But the big disadvantage of natural fibers is that they do not have same consistency in quality as compared to synthetic fibers. This inconsistency is due to variety of reasons such as climate, crop variety, retting process, and processing equipment used for fibers (Thomsen et al., 2006).

The processing of flax fibers from the stem is usually conducted by passing the straws through series of rollers under pressure exerted by the rollers. This action helps the outer skin, shives and other non- fibrous parts to detach from the fibers and the resultant product is a clean long fiber; the process is called decortication (Sharma and Van Sumere, 1992). In decortication of non- retted flax stems, the resultant fibers are of inferior quality with impurities remaining, because flax fibers are attached between themselves and the stem with chemical bonds such as pectin

bond, which cannot be broken completely by applying mechanical pressure. In order to release the fiber completely from the stem, these stems have to undergo a process called retting. Retting process employs the action of micro-organisms and moisture on plants to destroy the cellular tissues and pectin surrounding bast-fiber bundles, and hence facilitating separation of the fiber from the stem (Thomsen et al., 2006). Two primary methods for retting, namely water and dew retting have been traditionally used to extract fibers for textile and other commercial applications (Foulk et al, 2001). According to available literature, dew retting is considered to be the oldest method of retting. The quality of dew-retted fiber is inferior than water retted fiber, but due to the lower labor costs and high fiber yield, it remains as an attractive practice for the farmers. In dew retting, the stems are pulled and spread uniformly on the ground in a thin layer for 3-4 weeks. Changes in moisture and temperature result in the colonization and partial degradation of flax stems, mainly by saprophytic fungi. The main disadvantage of dew retted flax fiber is its poor and inconsistent qualities. The field use of 3-4 weeks is also another drawback of the process (Sharma, 1988). In water retting, straw is submerged in water tanks, where a pectinolytic bacterial community develops (Baley, 2002). *Bacillus* species are dominant for 10 to 40 hours after the start of the water retting process, and are followed by spore-forming anaerobic *Clostridium* spp. when oxygen concentration in water tanks becomes lower. Clostridia, the major group of bacteria, which shows pectin-degrading activity, are responsible for water retting (Akin et al., 2002). The sources of retting bacteria are suspected to be adhering soil particles, stem dust, air, and water. In water retting, consistent conditions for bacterial growth and activity exist, which results in the evenness of inoculum and colonization by bacteria and in turn the quality of the retted fiber. Though water retting produces the highest quality flax fiber, the environmental pollution caused by it forced the industries to regulate the procedure and find other alternatives like enzyme assisted retting, steam explosion and electromagnetic energy assisted retting (Akin, 2013).

The objective of this study was to understand the effect of water retting at controlled temperature on the physical properties of Polish flax variety Modran.

3.3 Experimental Section

3.3.1 Flax Straw

Non- retted flax straws were collected from the Institute of natural fibers and medicinal plants, Poznan, Poland. The average technical length and thickness was measured by taking average of 100 samples. The technical length is the distance between the beginning of root and first branch. Thickness of the straw was measured at the middle of the straw samples.

The average technical length of the flax straw was 60.42 ± 1.02 cm and the average thickness of the straw was 1.54 ± 0.13 mm. The color of the flax straw bundle was 60% yellowish and 40% greenish, which threw light on the maturity of the flax stems, because yellow stem indicates maturity and the green stem relatively less maturity. The color analysis was carried out by visual analysis.

3.3.2 Non- Retted Flax Fiber

Non- retted flax fibers were processed from non- retted flax stems at the Institute of Natural Fibers. The decorticated flax fiber contained high percentage of shives, dust and other impurities.

3.3.3 Water Retting of Flax Straw

Water retting chamber was a stainless rectangular chamber of 2m x1m dimension. The chamber was connected to a temperature control system, which maintains the temperature of the water in the chamber during retting. The samples were kept in the retting chamber and concrete bricks were placed on the top of the straw bundles to avoid the straw from floating. After keeping the samples inside the chamber, the chamber was filled with water until all the samples were submerged in water. The temperature of the treatment was controlled at 32° C for better bacterial activity and the duration of treatment was 72 hours. The chamber after 72 hours is as shown in Figure 3.1. After the treatment duration of 72 hours the water was drained out and retted samples were rinsed. The samples were then passed through a roller press twice before subjecting them to drying. The samples were transferred to a hot air oven for 24 hours at 80° C. Once the drying process was completed, the samples were taken out of the oven and kept at room temperature for 72 hours before further processing. This is needed to acclimatize the fibers

to the processing temperature and reduce any impact of processing on the physico-chemical properties of the fiber.

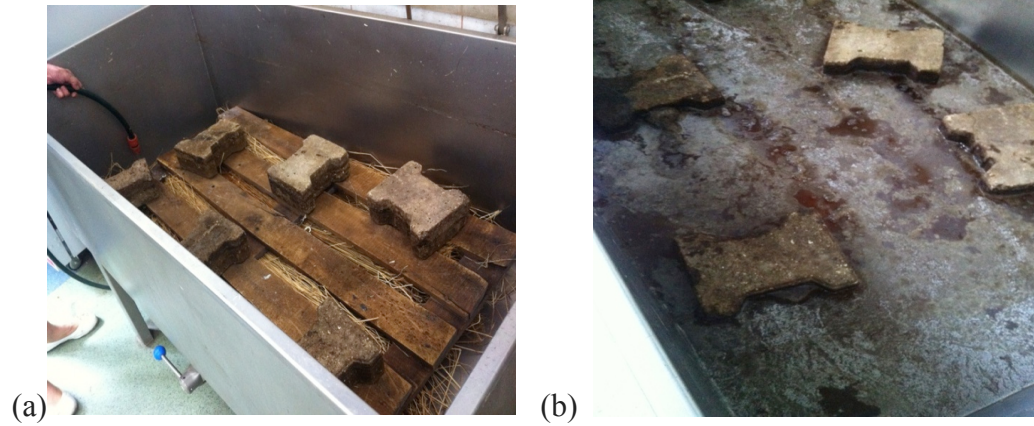


Figure 3.1 (a)Water retting of flax stems. (b) retted flax stems after 72 hours

After three days, the dried samples were passed through a turbine-scutching machine, which separates long and short fibers from the flax stems.

3.3.4 Measurement of Impurity

Impurities were separated from a known quantity of flax fiber samples and the impurities were weighed. Impurities included shives, dust, wax etc. If the total mass of sample is represented as M and the weight of impurities was m_i , the percentage of impurity is calculated using the following equation.

$$\text{Percentage of impurities (\%)} = \frac{m_i}{M} \times 100 \quad (3.1)$$

3.3.5 Scanning Electron Microscope (SEM) Analysis of Fiber Structure

The cross sectional and longitudinal analysis of flax fibers was performed using a SEM (Hitachi S- 3400 N). The flax fiber samples were prepared and attached on a metal plate as shown in Figure 3.2 and the plate was transferred to a chamber for gold coating. The samples were then inserted in the SEM chamber and magnified to study the structural properties.

3.3.6 Weighted Average Length of Fiber

The length of the fiber was analyzed manually using a cloth as shown in Figure 3.3. The climatic condition for the experiment was set at a: temperature of $20 \pm 2^\circ \text{C}$ and $65 \pm 2\%$

relative humidity. The flax fiber samples were weighed to measure their mass and separated manually in various ranges or classes starting from 0-2 cm, 2-4 cm up to 68-70 cm.

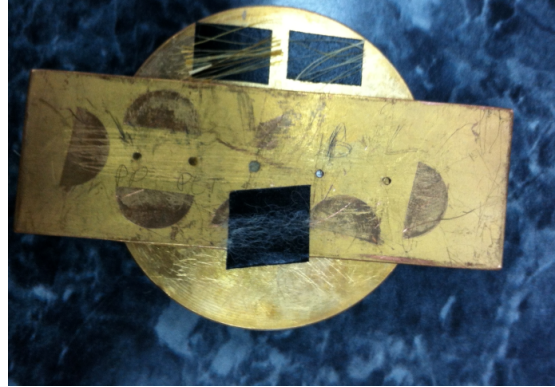


Figure 3.2 Flax fiber samples prepared for SEM analysis.

After the process of separation, the flax fibers in each class were weighed to nearest 0.001 g and the percentage by weight in each section was documented (Akin et al., 2001).

The length of the average weight was calculated by using the following equation:

$$\text{Weighted average length} = \frac{\text{Sum of (average length of the class} \times \text{mass of the fibre)}}{\text{total mass of the fibre}} \quad (3.2)$$

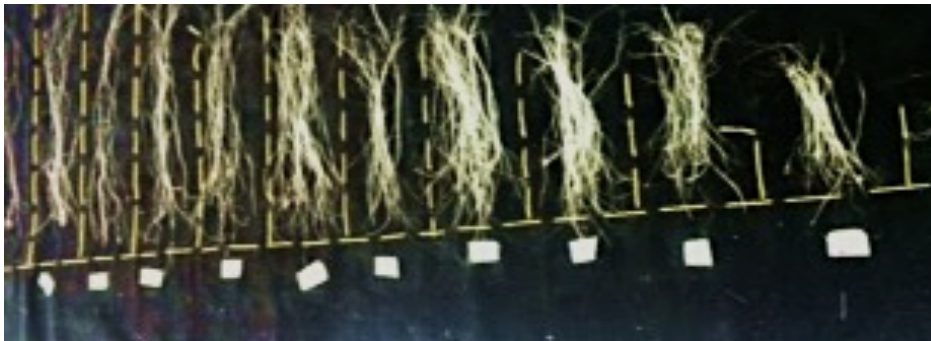


Figure 3.3 Weighted average length of flax fiber

3.3.7 Linear Density (Thinness)

The linear density or thinness of the fiber determines its fineness, and it is expressed as “Tex” (Wang et al., 2007). Prior to linear density analysis, the samples were acclimatized under ambient conditions of temperature of $20 \pm 2^\circ \text{C}$ and relative humidity of $65 \pm 2\%$. Samples were prepared by cutting sections of 10 mm length from the middle portion of the flax fibers to ensure

the evenness in analysis. From the samples, 100 fibers were separated in such a way that if a given fiber splits into two up to half of the length of the fiber, it should be considered as two separate fibers and should be counted as 2 fibers. Sometimes from one-fiber sample, we could get 3 or more separate fibers. After counting 100 fibers, the samples were weighed to nearest 0.1 mg and linear density was estimated using the following equation.

$$\text{Tex} = \frac{\sum m}{n} \quad (3.3)$$

Where, m is the mass of the samples and n is the number of samples. The experiment was repeated five times for a better statistical validation.

3.3.8 Tenacity and Elongation

Breaking tenacity and elongation were measured using STATIMAT ME testing machine (Textechno Herbert Stein GmbH & Co. KG, Germany). The acclimatized flax fiber samples without any impurities on the basis of mass (20 Tex) were taken and the length of the samples were fixed at 7 cm. Each sample was then mounted on the testing machine with a gauge length of 3 mm. 100 N load cell and the test speed of 10 mm/min was used to estimate the breaking tenacity, elongation and coefficient of variation of breaking force.

3.4 Results and Discussion

The fibers obtained from decortication without retting and long and short fibers after retting were tested for their physical properties and are reported here.

3.4.1. Impurities

The impurities in non- retted flax fibers and retted flax fibers were measured and tabulated in Table 3.1.

Table 3.1 Percentage Impurities in fibers.

Fibers	Impurity (%)	SD
Non retted	38	0.05
Retted (long)	0.3	0.01
Retted(short)	16.5	0.03

From the table, it can be observed that the percentage of impurities was maximum in non-retted decorticated flax fibers and minimum in retted turbine scutched long fiber (Akin, 2005). In non-retted flax fiber, the stem parts are attached closely to the fiber bundles by strong pectin bonds (Sharma, 1988). Hence, it was concluded that decortication process without retting is not enough to obtain pure fibers.

3.4.2 SEM Analysis

The SEM cross-sectional views of non- retted and retted fibers are shown in Figure 3.4.

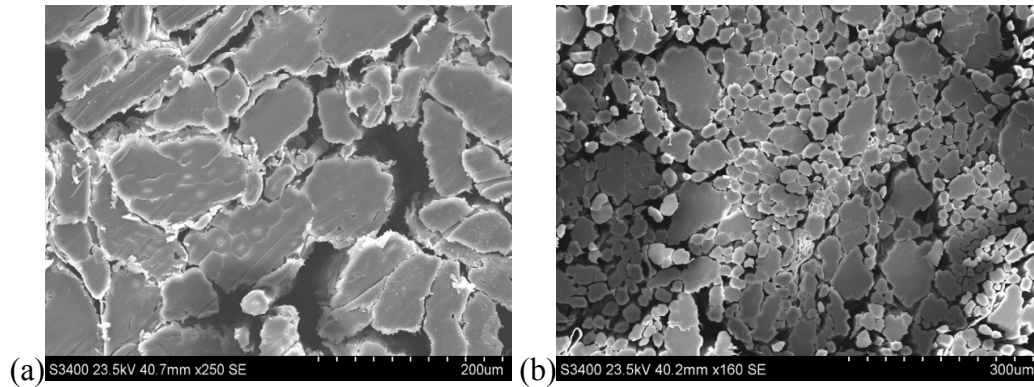


Figure 3.4 Cross- sectional view of (a) non retted and (b) retted flax fiber (a)

It can be observed that in non- retted flax fiber (Figure 3.4a), the fibers were bundled because waxes, shives and other impurities were attached to them (Akin et al., 1996), but the retted fibers (Figure 3.4b) were more separated and of smaller cross-section because of retting. The effect of retting in processing of flax fiber is illustrated in Figure 3.5. The non- retted flax fibers (Figure 3.5a) were rough and their surface contained lots of foreign particles like lignin, wood parts and dust. But retted flax fibers (Figure 3.5b) were clean and of high visual quality.

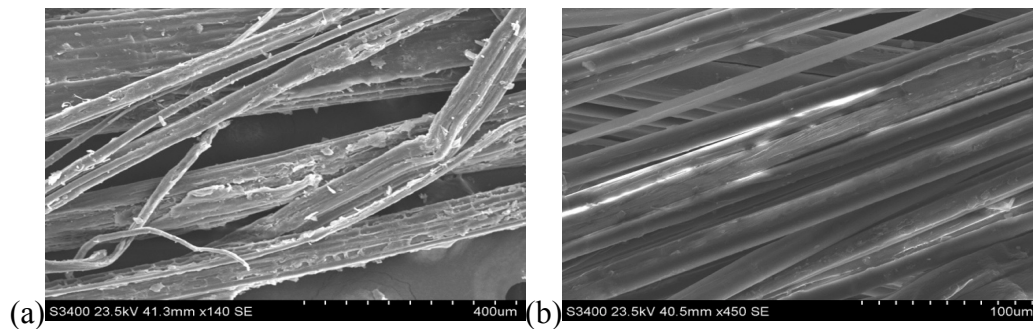


Figure 3.5 Longitudinal SEM view of (a) non- retted and (b) retted fiber

3.4.3 Weighted Average Length

Figures 3.6-3.8 represent the percentage weighted average length of non-retted and retted short and long fibers

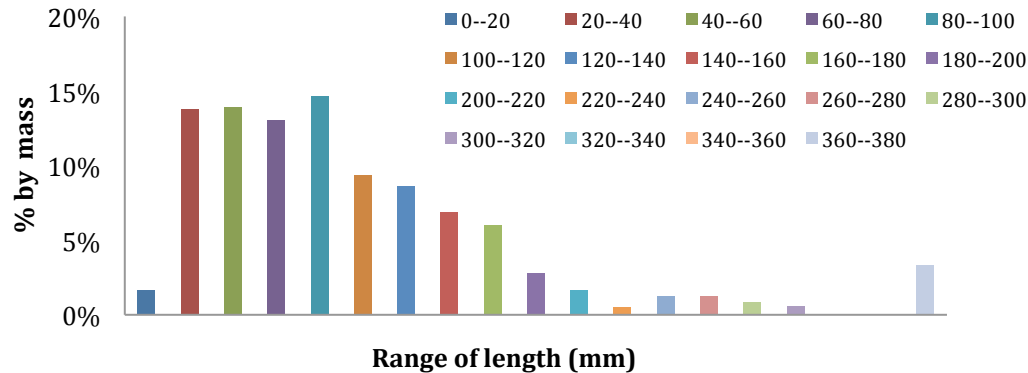


Figure 3.6 Percentage of lengths by mass – non-retted flax fiber

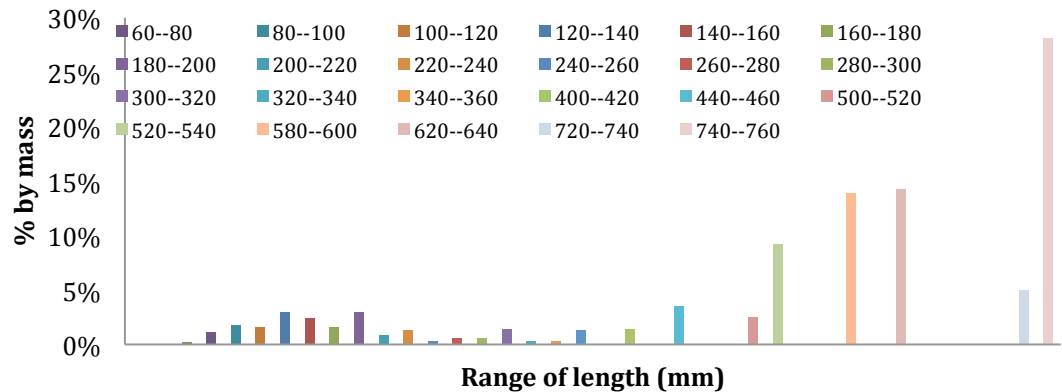


Figure 3.7 Percentage of lengths by mass – retted flax fiber (long)

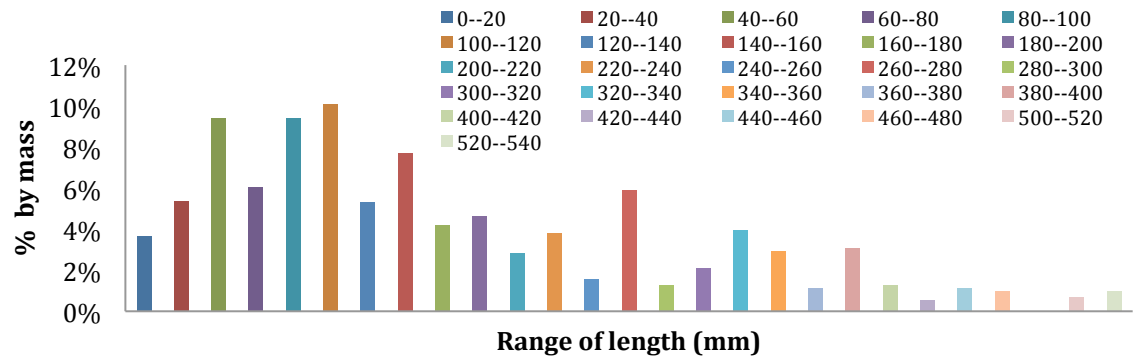


Figure 3.8 Percentage of lengths by mass – retted flax fiber (short)

50% of non- retted flax fibers were of the length between 20 mm to 100 mm and 30% of retted long fibers were within the range of 740-760 mm. 50% of retted short fibers were located within 20 mm to 160 mm range. The weighted average length of the flax fibers were, 108.5mm, 543.9 mm and 175.1 mm for non- retted, retted long fiber and retted short fiber respectively. The weighted average length signifies the application of fibers; long fibers are used mainly in textile industries whereas short fibers are used in bio-composites and paper industries (Foulk et al., 2001).

3.4.4 Linear Density (Thinness) of the Flax Fibers

Table 3.2 represents the linear density (thinness) of all the flax fibers. It can be observed that retted long and short fibers had the lower linear density in comparison to non-retted flax fibers. Similar result was observed in the SEM analysis of the fibers.

Table 3.2 Linear densities of flax fibers

Samples	Linear density (Tex)	Coeff. of variance (%)
Non retted	3.26	19
Retted (long)	2.54	9
Retted (short)	2.3	19

3.4.5 Tenacity and Elongation

Maximum load, elongation, work to rupture, bundle strength and time to rupture are tabulated in Table 3.3.

Table 3.3 Strength test result comparison of retted and non- retted fibers

Samples	Force (N)	Elongation (%)	Work to rupture (N.cm)	Bundle strength (daN/mg)	Breaking force cN/Tex	Time to rupture (sec)
Non- retted	58.75	41.35	4.012	2.218	39.73	12.16
Retted (long)	72.76	44.67	11.09	2.73	39.97	29.78
Retted (short)	65.64	42.9	4.74	2.38	41.37	13.37

The breaking force was 39.73 cN/Tex for non- retted fiber, 39.97 cN/Tex for retted long fiber and 41.37 cN/Tex for retted short fiber. It was concluded that the strength of the retted fiber was more than that of non- retted flax fiber. There are not much difference among the elongation percentage of all the samples. The strength analysis revealed that, retting improved the bundle strength, breaking force, work to rupture and elongation.

3.4.6 Industrial Applications of Biofibers

Flax fibers have many applications depending on their physical qualities; some of the major applications are discussed below.

Speciality Paper and Pulp

Flax fibers are used to make high quality papers for currencies, cigarettes, filter media, condenser and battery separator pages. Hammer milled non-retted oilseed flax fibers are used to make speciality pulps for high quality papers (Foulk et al., 2008).

Insulation

Non- retted flax fiber composites are used as both sound and thermal insulators. Bio-based fiber reinforced mats are recommended mainly because of their high degradability which helps in reducing environmental pollutions (Reddy and Yang, 2005).

Geotextiles

Geotextiles are used for making ground cover to suppress weeds, control erosion by keeping the top-soil, rain water filtration and should be degradable as well. Non- retted flax fibers could be used as geotextiles while considering its strength, hydrophilic nature, and degradability (Foulk et al., 2008).

Building Products

Flax fiber composites are used for making various types of building materials replacing concrete blocks to make houses, substitutes for wooden materials, and plastic materials (Mohanty et al., 2002).

Textiles

Retted long fibers are used in the textile industry. The processed flax fibers is subjected to various processing steps like bleaching, coloring, weaving to obtain the final product (Turner, 2008).

Bio-Plastic Composites

Retted long and short fibers are used in the plastic composite industry; Composite industry includes lots of possible end-use applications ranging from airplane bodies to pipes, to mining slurry containers to pocket calculator bodies. Bio- plastic composites are fiber-resin matrix, which is made by compression molding, vacuum molding, sheet compound molding, rotation molding, extrusion molding, injection molding and shoot and spray molding (Alix et al., 2008).

3.5 Conclusion

From the analysis of physical qualities of retted and non- retted flax fibers, it can be concluded that retting is the most important step in the processing of flax fiber in terms of its physical and structural qualities. The fibers from retted flax straws could be used for high end applications like in textile and automotive industries, whereas the fibers from non- retted flax stems can be used for products like door mats, geotextiles.

CONNECTING TEXT

Preliminary studies on water retting proved the role of retting in the processing of flax fiber. After learning the physical and structural changes associated with retting for flax stems, next objective was to develop a novel retting method for the processing of flax stems by applying microwave energy on the pre- soaked flax stems for short durations. Next chapter discusses the application of microwave energy in retting of flax stems and the analysis of the physical and compositional changes of fibers extracted from the stems.

CHAPTER 4

MICROWAVE-ASSISTED RETTING - A NOVEL METHOD OF PROCESSING OF FLAX STEMS

4.1 Abstract

A new method for retting of flax stem was introduced by using microwave energy. The combined effect of pre- soaking, microwave volumetric heating and the non- thermal effect of microwave energy were applied in the retting of flax stem. Effective retting was observed in various combinations of pre-soaking, microwave treatment times and microwave energy. The samples soaked for 24 and 36 h with microwave treatments of 20 minutes showed better retting efficiency when compared to 12 h soaked samples. Fried tests, near infrared analysis and fiber diameter distribution analysis were subjected to analysis in order to find out the retting efficiency. Experiments were conducted on microwave- assisted retting and the effect of non-thermal effect of microwave was proved experimentally. Colorimetric tests and tensile strength tests were conducted to compare the quality of fibers after microwave retting and no significant changes in the physical qualities were observed. The remaining water after microwave- assisted retting was not contaminated because of less microbial activity in short duration of the entire process. From industrial point of view, this method is acceptable because of the ease of recyclability of the pre-soaked water and comparably short duration of the process.

4.2 Introduction

Flax (*Linum usitatissimum*) is a fibrous plant, which is abundantly grown globally, and flax fiber is a natural fiber processed from the flax stems. It has potential applications in various sectors like apparel industries, paper industries, bio-composite industries etc. Flax fibers are of high quality and are being used as a replacement for synthetic fiber, but these fibers are expensive when compared to synthetic fibers. This is mainly due to various difficult stages involved in the processing of flax fiber from its stem. The most important and energy intensive step in the processing of flax stem is retting, which is the separation or loosening of bast fibers from shive and other non-fiber fractions, leading to a major problem in flax fiber processing (Sharma and Van Sumere, 1992; Foulk et al, 2001). Retting should be done very carefully; otherwise the process will turn up either as an under- retted or over-retted stems. Under-retted flax produces

coarser low quality fibers with shive and cuticular fragments, and over-retting results in maximum destruction of cellulose that leads to excessive thinning of fiber. Two conventional retting methods, namely water retting and dew retting have been used to extract fibers for textile and other commercial applications. The duration of these processes range from 1-2 weeks depending upon the variety of flax. Even though the quality of fiber by water retting is much higher than that of newer methods, this practice has been largely discontinued everywhere due to the high costs and the pollution and contamination arising from fermentation of the plant material. Enzyme assisted retting is a relatively new process which is considered to be a replacement for the conventional retting methods. Enzyme assisted retting is performed by introducing enzymes like pectinases to the plant stem surface which disintegrate pectin and hemicellulose which then separate fiber from the non-fiber tissues (Akin et al, 2005). The duration of this process ranges from 8 hours to 24 hours. Non-reusability of enzymes is a main concern, which affects the cost effectiveness of the process. This made us think about an alternative physical method for the retting of flax stem, which involves no chemical interaction and no environmental pollution. There are some studies, which have attempted to quantify non-thermal effect of microwave in biomass processing. Therefore microwave energy could be applied to release the fiber from the plant cell walls of flax. Microwaves are part of the electromagnetic spectrum and microwaves are considered to be ranging in frequency from 300 MHz to 300 GHz. This non-ionizing electromagnetic radiation is absorbed at molecular level and manifests as changes in vibrational energy of the molecules or heat (Banik et al., 2003). Microwave is widely used for heating in various post harvest processing industries (Kim et al, 2011). There are evidences of biological changes caused by application of microwaves. These changes are attributed to thermal effect of microwaves (Gandhi, 1987). Later research threw some light on the area of non-thermal effects of microwaves in terms of the energy of the alterations of molecular structures in the presence of microwave energy. When lignocellulosic materials like flax stems are placed in an electric field for dielectric treatment, dipole molecules such as water molecules inside the flax stem rotate vigorously to orient in the electromagnetic field. Inside electromagnetic field, flax stem acts as a non-homogenous material that allows more polar components to absorb more energy that creates “hot spots” in flax stem. According to the hypothesis, this unique method of heating results in an “explosion” effect in the particles and leads to the disruption of the lignocellulosic structures of flax stem. Apart from that, the

non-thermal effects of electromagnetic field accelerate the disintegration of the lignocellulosic compounds (de la Hoz et al., 2005, Yin , 2012). By applying Planck's law at 2450 Hz, which is the frequency of commercial microwave radiation, the energy carried by microwave photons is only around 1 joule per mole. This energy is way too low to initiate any chemical activity in materials. Therefore, microwave radiation alone cannot achieve any structural and chemical changes in materials. However, when the material to be treated exposed to microwaves containing polar molecules and ions, the radiation can accelerate chemical, biological and physical processes (Sridar, 1998). However this concept is debatable and needs further intensive studies. In light of this scenario, the objective of this paper is to study microwave assisted retting process of the flax stems.

4.3 Materials and Methods

The materials used and the methods adopted for the study are discussed in this section.

4.3.1 Flax Stems

The non-retted flax straws used in all experiments were received from LENAUPÔLE fiber, Montreal. The stems were cut in to 5 cm length in order to fit it inside a test tube. The moisture content of the flax stems was 3.93% w.b. The middle part of the plant stem was chosen for the experiment to ensure uniformity in carrying out drying tests. Flax straw samples (5 g) were placed in a test tube of 50 ml capacity container full of water for various soaking times at room temperature to ensure fully wet conditions.

4.3.2 Microwave Apparatus

The retting of flax straw was performed using a microwave apparatus designed in the post harvest technology lab, Macdonald Campus, McGill University (Fig 4.1). The microwave generator operated at 2450 MHz with a variable power from 0 to 750 W. The temperature of the flax stem was measured with the help of an optical fiber probe (Nortech EMI-TS series, Quebec City, Canada). The temperature probes were connected to an Agilent 34970A data acquisition unit and that unit was connected to a computer. A hot air supply was attached to the microwave oven to pass hot air through the microwave oven to remove the moisture generated by the samples (Nair et al., 2012).

4.3.3 Experimental procedure

The procedures followed for various experiments are discussed in this section.

4.3.3.1 Microwave treatment

Non-retted flax stems of 5 g each were soaked in water at room temperature in separate test tubes of 50 ml capacity. The soaking periods were 12, 24 and 36 hours. The pre-soaked flax stems of 5 g containing 50 ml water were subjected to microwave treatment in the microwave chamber at varying times and power levels. Water is used as a solvent in this treatment, because water is a readily available commodity and it is an environment friendly solvent for microwave assisted treatment; also water soaking ensures removal of inorganic salts, colored materials and soil particles from the flax stems (Akin et al., 2003).

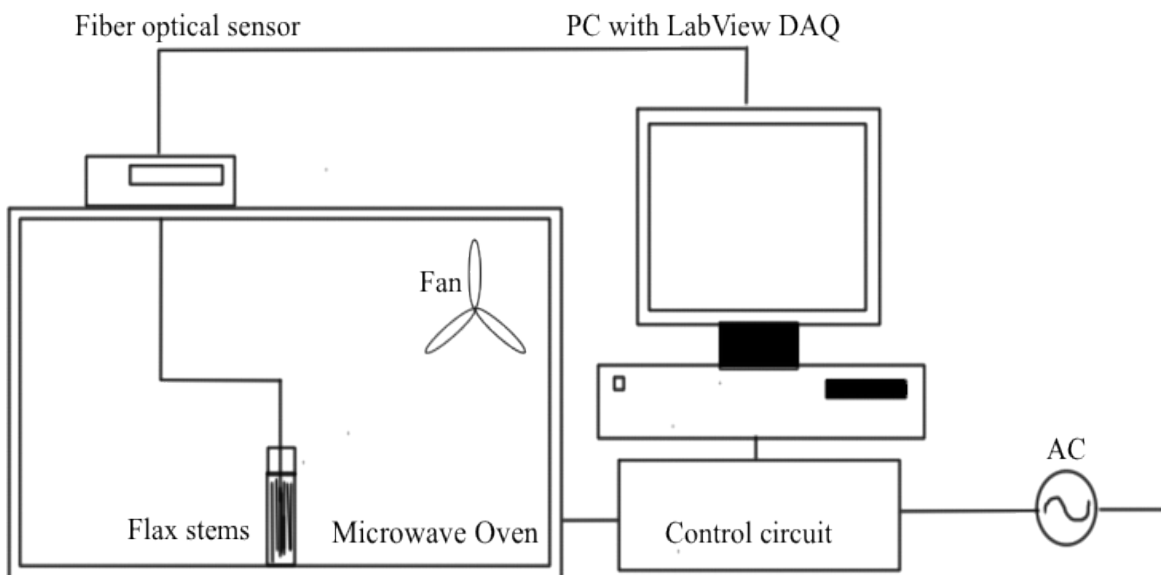


Figure 4.1 Microwave apparatus for retting of flax

Pre-soaking ensures equal distribution of water inside the stems which helps in effective retting by reducing the glass transition temperature of compounds like pectin, hemicelluloses and lignin (Tsubaki and Azuma, 2011). The pre-soaked flax stems were subjected to microwave treatment in the microwave chamber at varying time and power levels. The power levels were 1, 1.5 and 2 W/g and the residence time of retting was 10, 15 and 20 min. The temperatures were not controlled and monitored during the whole microwave treatments.

The experimental design of the treatment is shown in Table 4.1. A full factorial design was established with 3 levels and 3 factors and the experiments were replicated thrice.

Table 4.1 Experimental design of microwave- assisted retting of flax

Factors	Levels	Description
Pre-soaking time	1	12 h
	2	24 h
	3	36 h
Microwave retting power	1	1.0 Wg ⁻¹
	2	1.5 Wg ⁻¹
	3	2.0 Wg ⁻¹
Microwave retting time	1	10 min
	2	15 min
	3	20 min

4.3.3.2 Measurement of Retting Efficiency

The treated flax stem samples were subjected to a Fried test, which is, the test to find out the retting efficiency. Four flax stems were taken in a test tube, and 8 ml of boiled water was added into it. Then the closed test tube was vortexed for 10 seconds. After that, the test tube was shaken hard vertically for 4 times. Then the test tube was opened and retting efficiency was checked. Retting efficiency was measured on a scale of 0-3. After Fried test, if no fiber peeled off from the stem, the value is 0, at the same time if all the fiber peels off, the reading is 3 (Van Sumere, 1992; Henriksson et al., 1997; Akin, 2013).

Then the samples were dried and the fibers were taken out manually. The physical qualities of fiber such as color, fiber contents, diameter distribution and tensile strength were measured.

4.3.3.3 Near Infrared Spectrometer (NIR) analysis

In Fried test, retting was explained as a visual score ranged from 0 to 3, but in NIR spectrometer analysis, the retting efficiency was determined on the basis of the changes in the compounds in the flax fiber related to non retted samples (Sohn et al., 2004). So the flax fibers after retting were subjected to near infrared analysis using a NIR spectrometer. The model used for the

analysis was Nicolet Antaris FT-NIR analyser at BRI, Montreal, Canada. 3 g of flax fiber samples were mounted on the apparatus and test was done. The analyzer makes 300 scans to analyse the sample. The results are logged into the computer connected to the spectrometer. The NIR spectroscopy result will indicate how the chemical composition has changed when compared to the control. It helps in analyzing the changes in the composition of lignin, hemicelluloses (impurities), cellulose (to analyze strength) etc.

4.3.3.4 Colorimetric Measurements

Changes in the color of flax fibers after microwave assisted retting with respect to non-retted samples were compared. Color was assessed within the CIE 1976 L^* , a^* , b^* color space (CIE, 2007) using a tristimulus colorimeter (Minolta Co. Ltd., Japan). Color values, expressed as L^* (whiteness or brightness/darkness), a^* (redness/greenness) and b^* (yellowness/blueness) were determined for all samples.

Twenty millimeter thick flax fiber samples were placed on a table, and the L^* , a^* , b^* values were measured by pressing the measuring head on the top of the samples. Three replicates of each sample were measured. Non-treated flax fiber samples were taken as standards and color change after the retting of the flax fiber was calculated with respect to the standards. Color difference values of ΔL^* , Δa^* and Δb^* were calculated by subtracting the respective standard color values from the measured values for each set of retted experimental samples (Nair et al., 2012).

The total color difference ΔE is measured as (Minolta, 1991):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (4.1)$$

4.3.3.5 Fiber Diameter Distribution Analysis

The cross sectional shape of a single flax fiber is almost an irregular polygon but it is represented as almost circular for its characterization in terms of its diameter (Grishanov et al., 2006; Bourmaud et al. 2013). Diameter of the fiber has to be analysed to understand the effectiveness of retting. An effective retting gives maximum percentage of fine fibers rather than coarse fibers (Fouk et al., 2011). The diameter distribution of the fiber was conducted as per ASTM Standard D7025 by using fibershape version 5.2 image analysing software. Fiber portions were taken randomly from the fiber bundle and those fibers were spread on a glass slide

and inserted into a Nikon scanner. The image showed by the scanner was analysed by a computer connected to the scanner with the help of software named Fibershape Version 5.2.

4.3.3.6 Tensile Strength

Five samples of flax fibers were randomly selected from the retted fibers and each samples were tested three times (ASTM D3822-07). For the tensile strength test, the desired length of the fiber was 75 mm, with a gauge length of 50 mm. The fiber was fixed on a 50 mm × 10 mm sheet of paper with epoxy, so as to maintain the fiber in a straight and extended position. The flax fiber attached to the paper was mounted on the tensile test machine, the top end being attached to the machine with the help of a high-grip clip and the other end being connected to the chuck at the bottom. After mounting on the machine, the edges of the paper were carefully cut away and force applied in tension until the fiber broke into two. The force and displacement were recorded (Yuan et al., 2001; Nair et al., 2011). Five sets of experiments were done, each with three replicates. The experiments were repeated for retted and non-retted samples and the results analyzed.

The tensile strength of the flax fiber was calculated using the equation:

$$\sigma_t = \frac{F_{\max}}{A} \quad (4.2)$$

where,

σ_t is the tensile strength in (Pa) N m⁻²,

$F_{\max}$ is the maximum force applied (N), and

A is the cross sectional area of the fiber (m²)

4.3.4 Statistical Analysis

The statistical analysis of variance (ANOVA) of the samples was performed to assess which treatments had significant ($P \leq 0.05$) effects on measured parameters using SAS. Means were compared using Duncan's Multiple Range test ($P \leq 0.05$).

4.4 Results and Discussion

The results and discussion related to this study are presented in this section.

4.4.1 Microwave Treatment and Retting Efficiency

Microwave assisted retting was carried out with pre-soaked flax straw samples with variable treatment conditions. The flax stems were subjected to Fried tests to find out the retting efficiency. The result of the Fried test was in the scale from 0-3, where 0 represents no fiber separated from the stem and 3 represents 100% separation. The result is presented in Fig 4.2. From the figure, the treatments 36 hours pre-soaked, 2W/g microwave treated for 20 minutes (36h-2W-20 min) samples and 24h- 2W-20 min samples showed almost 100 % retting efficiency. All the 3 sets of samples (12 hours pre-soaked, 24 hour pre-soaked and 36 hour pre-soaked) showed an increasing trend in retting efficiency within their groups. The 24 hours pre-soaked flax stems treated with a microwave power of 2W/g showed maximum retting efficiency and therefore it is considered as an optimum method in terms of retting efficiency.

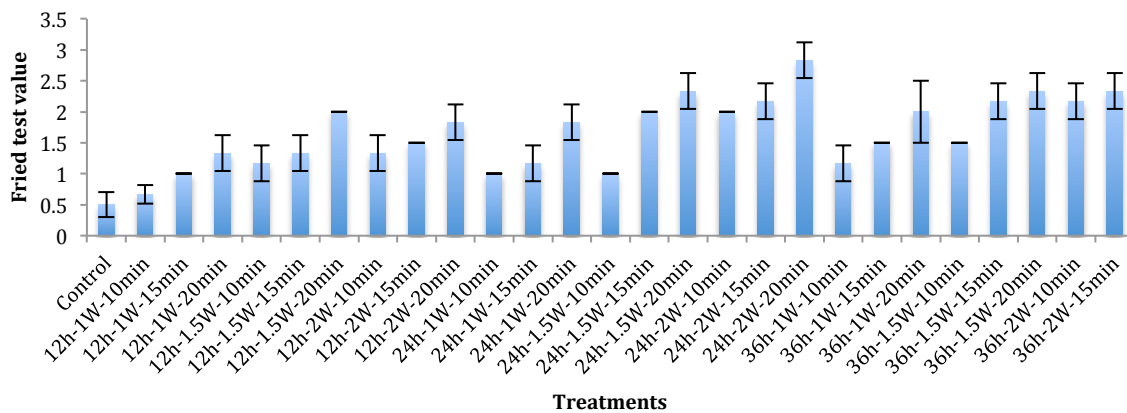


Figure 4.2. Retting efficiency of various treatments (Fried test)

The experiments showed that retting efficiency increased with microwave treatment for all the levels of experiments. This is because of the effect of microwave in breaking the strong pectin bonds attached to the flax fiber, which is termed as “non thermal- effect” of microwave processing. The effect of microwave assisted retting is a combination of both thermal and non-thermal effect, ie, volumetric heating, selective heating, hot spots, and non- thermal effect of highly polarizing field together helped to achieve the retting process (de la Hoz et al., 2004). Selective heating was explained based on the heterogeneity of the flax stem in terms of its compounds where polar substances were heated up faster than non polar substances and as a result, there was formation of hot spot within the plant stem where the temperature was more

than that of the surrounding areas (Lukasiewicz, 2003). From the earlier studies, it is revealed that microwave photons cannot induce any chemical bond breaking (Stuerga and Guillard, 1996). But the observed effect is due to the combined effect of microwave power, incident time and thermal and non- thermal effects in combination. However, the effect of non- thermal occurrence independent of other parameters is difficult to separate.

Microwave assisted retting is influenced by the pre-soaking time, microwave energy and the treatment duration. Pre-soaking time is the first factor to be considered. Pre -wash helped to remove contaminating inorganic salts, coloured materials, and soil (Sharma and Van Sumere, 1992). Akin et al. in 2003 conducted studies on enzyme retting of pre- soaked and control flax stems. They found that the pre-soaked flax stems eased the retting process and the resultant fiber was of fine quality. Results presented from the analysis of pre- soaked water indicate that the water extract from these flax samples is a complex mixture of compounds, including sugars and aromatics representative of the type found in intact plants (Akin et al., 1996). Pre- soaking led to the water intake through the outer skin. So, due to pre- soaking, the flax stems were highly moist so that there were plenty of free water molecules inside the plant cell. An increase in moisture decreases the glass transition temperature of the binders like pectin because of the breaking of intermolecular hydrogen bonding; hence the pectin hydrolyses easily with the thermal and non-thermal effect of microwave power (Tsubaki and Azuma, 2011). Temperatures of the treatments were monitored and since the residence time was short, there wouldn't be any effect of temperature in retting process. The experiments were conducted on the pre –soaked flax stems in a hot water bath at 100° C and no visual changes were observed during the process.

NIR spectrometer was used to analyze cellulose, lignin and hemicellulose content of the fibers from various processes and compared with the control sample. Figure 4.3 demonstrates the cellulose content of the fibers obtained from different treatments, which is compared to the non-microwave treated flax fiber soaked for 24 hours. Control samples were prepared after subjecting them to pre-soaking for 24 hours. From the graph, it is seen that there was an increase in the cellulose content in all the samples compared to control. But the difference in the cellulose content was not statistically significant. The increase in cellulose content is attributed to the microwave treatment on those pre-soaked flax stems. The increase in cellulose in the treated flax is the symptom of effective retting because it is the indication of the release of cellulosic fibers from the matrix. It is experimentally proven that, cellulose content increases

with an increase in the retting efficiency (Hessler, 1945; Putnina and Kukle, 2011). The minimum cellulose content in the control sample was clearly a sign of improper retting where bast fibers were surrounded by non- cellulosic materials.

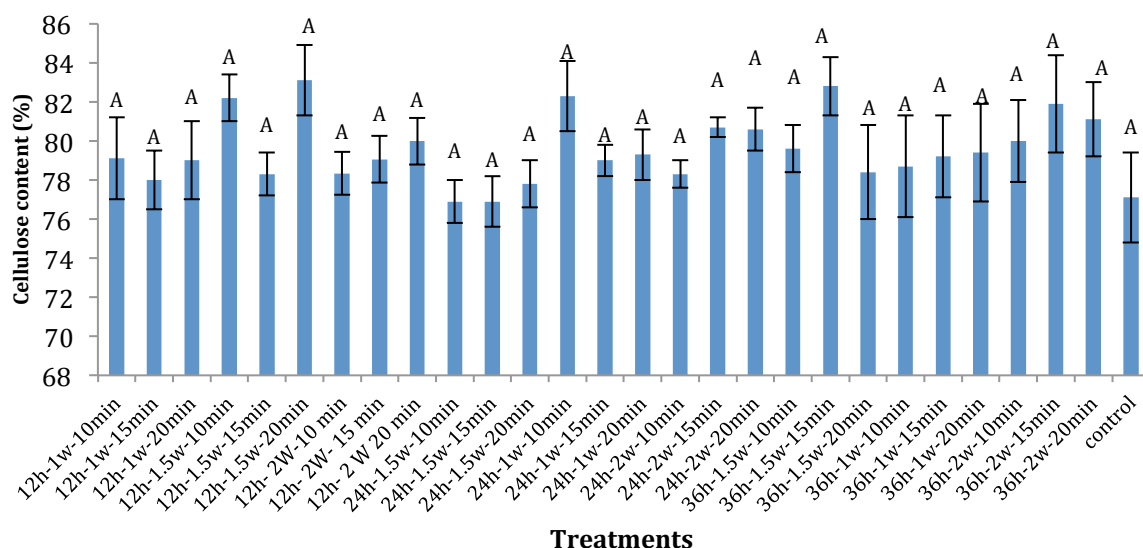


Figure 4.3 NIR analysis of cellulose content in flax fibers

NIR analyses of hemicellulose in the flax fiber samples are as shown in Fig 4.4. The hemicellulose content in the control sample was 12% and that was the maximum among all the others. It clearly indicates a decrease in hemicellulose content due to microwave assisted retting.

But when we consider 12 hour soaked flax stems with microwave retting, there was no significant difference between control and MW treated samples. But the 24 hours soaked and MW treated samples showed significant difference in the percentage of hemicellulose content. This proves the effect of microwave treatment in the removal of hemicellulose, because our control sample itself was soaked for 24 hours. 24 hour soaking left 12% of hemicellulose in the flax fiber, but with microwave treatment, it went down to 6 % for the 36 hours soaking and MW treatment

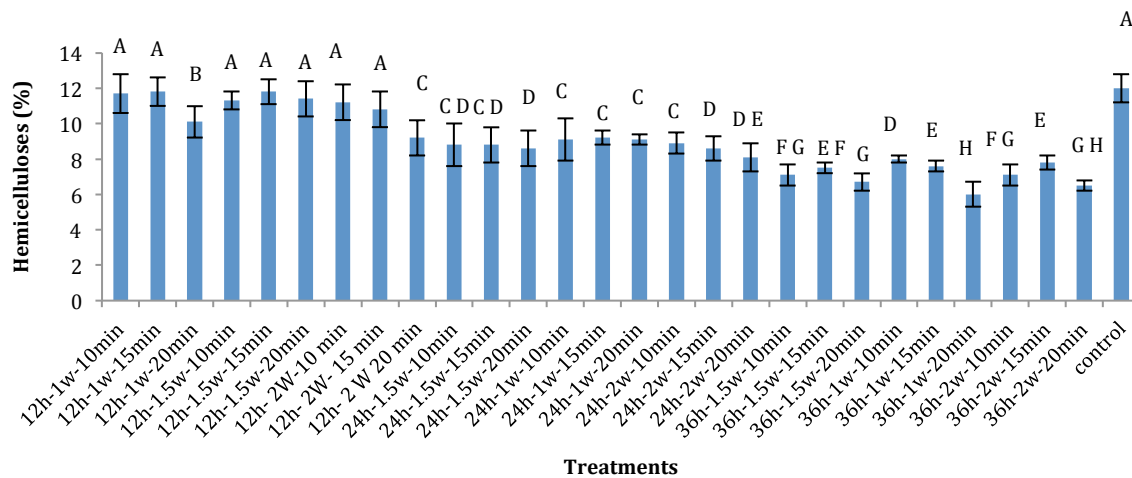


Figure 4.4. NIR analysis of hemicellulose in flax fibers

Maximum decrease in hemicellulose percentage was shown by 36 hours soaked MW treated samples and minimum changes were noted in 12 hours soaked samples. This indicates the effect of soaking in the MW assisted retting of flax. In an effective retting process, hemicelluloses are to be removed so as to release the fiber bundles to individual fibers (Garcia- Jaldon et al., 1995; Shamolina et al., 2003).

NIR analyses of lignin content in the various flax samples are as shown in Fig. 4.5

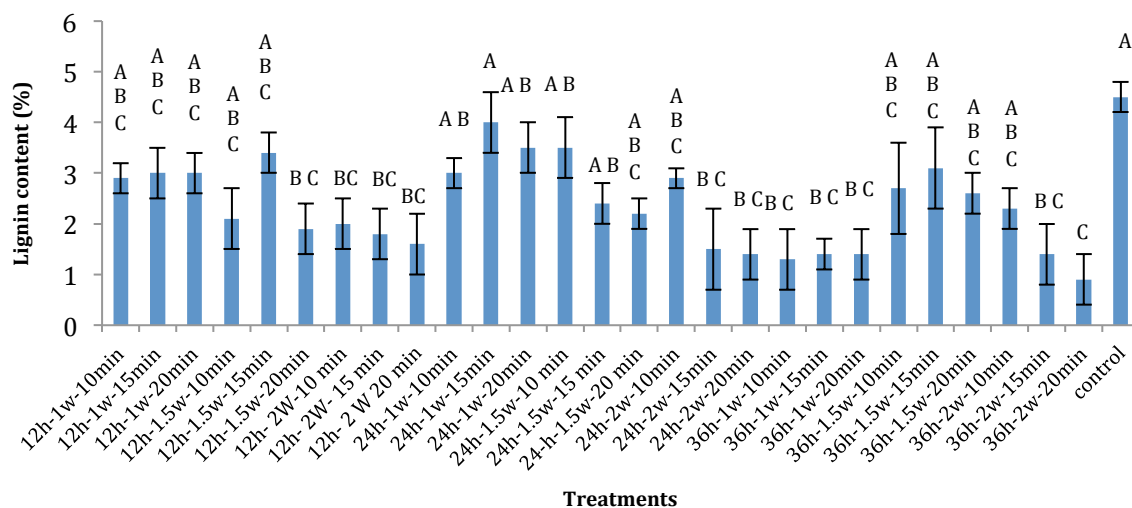


Figure 4.5 NIR analysis of lignin in flax fibers

The control sample contained 4.5 % lignin and with microwave assisted retting, the percentage of lignin decreased. The decrease was significant in 24 hour soaked and 36 hour soaked flax samples. So, it is seen that the effect of soaking also played a very pivotal role in removal of lignin, which initiated the release of fiber from the stem.

With the NIR spectrometer analysis, the combined effect of microwave and soaking in the retting process of flax stem was established. Retting efficiency influenced pre-soaking time, microwave energy and the treatment duration. Pre-soaking time is the first factor to be considered. Pre -wash helped to remove contaminating inorganic salts, colored materials, and soil (Sharma and Van Sumere, 1992). Akin et al. in 2003 conducted studies on enzyme retting of pre- soaked and control flax stems. They found out that the pre-soaked flax stems eased the retting process and the resultant fiber was of fine quality. Results presented from the analysis of pre- soaked water indicate that the water extract from these flax samples is a complex mixture of compounds, including sugars and aromatics representative of the type found in intact plants (Akin et al., 1996). Pre- soaking led to the water intake through the outer skin. So, due to pre-soaking, the flax stems were highly moist so that there were plenty of free water molecules inside the plant cell. An increase in moisture decreases the glass transition temperature of the binders like pectin because the water molecule breaks intermolecular hydrogen bonding; hence the pectin hydrolyses easily with the thermal and non-thermal effect of microwave power (Tsubaki and Azuma, 2011).

In flax stem, flax fibers are situated in the middle lamella, which mainly contains pectin with minimum amount of lignin, which results in a bundle cohesion. In the primary cell wall, cellulose microfibrils are embedded in pectin matrix, hemicelluloses and small amount of the lignin. In the secondary layer, pectin and hemicellulose are forming interphase between cellulose microfibrils (Morvan et al., 2003). Following the NIR result, one can observe that the amount of cellulose was increased, and simultaneously the percentage of hemicellulose and lignin reduced significantly which is a clear indication of fiber release from the bundle. This increase in the fiber release was due to the non- thermal effect of microwave which broke down the matrix contained hemicellulose, lignin and pectin in order to release cellulosic fiber. Because, by keeping the flax stems in a hot water bath of 80° C for 20 minutes did not make any visible changes in terms of fiber release. It is therefore attributable to the non- thermal effect of microwave assisted retting.

4.4.2 Colorimetric Analysis of Flax Fibers

The color of the flax fiber samples were measured after the microwave treatment and compared with the control to study the effect of microwave- assisted process in the color change of the fiber. The results are as shown in Fig 4.6. The color difference in terms of ΔE did not show any particular trend as expected. The color differences ranged between 1.3 and 5.67. In the graph, the treatments with A values had maximum color difference and the treatments did not show any significant difference among themselves. By analyzing the L^* , a^* and b^* values, the L^* values ranged from 55.8 (control) to 61.4 (24h-2W- 20 min), a^* values ranged from +3.3 (36h-1W- 10 min) to +5.7 (24h- 2W- 10 min) and b^* values ranged from +19 (12h-1W-15 min) to +23.9 (36h- 2W-15 min).

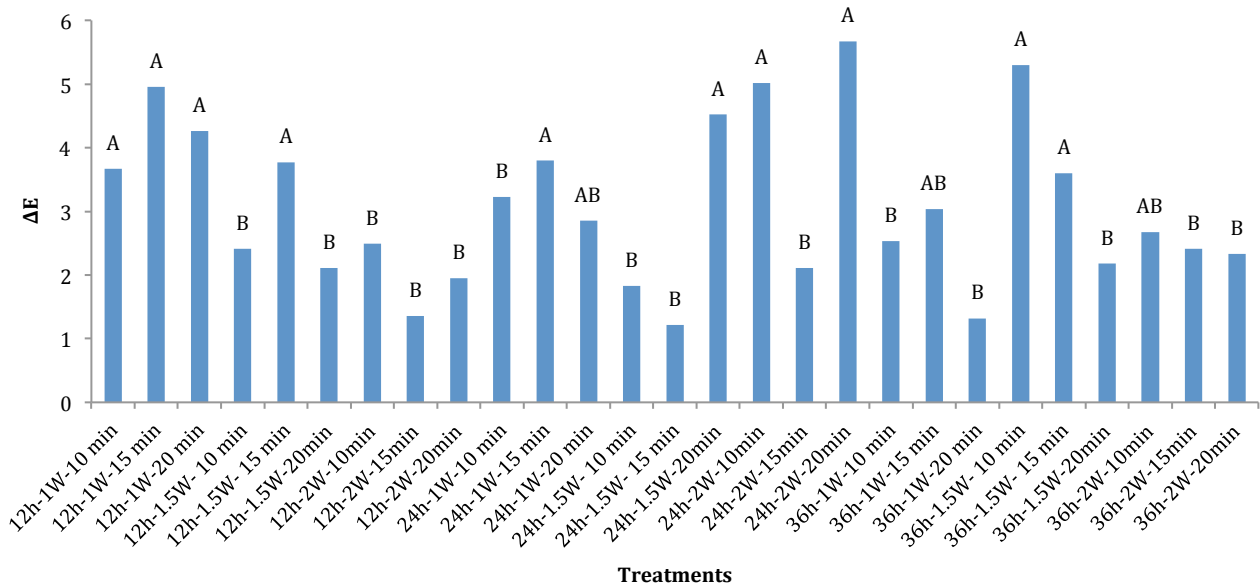


Figure 4.6 Colorimetric analyses of flax fibers

These ranges of color differences were comparatively low for human eyes. This proved that the changes in color of flax fibers due to microwave assisted retting did not make any adverse effect on its industrial acceptability.

4.4.3 Diameter Distribution of Flax Fibers

The diameter distributions of flax fibers were analyzed with respect to ASTM Standard D7025 and presented in Table 4.2. According to Panigrahi et al (2012), the average diameter of fine

flax fiber is 19.3 μm with a standard deviation of 9, that of medium fiber is 26.1 with a standard deviation of 17.2 and the rest of the fibers are called as coarse fibers (Panigrahi et al., 2012). From the table, the control sample had 30% of its diameter within the range of 0- 23 μm where all the retted samples had more than 50% of fiber diameter below 23 μm . This result again indicated that microwave assisted retting released elementary fibers from large fiber bundle effectively and hence proved the effectiveness of the process.

4.4.4 Analysis of Tensile Strength of Flax Fibers

Tensile strengths of flax fibers were analyzed by using Instron machine and are as shown in Fig 4.7.

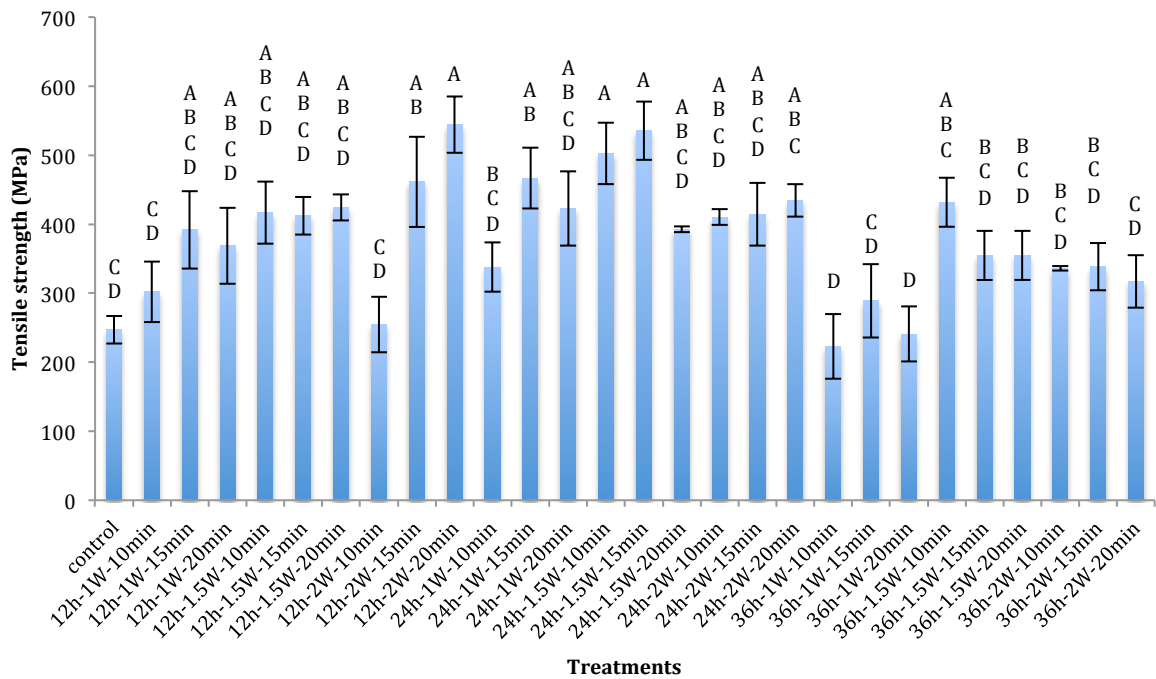


Figure 4.7 Analysis of tensile strength of flax fiber

Table 4.2 Diameter Distributions of flax fibers

Diameter (μm)	Control	12h- 1W- 10 min	12h- 1W- 15 min	12h- 1W- 20 min	12h- 1.5W- 10 min	12h- 1.5W- 15 min	12h- 1.5W- 20 min	12h- 2W- 10 min	12h- 2W- 15 min	12h- 2W- 20min
6 to 12	4%	11%	12%	16%	11%	9%	16%	14%	10%	12%
12 to 17	14%	17%	28%	35%	24%	15%	38%	21%	22%	24%
18 to 23	12%	15%	18%	21%	14%	13%	22%	14%	17%	16%
24 to 29	9%	10%	9%	8%	7%	7%	9%	8%	11%	8%
30 to 35	6%	6%	8%	5%	5%	5%	4%	6%	4%	7%
36 to 49	13%	11%	10%	6%	11%	12%	5%	9%	8%	11%
50 to 99	28%	22%	12%	8%	23%	27%	5%	20%	17%	17%
100 to 249	14%	8%	2%	1%	6%	11%	1%	8%	11%	6%

Diameter (μm)	Control	24h- 1W- 10 min	24h- 1W- 15 min	24h- 1W- 20 min	24h- 1.5W- 10 min	24h- 1.5W- 15 min	24h- 1.5W- 20 min	24h- 2W- 10 min	24h- 2W- 15 min	24h- 2W- 20min
6 to 12	4%	11%	14%	11%	13%	9%	12%	11%	16%	13%
12 to 17	14%	22%	29%	23%	23%	16%	20%	24%	21%	22%
18 to 23	12%	16%	17%	16%	16%	11%	14%	17%	13%	16%
24 to 29	9%	8%	9%	9%	8%	6%	7%	9%	8%	7%
30 to 35	6%	4%	6%	6%	5%	4%	5%	5%	5%	3%
36 to 49	13%	8%	7%	11%	9%	14%	9%	9%	10%	7%
50 to 99	28%	20%	14%	19%	19%	31%	23%	19%	19%	22%
100 to 249	14%	12%	4%	5%	7%	8%	10%	6%	7%	10%

Diameter (μm)	Control	36h- 1W- 10 min	36h- 1W- 15 min	36h- 1W- 20 min	36h- 1.5W- 10 min	36h- 1.5W- 15 min	36h- 1.5W- 20 min	36h- 2W- 10 min	36h- 2W- 15 min	36h- 2W- 20min
6 to 12	4%	13%	7%	14%	12%	9%	14%	8%	8%	13%
12 to 17	14%	23%	16%	32%	29%	19%	31%	17%	18%	29%
18 to 23	12%	15%	13%	19%	19%	18%	23%	12%	15%	22%
24 to 29	9%	8%	9%	7%	8%	9%	9%	11%	12%	8%
30 to 35	6%	7%	6%	3%	4%	7%	5%	6%	7%	4%
36 to 49	13%	10%	13%	7%	8%	10%	7%	13%	10%	7%
50 to 99	28%	19%	30%	14%	16%	20%	8%	23%	23%	13%
100 to 249	14%	6%	7%	2%	4%	8%	3%	10%	7%	3%

From Fig 4.7, it is clear that the tensile strength showed an increase with the microwave power and residence time. But those trends were only for 12 hours and 24 hours soaked samples. For 36 hours soaked flax samples, the tensile strength was lower than the other samples. This may be because of the effect of water, which made the decomposition of binding compounds, resulted in less strength when compared to other samples. The tensile strengths of most of the samples were not significantly different, but the difference was because of the difference in the diameter of individual fibers subjected to tests (Nair et al., 2012).

4.5 Conclusion

A novel method of retting/ degumming of flax stems was established. The microwave- assisted process was proven to be efficient through the analysis of the compositional changes of the flax fibers after the retting process when compared to the composition before the retting process. The retting efficiency was analyzed and the process was optimized in terms of retting efficiency. 24 hours soaked samples treated at 2 W/g power for 20 minutes showed the maximum retting efficiency of 100%. The combined thermal and non- thermal effects of microwaves are studied here, but the introduction of electromagnetic energy in retting of flax is in its beginning stage, there are many future studies to be done for further modification of the process. Possibility of scaling up of the process, processing at higher temperatures with different pressure levels etc. are to be studied and verified in future investigations. These attributes help microwave assisted retting methods to be useful for the industrial application, because microwave assisted retting method has capability to address the issues related to environmental pollution due to retting, time and energy utilization without compromising the quality of the final product.

CONNECTING TEXT

Flax is a fibrous plant, which contains fiber in its stems, and Canada is the largest producer of flax. Hemp is also a similar type of plant with fibrous stem and the qualities of both fibers are close to each other. The production of hemp was restricted in most of the countries in the past, and recently the production of industrial hemp has been allowed with licensing activities. Since hemp is also available in Canada and other countries, next chapter discusses the studies on the application of microwave in the degumming or retting of hemp stems. Hemp stems are of much bigger diameter of the order of one cm whereas flax stems are of 1-2 mm in diameter. According to the available literature, slight differences were reported in the compounds presented in both the stems, especially lignin. High lignin content was found in hemp when compared to flax. These factors initiated the need for conducting separate sets of experiments for microwave-assisted retting of hemp.

CHAPTER 5

APPLICATION OF MICROWAVE ENERGY IN DEGUMMING OF HEMP STEMS

5.1 Abstract

Microwave assisted- degumming/retting of hemp stems was established and the changes in the components like cellulose, hemicellulose and lignin during microwave treatment were studied by Near Infrared (NIR) analysis of the fibers processed from the treated hemp stems. Pre-soaked hemp stems subjected to microwave assisted degumming/retting at various power levels showed significant increase in the cellulose content from 72.1% to 79.8% when compared with the control samples. The percentage of hemicellulose and lignin were the key factors in binding the fibers together, which showed significant decrease when subjected to microwave treatment. Hemicellulose decreased from 14.5% to 12.1% and lignin from 8% to 5.5%. These compositional changes proved the effect of microwave energy in fiber separation. Tests like diameter distribution, tensile strength and colorimetric analysis were also performed to verify the effect of microwave assisted retting on the physical qualities. The diameters of the control hemp fiber samples were 35% at 0-23 μm where all the microwave- assisted retted samples contained more than 50% of fiber diameter below 23 μm . Colorimetric tests and tensile strength tests did not show any specific trend, but the results confirmed that the microwave energy did not have any significant influence in the changes of the physical qualities during the process. The above studies proved the efficiency of microwave treatment on the degumming of hemp fibers.

5.2 Introduction

Hemp (*Cannabis sativa* L.) is a fibrous plant, which is grown in many countries like China, France, Chile, Russia, Turkey, United States and Canada. The cultivation of hemp is restricted by licensing in most of the countries due to its similarity with marijuana, which belongs to the same Cannabis family. But industrial hemp contains 0.3-1.5% of tetrahydrocannabinol (THC), while marijuana contains about 5-10% of THC, and this is the reason why marijuana is used as a psychoactive drug or medicine (Wayne and Wendy, 2000). Hemp has a lot of potential applications in various areas like apparel industries, paper industries and bio-composite

industries (Ouajai and Shanks, 2005). Hemp stems can be separated into two components: the stem tissues outside the vascular cambium (bark) and the stem tissues inside the vascular cambium (core). The bark consists of the epidermis, the cortex and the phloem. In the phloem, sieve tubes and primary bast fibers are arising from the prodesmogen. The phloem may contain secondary bast fibers arising from the cambium. Hemp fibers are of high quality and are widely used as a replacement for synthetic fiber, but these fibers are expensive as compared to synthetic fibers (Kymalainen, 2004). This is mainly due to various difficult stages involved in the processing of hemp fiber from its stem. The most important and energy intensive step in the processing of hemp stem is degumming/retting, which is the separation or loosening of bast fibers from shive and other non-fiber fractions, leading to a major problem in natural fiber processing (Sharma and Van Sumere, 1992; Foulk et al, 2001). Microwave energy can be used to release the fiber from the plant cell walls of hemp to separate the fibers from plant stem. Microwaves are a form of electromagnetic radiation with frequency ranging between 300 MHz to 300 GHz. (Banik et al., 2003). Microwave energy is primarily used for heating in various post harvest operations (Kim et al, 2011). Biological changes that occurred in plant materials due to microwave energy is due to its thermal effects (Gandhi, 1987). Under the influence of microwave energy, soaked hemp stems are subjected to dielectric heating, which takes place when dipole molecules inside the hemp stem try to rotate vigorously in order to orient itself to the direction of applied electric field. Under electromagnetic field treatment, hemp stem acts as a non-homogenous material that allows more polar components to absorb microwave energy that creates “hot spots” in hemp stem. According to our hypothesis, this unique method of heating results in an “explosion” effect in the particles and leads to the disruption of the lignocellulosic structures of hemp stem. Apart from that, the non-thermal effects of electromagnetic field accelerate the disintegration of the lignocellulosic compounds (de la Hoz et al., 2005, Yin, 2012). By applying Planck’s law at 2450 MHz, (frequency of commercial microwave oven) the energy carried by microwave photons is approximately 1 joule per mole. This energy is way too low to initiate any chemical activity in the material. Therefore, microwave radiation alone is not able to attain any structural and chemical changes in biomaterials. When a biomaterial to be treated is exposed to microwaves containing polar molecules and ions, the radiation can accelerate chemical, biological and physical processes (Sridar, 1998).

The objective of this study is to optimize microwave assisted retting process of the hemp stems.

5.3 Materials and Methods

The materials and methods used for the study are discussed in this section.

5.3.1 Hemp Stems

The non-retted hemp straws were obtained from National Research Council, Royalmount Avenue, Montreal. The stems were cut into 8 cm length in order to fit inside a test tube. The initial moisture content of the hemp stems was found to be 3.93% w.b. by oven dry method. The middle part of the plant stem was chosen for the experiment to ensure uniformity in carrying out retting experiments. Hemp straw samples (5 g) were placed in a test tube of 50 ml capacity containing water for various soaking times at room temperature to ensure fully wet conditions.

5.3.2 Microwave- Assisted Retting Apparatus

The apparatus used for microwave- assisted retting of hemp was the same as that used for retting flax, which is discussed in section 4.3.2.

5.3.3 Experimental Procedure

Experimental procedure was similar to that of microwave- assisted retting of flax stems, which is discussed in section 4.3.3 except the retting efficiency (Fried test). Fried test is applicable only for flax stems.

5.4 Results and Discussion

Pre-soaked hemp stems were subjected to short-duration microwave treatments, and the treated stems were dried using microwave energy. Fibers were separated manually from the dried stems using a hackler after crushing. Hackler was a type of comb having iron brushes, and the non-fibrous materials were separated when the fibers pass through the hackler. The fibers obtained were subjected to various tests to analyze the effect of microwave on release of fiber.

5.4.1 NIR Spectrometer Analysis

NIR spectrometer analysis of cellulose, lignin and hemicellulose content of hemp fibers was performed and the results were analyzed. The results demonstrated a significant difference in the cellulose content between the microwave- treated and non-treated hemp fiber samples (Figure 5.1). But among the 24 and 36 hour soaked microwave- treated samples, there was no

significant difference in the cellulose content which proved both 24 h and 36 h soaking was acceptable in terms of cellulose content in the resultant fiber. From Figure 5.1, it can be observed that there was an increasing trend in the cellulose content of all the hemp fiber samples compared to control fiber samples. The significant difference in the cellulose content of microwave- treated samples when compared with the control sample was an evidence of the role of microwave in the increase in cellulose content in the resulting fiber. Hemp fibers are cellulose rich materials with a complicated inner structure, in which cellulose microfibrils were trapped in a matrix of lignin, pectin and hemicellulose. With retting, combined thermal and non- thermal effects of microwave initiated the breaking of lignin, pectin hemicellulose matrix which resulted in the increase in cellulose content in the hemp fiber. The increase in cellulose in the microwave-treated hemp fibers could be expressed in terms of effectiveness of retting in such a way that, the presence of cellulose in the fibers indicated a decrease in the non- cellulosic materials and impurities in the fibers.

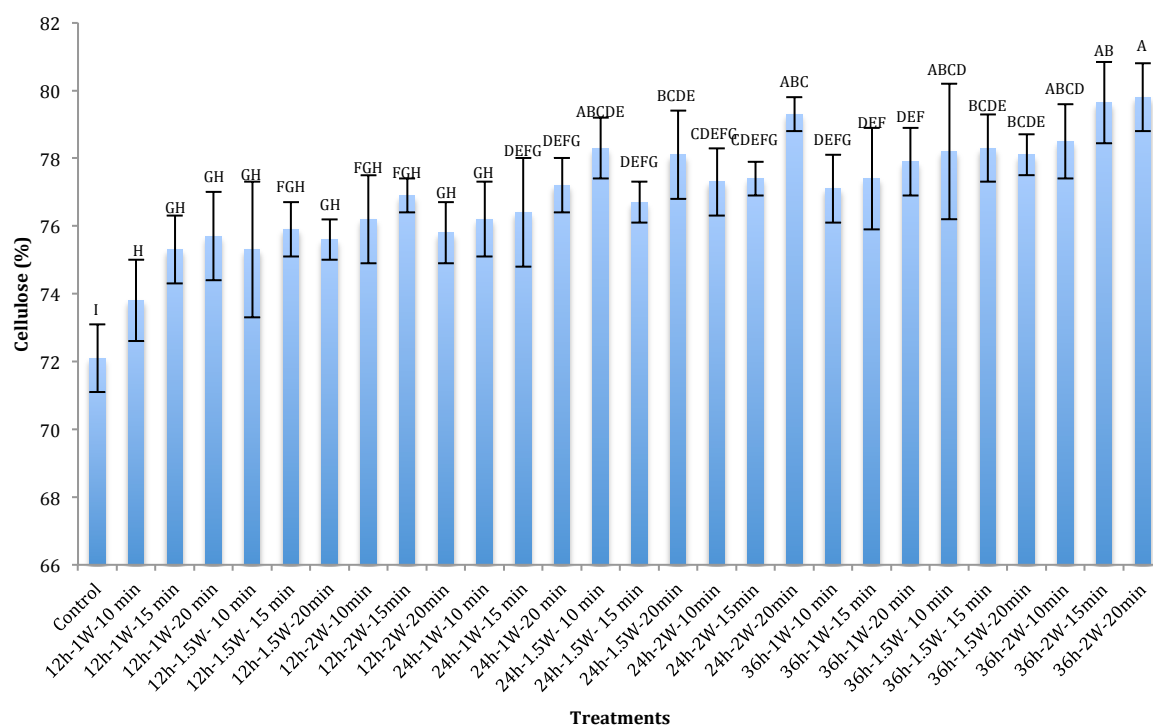


Figure 5.1 Cellulose content in hemp stems

Earlier experiments proved that the cellulose content increases with an increase in the retting efficiency (Hessler, 1945; Putnina and Kukle, 2011). The minimum cellulose content in the control sample proved the improper degumming of hemp stems, because the bast fibers were found to be surrounded by non-cellulosic materials.

Figure 5.2 represents the NIR analysis of hemicellulose in the hemp fiber. Hemicellulose content in the control sample was the maximum and was decreased with the increase in pre-soaking time and microwave energy. But there was no significant difference in the hemicellulose content between the control sample and the microwave-treated samples except that of 36 h soaked microwave treated samples. The 24 h- 2W-20 min sample (24 h soaked and microwave treated for 20 minutes at 2 Wg⁻¹) showed a significant difference with the control sample in the case of hemicellulose content.

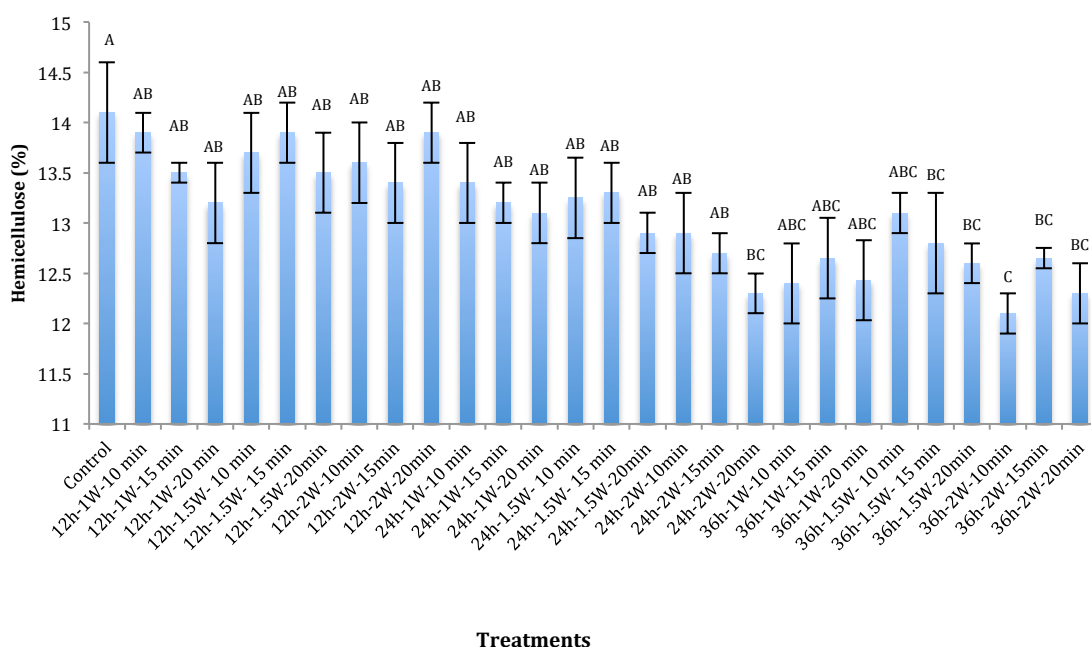


Figure 5.2 NIR analysis of hemicellulose in the hemp fiber

Zang et al. in 2008 conducted studies on seawater retting and found the hemicellulose content of the non-retted hemp was decreased from $18.2 \pm 0.4\%$ to $9.8 \pm 0.3\%$ after seawater retting. While, in the current study, the maximum hemicellulose content was 14% (control sample) and the minimum hemicellulose content was 12.1 (36-2W- 10 min sample). It has been experimentally proved that in an effective retting or degumming process, hemicelluloses are to

be removed so as to release the fiber bundles to individual fibers (Garcia- Jaldon et al., 1995; Shamolina et al., 2003; Zang et al., 2008).

NIR analyses of lignin content in the various hemp samples are as shown in Figure 5.3. The lignin content in hemp fibers showed a decreasing trend with microwave treatment at various soaking levels. The control hemp fiber sample had 8.1 % lignin and it decreased with the treatment with a minimum of 5.5% for 36 h- 2W- 20 min hemp fiber samples. The decrease was significant in 24 hour soaked and 36 hour soaked hemp samples. So, it was clear that pre-soaking also played a very pivotal role in removal of lignin, which initiated the release of fiber from the stem.

The NIR spectrometer analysis of cellulose, hemicellulose and lignin in hemp fibers explained the combined effect of microwave energy, treatment time and pre- soaking time in the degumming process of hemp stem. Pre-soaking of hemp stems also resulted in elimination of contaminating inorganic salts, colored materials, and soil (Sharma and Van Sumere, 1992; Akin et al., 1993). In 2003, Akin et al. reported that the pre-soaked stems eased the further enzymatic retting process and the resultant fiber was of fine quality.

Increase in the moisture level led to a decrease in the level of glass transition temperature of binders like pectin, since water molecule breaks intermolecular hydrogen bonding inside the plant cell, pectin hydrolyses easily with the thermal and non-thermal effect of microwave energy (Akin et al., 1996; Tsubaki and Azuma, 2011). In hemp stems, elementary fibers are thick-walled and polygonal in cross section, with joints, cracks, swellings, and other irregularities on the surface (Garcia et al., 1998; Morvan et al., 2003). NIR analysis revealed that the amount of cellulose was increased, and simultaneously the percentage of hemicellulose and lignin reduced significantly which is a clear indication of fiber release from the bundle. The increase in components was due to the non- thermal effect of microwaves. Pre- soaked hemp stems were subjected to retting in a hot water bath without microwave at 95° C for 20 minutes (Table 5.1).

Table 5.1 Components of hot water treated pre- soaked hemp stems

Soaking hours (h)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Control	72.1	14.1	8
12	72.4	14.1	7.8
24	73.2	14	7.8
36	74.1	14	7.5

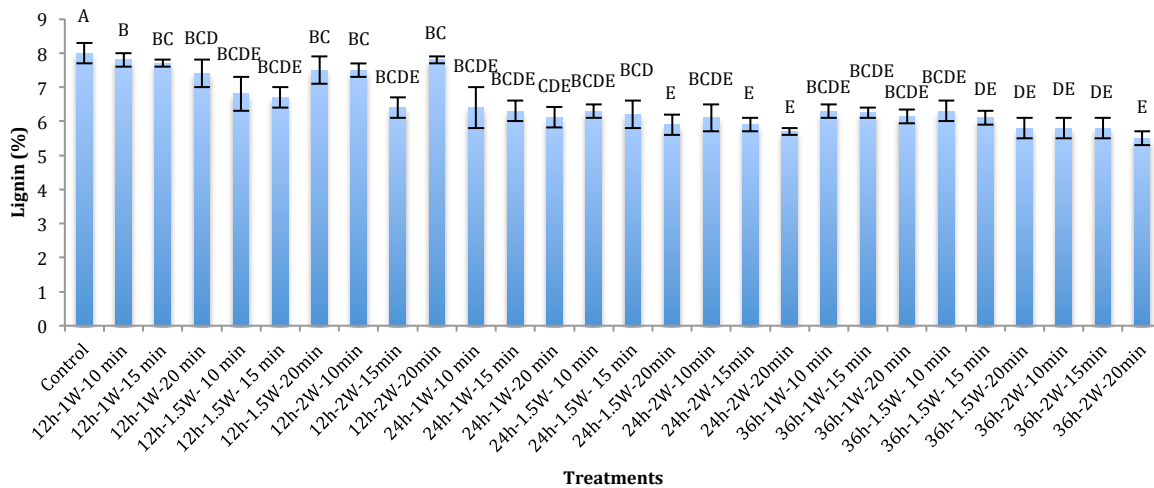


Figure 5.3 NIR analysis of Lignin in the hemp fiber

Cellulose, hemicellulose and lignin % did not show any remarkable differences due to pre-soaking and hot water treatment when compared to microwave- assisted retting. It proved the non- thermal effect of microwave assisted retting.

5.4.2 Colorimetric Analysis of Hemp Fibers

The color difference in the hemp stems were estimated and the results are as shown in Figure 5.4.

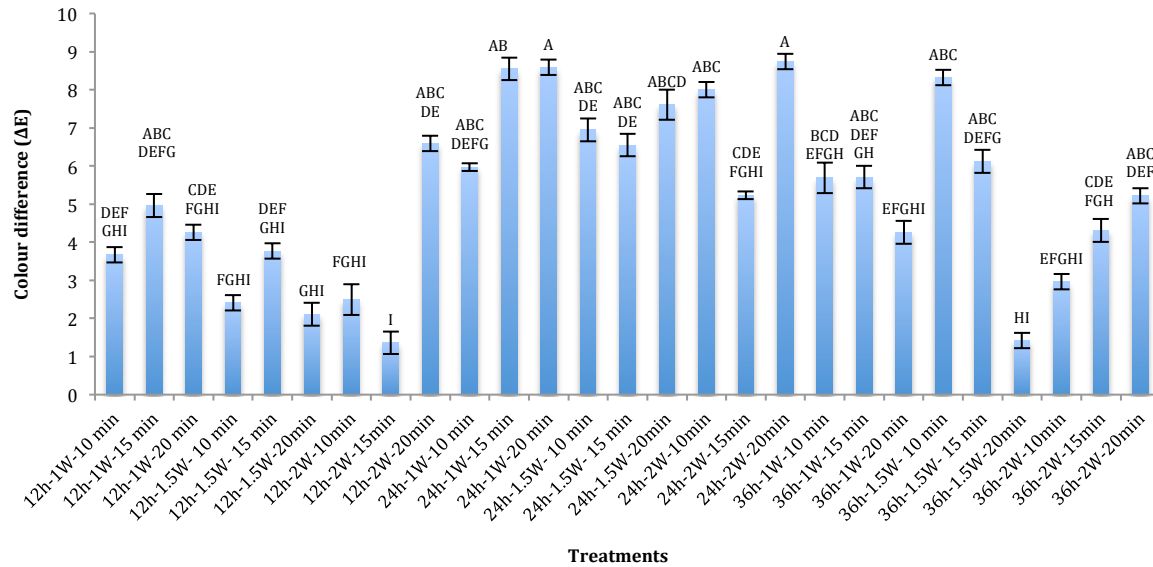


Figure 5.4 Colorimetric analyses of hemp fibers of various treatments

The color difference in terms of ΔE did not show any particular trend. The maximum color difference was found in 24 h- 1 W- 20 min and 24 h- 2 W- 20 min hemp fibers whereas the minimum color difference was shown by 12 h- 2 W- 15 min hemp fiber samples. The color differences ranged between 1.36 and 8.74. The 12 h soaked hemp fibers showed less changes in its color when compared to control samples and 24 h soaked hemp fibers had the maximum color difference after the treatments.

5.4.3 Diameter Distribution of Hemp Fibers

The diameter distributions of hemp fibers were analyzed with respect to ASTM Standard D7025 and presented in Table 5.2. Panigrahi et al (2012) estimated that the average diameter of fine fiber is 19.3 μm with a standard deviation of 9 and that of a medium fiber is 26.1 with a standard deviation of 17.2, the rest of the fibers were called as coarse fibers (Panigrahi et al., 2012). From the table, the control sample had 35% of its diameter within the range of 0-23 μm whereas all the retted samples had more than 50% of fiber diameter below 23 μm . This result too indicated that microwave assisted retting effectively released elementary fibers from large fiber bundle.

5.4.4 Analysis of Tensile Strength of Hemp Fibers

Tensile strength of hemp fibers were analyzed by using Instron machine and are as shown in Figure 5.5.

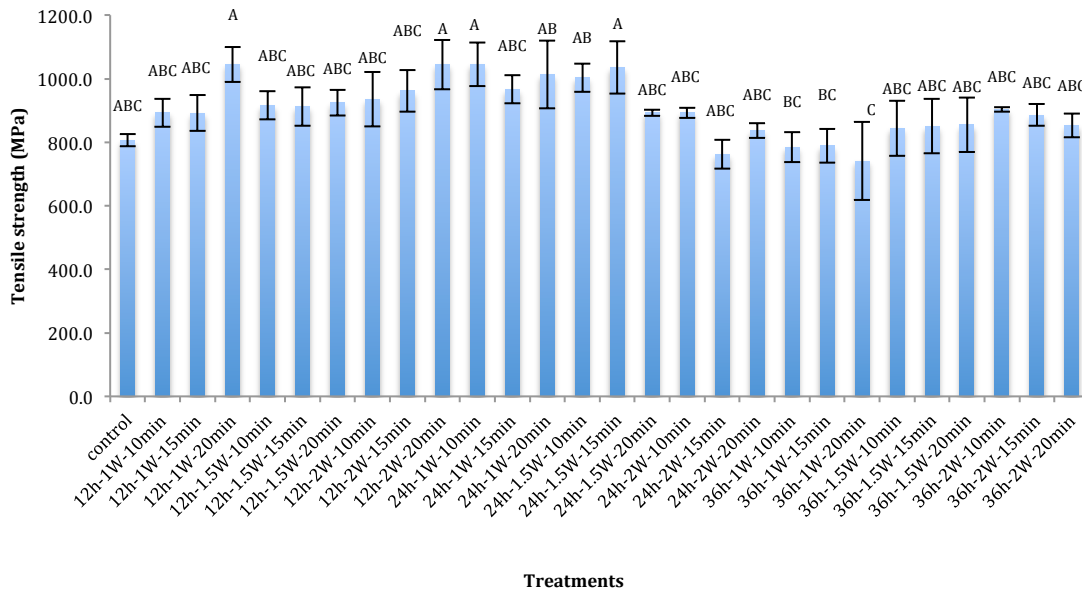


Figure 5.5 Tensile strength of hemp fibers

Tensile strength is one of the most important parameter that determines the quality of the fiber (Nair et al., 2012). From Figure 5.5, it can be observed that the maximum tensile strength was shown by 12 h- 1 W- 20 min, 12h- 1.5W- 20 min, 24 h1 W- 15 min and 24 h-1.5 W- 15 min hemp fiber samples whereas hemp fiber samples 36 h- 1 W- 20 min showed the minimum tensile strength. The tensile strength of the hemp fibers ranged between 740.8 and 1044.9 MPa, which was within the average tensile strength of 700- 1000 MPa reported for hemp fibers (Shahzad, 2013).

Table 5.2 Diameter distributions of hemp fibers

Diameter (μm)	Control	12h- 1W- 10 min	12h- 1W- 15 min	12h- 1W- 20 min	12h- 1.5W- 10 min	12h- 1.5W- 15 min	12h- 1.5W- 20 min	12h- 2W- 10 min	12h- 2W- 15 min	12h- 2W- 20min
6 to 12	8%	9%	10%	9%	11%	9%	8%	11%	11%	11%
12 to 17	14%	20%	17%	16%	18%	20%	18%	19%	21%	19%
18 to 23	13%	17%	16%	13%	13%	18%	18%	19%	15%	14%
24 to 29	11%	14%	15%	12%	13%	14%	14%	14%	12%	13%
30 to 35	8%	10%	11%	10%	9%	11%	10%	9%	9%	11%
36 to 49	13%	15%	15%	17%	14%	13%	13%	12%	14%	15%
50 to 99	20%	12%	14%	20%	19%	13%	17%	13%	17%	15%
100 to 249	4%	2%	2%	3%	3%	2%	2%	2%	2%	2%

Diameter (μm)	Control	24h- 1W- 10 min	24h- 1W- 15 min	24h- 1W- 20 min	24h- 1.5W- 10 min	24h- 1.5W- 15 min	24h- 1.5W- 20 min	24h- 2W- 10 min	24h- 2W- 15 min	24h- 2W- 20min
6 to 12	8%	10%	9%	7%	9%	10%	9%	8%	8%	10%
12 to 17	14%	19%	14%	15%	20%	14%	19%	21%	17%	15%
18 to 23	13%	16%	16%	17%	18%	15%	16%	20%	17%	14%
24 to 29	11%	14%	15%	16%	12%	10%	15%	13%	13%	13%
30 to 35	8%	10%	10%	12%	8%	10%	9%	9%	11%	11%
36 to 49	13%	15%	15%	16%	14%	17%	14%	13%	14%	18%
50 to 99	20%	15%	18%	14%	15%	23%	15%	13%	17%	17%
100 to 249	4%	1%	3%	2%	3%	2%	3%	3%	3%	3%

Diameter (μm)	Control	36h- 1W- 10 min	36h- 1W- 15 min	36h- 1W- 20 min	36h- 1.5W- 10 min	36h- 1.5W- 15 min	36h- 1.5W- 20 min	36h- 2W- 10 min	36h- 2W- 15 min	36h- 2W- 20min
6 to 12	8%	8%	11%	9%	10%	10%	8%	10%	9%	9%
12 to 17	14%	20%	20%	18%	23%	19%	18%	20%	18%	20%
18 to 23	13%	19%	14%	17%	20%	18%	17%	19%	19%	19%
24 to 29	11%	15%	12%	15%	14%	16%	16%	14%	14%	14%
30 to 35	8%	11%	8%	11%	10%	12%	12%	11%	10%	10%
36 to 49	13%	15%	14%	14%	13%	16%	16%	13%	14%	13%
50 to 99	20%	11%	18%	14%	9%	10%	13%	12%	14%	13%
100 to 249	4%	1%	3%	2%	1%	1%	1%	1%	2%	2%

5.5 Conclusion

Microwave- assisted degumming of hemp stems was established. This process was proven to be efficient by analyzing the compositional changes of the hemp fibers after the retting process when compared to the composition before the retting process. 36 h soaked hemp stems, treated in the microwave- chamber at 2 W/g power for 20 min showed maximum retting in terms of changes in cellulose, hemicellulose and lignin with microwave- assisted retting. Loosening of fibers occurred due to combined thermal and non- thermal effects of microwave energy on pre-soaked hemp stems. Pre- soaking of hemp stems led to weakening of the strong pectin bonds, which cemented fibers to the stems. With the application of microwave energy, the water inside the plant stems increases the pressure, and with the energy dissipated by microwave led to the breaking of already weakened bonds and hence release of the fibers from the stems. Scale up, treatments at higher pressure levels and with different electro- magnetic wavelengths are the future investigations to be done in this area. These attributes help microwave assisted degumming methods to be useful for industrial application, because microwave assisted degumming could address the issues related to environmental pollution due to conventional retting practices.

CONNECTING TEXT

Microwave- assisted retting of flax and hemp stems was introduced and various properties of the fibers were analyzed in the previous chapters. Combined effect of thermal and non- thermal properties of microwave led to the loosening of fibers from the stems. Fibers are attached in flax and hemp stems by strong chemical bonds called pectin bonds. Pectin is a long chain polysaccharide, which is strategically located in the plant stems cementing the fibers together and with the shives. So, the removal of pectin is the most important constraint determining the efficiency of retting. In the next chapter, chemical analysis of pectin, lignin, hemicellulose and cellulose presented in the flax fibers are carried out to find the efficiency of microwave- assisted retting and hence the process was optimized by analyzing the various parameters. Chemical analysis was conducted on flax fibers since flax and hemp stems showed similar characteristics with the use of microwave- assisted process.

CHAPTER 6

ANALYSIS OF CHEMICAL COMPOSITION CHANGES DURING MICROWAVE- ASSISTED RETTING AND OPTIMIZATION OF THE PROCESS

6.1 Abstract

Pre- soaked flax stems were subjected to microwave assisted retting at different power levels and the effectiveness of microwave assisted retting was studied by the analysis of chemical compounds presented in the retted flax fibers processed from the stems. Response surface statistical design was used for this study with JMP[®] 10 software. Chemical analyses were performed by gravimetric methods. Cellulose, hemicellulose, lignin and pectin concentrations of flax fibers and the sugar content in the solution obtained after the treatment were subjected to further analyses. The release of cellulose due to microwave –assisted retting was proved by the chemical analysis of cellulose percentage in the fiber, which increased significantly ($p < 0.0001$) with the increase of microwave power at various soaking levels. Percentage of hemicellulose, lignin and pectin concentrations were decreased significantly after microwave-assisted retting that explained the degree of retting with the help of microwave energy. This study used the change in chemical composition of the fibers, which was used as a tool to estimate the effectiveness of microwave- assisted retting and the results were used to optimize the process.

6.2 Introduction

Bio-fibers are widely used as a replacement for synthetic fiber in industries making speciality paper, bio-composite materials, apparel etc., which contribute to the successful commercial production of bio-fibers (Akin, Dodd et al. 2005; Akin, Foulk et al. 2001). Flax fiber is one of the most available bio-fiber and is cultivated all over the world from ancient times. Flax fibers are processed from its stems. The height of fully-grown flax plant varies from 50 cm to 150 cm with slender stems of 1 mm to 2 mm in diameter. The life of a flax plant is 90 to 180 days from sowing till cultivation, which depends on the weather and soil type (Day, Ruel et al. 2005). The main components that hold the fibers together inside the flax stem are waxes on the cell wall, pectin substances with traces of lignin in the primary cell wall, and the secondary cell wall

consists of cellulose. Inside the cell wall, cellulosic microfibrils are embedded in the matrix consisting of proteins, lignin, hemicelluloses and pectin (Kadla, F. et al. 2000). Retting is the process of the separation of fiber bundles from the non- fiber tissues in the stem (Pallesen 1996; Akin 2013; Morrison Iii; Akin et al. 1999).

Studies were conducted on microwave assisted retting at the Bioresource Engineering department, Macdonald campus, McGill University and the process was established by estimating the quality and physical properties of the retted flax fibers. Microwave energy was passed through pre-soaked flax stems, and due to the combined effect of microwave energy and heat energy released due to the dipole rotation, the fibers were separated by breaking the covalent bonds, those responsible for holding the fiber bundles together (de la Hoz, Ortiz et al. 2005, Yin 2012). Flax fiber after retting process was clean and without any impurities. One of the ways of analyzing the degree of retting was to find out the chemical composition of the retted fiber. As discussed, non-retted flax fibers are closely bounded by strong chemical bonds formed by pectin and non-methoxylated carboxyl groups on galacturonic acid which are often cross linked by Ca^{++} or other cations that form stable bridges across pectin molecules (Sakai, Sakamoto et al. 1993). Shives are from the woody core tissues in the central region of the stems where highly lignified cells are present (Akin, Gamble et al. 1996). Lignin contains recalcitrant compounds with a complex polyphenylpropanoid structure, which is a major cause for the limited degradation of plant carbohydrates as well as retting (Akin 1989). Hemicellulose is also found in the secondary cell wall of the non-retted flax fiber. In retted and clean flax fibers, pectin, hemicellulose and lignin are removed and the percentage of cellulose content is higher than that of non- retted fibers. The changes in the composition of flax fiber of various retting levels can be analyzed and the degree of retting can be found out on the basis of its chemical composition (Mooney, Stolle-Smits et al. 2001).

The objective of this study was to find out the efficiency of microwave- assisted retting of flax stems and to optimize microwave assisted retting by analyzing the chemical composition of flax fibers obtained from various treatments by gravimetric methods.

6.3 Materials and Methods

The materials and methods used for the study are discussed in this section.

6.3.1 Flax Stems

Non- retted lax stems were obtained from Lanaupôle Fibers, Montreal, and the samples were prepared by cutting 5 cm of length from the middle portion in order to fit into a 50 ml test tube and to ensure the uniformity of experiments. The initial moisture content of flax stems was found out by oven dry method and as 3.93% (w.b.).

6.3.2 Microwave Apparatus

Retting experiments were conducted using a microwave apparatus designed in the post harvest technology lab, Macdonald Campus, McGill University (Fig 6.1). The microwave generator frequency was 2450 MHz with a variable power from 0 to 750 W. Optical fiber probe was used to find the temperature of the flax samples (Nortech EMI-TS series, Quebec City, Canada) and temperature probes were connected to an Agilent 34970A data acquisition unit connected to a computer. A hot air supply was attached to the microwave oven to pass hot air through the microwave oven to remove the moisture generated by the samples (Nair, Liplap et al. 2011).

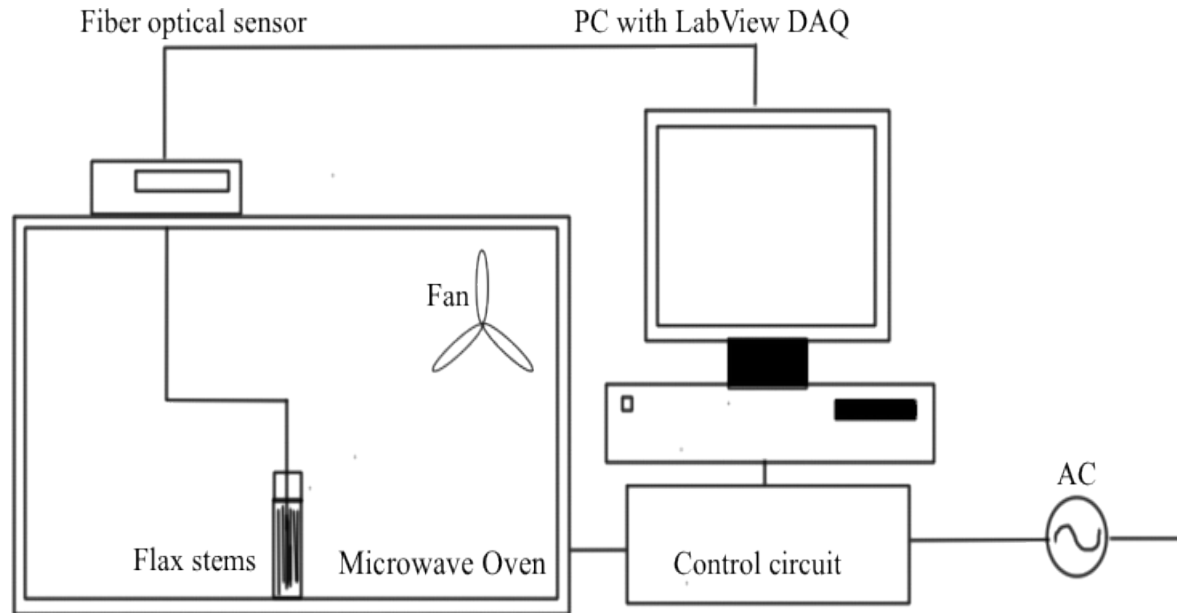


Figure 6.1. Microwave apparatus for retting process

6.3.3 Experimental Procedure

Experimental procedures of microwave assisted retting and chemical analysis are discussed below.

6.3.3.1 Microwave Assisted Retting

Flax stem samples (5 g) were subjected to soaking in a 50 ml test tube. The solvent used for soaking was water, which is the most common, readily available and environmental friendly solvent in the world and water soaking ensured removal of inorganic salts, colored materials and soil particles from the flax stems (Akin 2013). The response surface retting experiments were designed by using JMP[®] 10 software. The upper and lower limits of soaking were fixed as 12 hours and 36 hours where as the treatments were set between the intervals 0 to 3 where 0 was the treatment with hot water at a temperature of 100⁰ C for a duration of 20 minutes and 3 was microwave assisted retting fixing the microwave power as 2W/g. Treatment time and temperature was kept constant throughout the study because the treatment was occurred at boiling temperature throughout the processing time of 20 min. Total number of experiments was 40 and the experimental design is shown in Table 6.1.

6.3.3.2 Analysis of Compounds

Flax stems obtained after different conditions of retting were dried and the fibers were separated manually. Separated fibers were cleaned to ensure that there were no impurities and cut into very short pieces to perform the chemical analyses for obtaining the concentration of cellulose, hemicellulose, lignin and pectin. The solutions obtained after various soaking and retting treatments were analyzed to estimate their sugar content to determine the efficiency of retting in terms of sugar released during the treatments. Gravimetric methods were adopted to find out the compounds, which are simple and convenient for routine analysis of compounds present in biomaterials (Deschatelets and Yu 1986). Tukey's tests were performed to analyze the statistical significance of various treatments. Neutral detergent fiber (NDF) in flax is the cell wall components such as cellulose, hemicellulose, lignin and minerals. A neutral detergent solution was used to remove the components such as proteins and pectin. The neutral detergent solution contains sodium lauryl sulfate, ethylenediaminetetraacetate (EDTA), sodium hydroxide, sodium borate decahydrate, sodium phosphate, triethylene glycol, and sodium sulfite. A heat-stable

enzyme, amylase was also added to remove the starch from the samples. The residue obtained after refluxing the sample with the neutral detergent solution was washed with acetone and then dried to estimate the NDF. The residue obtained was used for the estimation of acid detergent fiber. Acid detergent fiber (ADF) in flax consists of mainly cellulose and lignin. It is estimated as the residue remaining after extracting the NDF sample material using the acid detergent solution containing 2% CTAB (cetyl trimethylammoniumbromide) in 1 N H_2SO_4 and acetone. Hemicellulose concentration was estimated by subtracting the ADF value from the NDF value. The residue obtained was used for the estimation of lignin and cellulose. Lignin was estimated by digesting the ADF with 72% sulphuric acid for 3 hours. The difference in ADF and lignin gave an estimation of cellulose in the sample. Pectin was estimated by gravimetric method. Pectin compound was precipitated as calcium pectate by adding calcium chloride to an acid solution. After thorough washing, the chloride ions were eliminated, and the precipitate was dried and weighed to estimate the percentage of pectin in the sample (Sadasivam and Manickam 1996). Liquid samples were analyzed using UV-Vis spectroscopy for the concentration of hexose and pentose sugars, sugar degradation products and lignin. Pentose sugar estimation was done using the para-bromoaniline method developed by Deschatelets and Yu in 1986. In this procedure, 0.2 mL of the sample was treated with 1.0 mL of parabromoaniline reagent, which formed a pink colored complex while heating the mixture at 70°C for 10 minutes.

6.4 Results and Discussion

In microwave-assisted retting, the soaking times were 12 hours, 24 hours and 36 hours where, microwave-assisted retting was termed as treatments 0, 1, 2 and 3 as per the response surface analysis. 0 was hot water retting for 20 minutes, 1 was microwave- assisted retting at a power of 1 W/g for 20 minutes, 2 was microwave- assisted retting at 1.5 W/g and 3 was microwave-assisted retting at a power of 2 W/g for 20 minutes. Experiments were conducted and concentration of the various polymeric components of flax fiber retted in the above conditions was estimated. The results are discussed in this section.

6.4.1 Cellulose Concentration

Cellulose content in the flax fiber after various treatments were analyzed and the results are shown in Figure 6.2. The primary cell wall of a flax stem consists of pectin that is strengthened

and dehydrated by the presence of lignin. The secondary wall consists of cellulose, which is attached to hemicellulose (Springer, 2002).

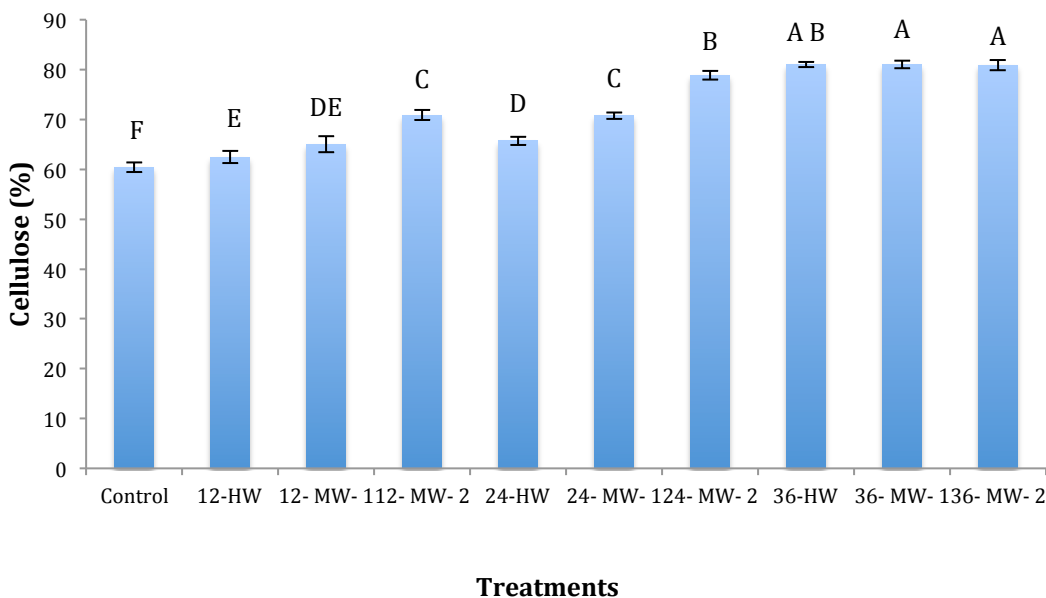


Figure 6.2. Cellulose percentage in flax fibers after various treatments

In non- retted flax fibers, the percentage of pectin, lignin and hemicellulose are higher than that of retted fibers. But after retting, because of the removal of pectin, lignin, hemicellulose and wax, the percentage of cellulose increases. Therefore, percentage of cellulose is directly proportional to the retting efficiency. Initial cellulose percentage of non-retted flax fiber i.e., control sample, was found to be 60.45%. There was a significant difference in the cellulose percentage between control sample and the treated samples. Cellulose percentage in flax fiber sample 12- HW (12 hour soaked and hot water retted for 20 minutes) showed a significant difference when compared with the cellulose release in 12- MW- 2 (12 hour soaked and microwave retted for 20 min at 2 W/g). Similar results were observed in 24 hour soaked sample as well. But 36 hour soaked flax fiber samples did not show any significant difference in the release of cellulosic fiber (Figure 6.2) compared to 24 h samples.

Response surface analysis of percent cellulose concentration with respect to soaking and retting is shown in Figure 6.3. It shows that, cellulose concentration was increased with an increase in treatments from 0 to 3. Cellulose concentration in the flax fibers increased with an increase in

soaking time from 24 h to 36 h as well.

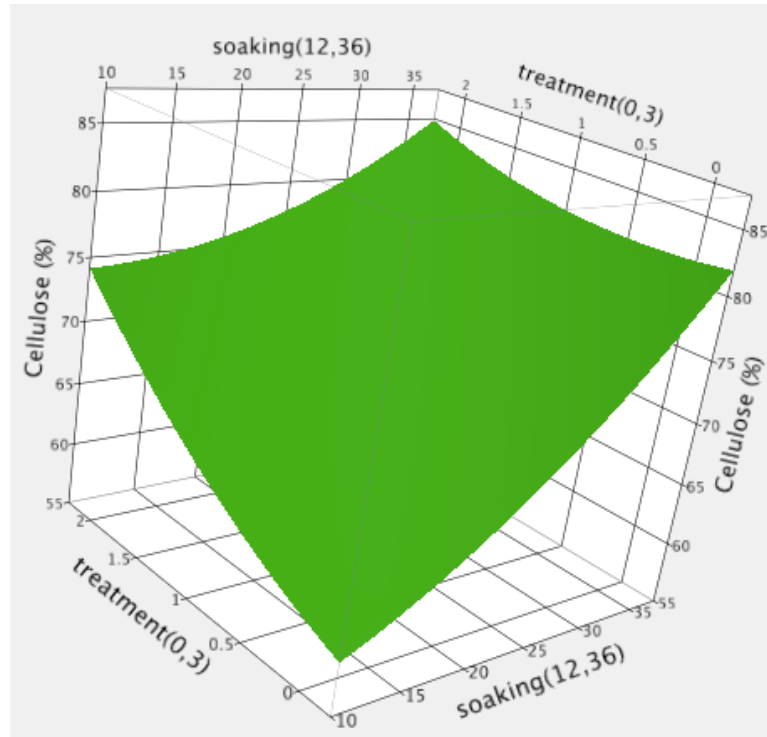


Figure 6.3 Response surface curve of cellulose percentage in flax fibers

The predicted cellulose percentage was estimated from the surface plot by using a polynomial equation.

$$\begin{aligned} \text{Cellulose}(\%) = & 71.929 + 8.332 (\text{Soaking}) + 4.21(\text{treatment}) \\ & -1.67(\text{soaking} \times \text{treatment}) \end{aligned} \quad (6.1)$$

R^2 value for the fit was calculated as 0.94, $P < 0.0001$ and RMSE (root means square error) as 2.0598. The comparison between the actual and the predicted values of cellulose concentration is tabulated in Table 6.1.

6.4.2 Hemicellulose Concentration

The results of the analyses showed that the hemicellulose concentration in the flax fiber decreased during the retting process. The decrease in hemicellulose resulted in the release of cellulosic fiber, which was bounded together as fiber bundles (Weiting 1951). The hemicellulose concentration in fibers from various treatments is as shown in Figure 6.4.

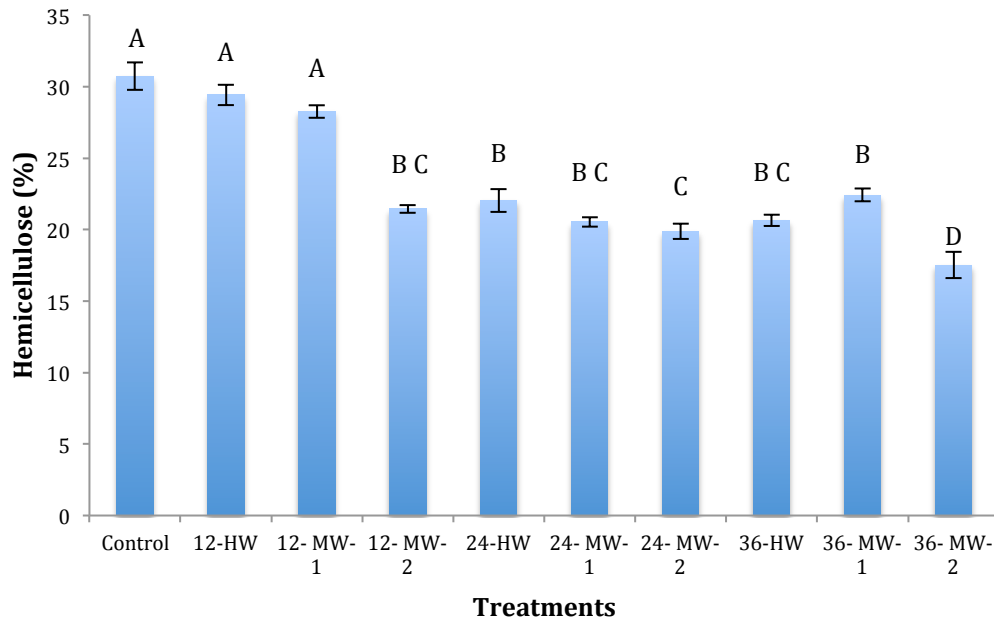


Figure 6.4 Hemicellulose percentages in flax fibers after various treatments

The concentration of hemicellulose showed a decreasing trend in all the levels of soaking except for 36 hours of soaking, but at the same time, there was a significant difference in hemicellulose concentration between the hot water treated flax fiber samples and microwave treated (2W/g) flax fiber samples which proved the role of microwave in the hemicellulose removal.

The control samples and the retted samples showed significant difference in hemicellulose concentration except for 12 hour soaked and hot water treated samples and 12 hour soaked microwave treated (1 W/g) samples.

Response surface curve for the hemicellulose concentration of flax fiber at various levels of treatment is as shown in Figure 6.5. Hemicellulose concentration was decreased with increase in soaking time and the microwave power used in the treatment. The equation for the hemicellulose concentration as per the surface plot is as follows:

$$\begin{aligned}
 \text{Hemicellulose (\%)} = & 22.0547 - 3.4159(\text{Soaking}) - 1.993(\text{Treatment}) \\
 & + 0.8599(\text{Soaking} \times \text{Treatment}) + 2.4561(\text{Soaking})^2 \\
 & - 1.5688(\text{Treatment})^2
 \end{aligned} \tag{6.2}$$

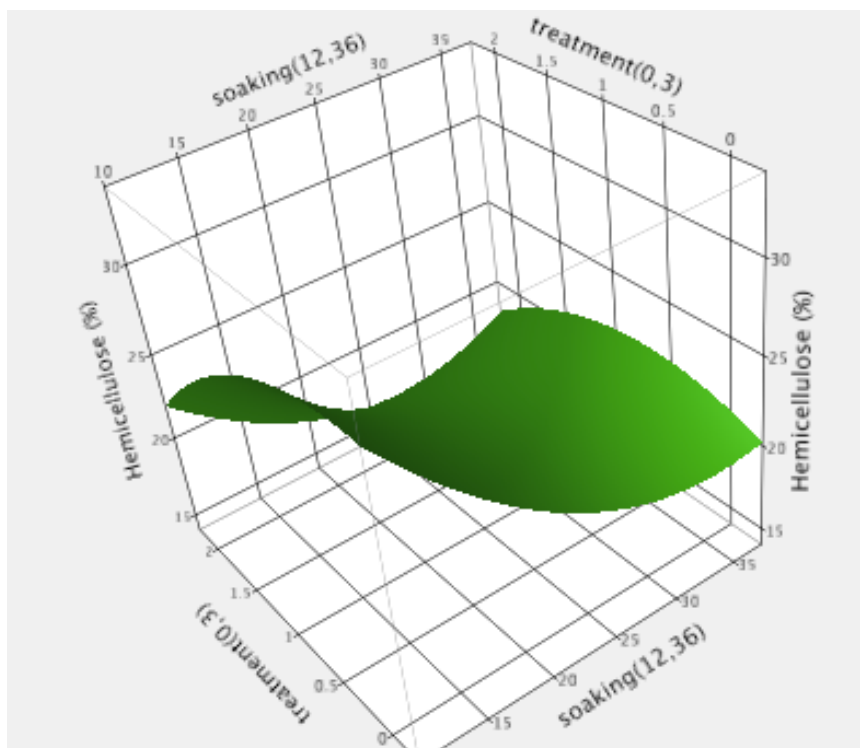


Figure 6.5 Response surface curve of hemicellulose percentage in flax fibers

The analysis of variance showed that the hemicellulose percentage was represented with a quadratic polynomial equation with an R^2 value of 0.92. The quadratic polynomial model was highly significant and sufficient to represent the actual relationship between the response and significant parameters with a p-value of 0.0001 and RMSE value of 1.1124 from the ANOVA.

6.4.3 Lignin Concentration

Lignin is present in the primary cell walls of the plant stem along with pectin whereas cellulose is present in the secondary cell wall of the plants (Pallese 1996). In non- retted fibers, lignin percentage was 2.98%. Lignin concentration in the flax fiber samples decreased during microwave assisted retting with all soaking durations. There was a significant difference in lignin concentration between hot water treated flax fiber samples and microwave assisted retted samples at all soaking levels and all the treatments were significantly different from that of control sample also (Figure 6.6).

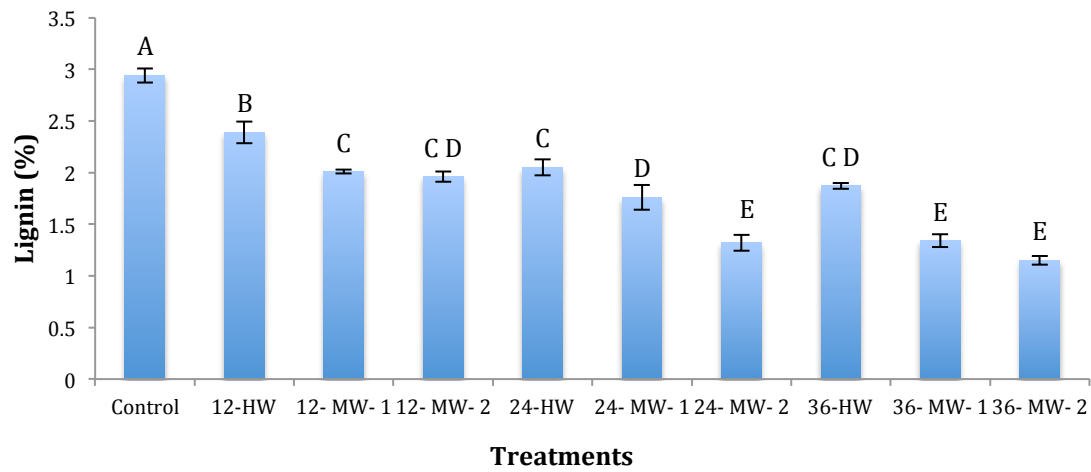


Figure 6.6 Lignin percentage in flax fibers after various treatments

The response surface curve of lignin concentration at various treatments is shown in Figure 6.7.

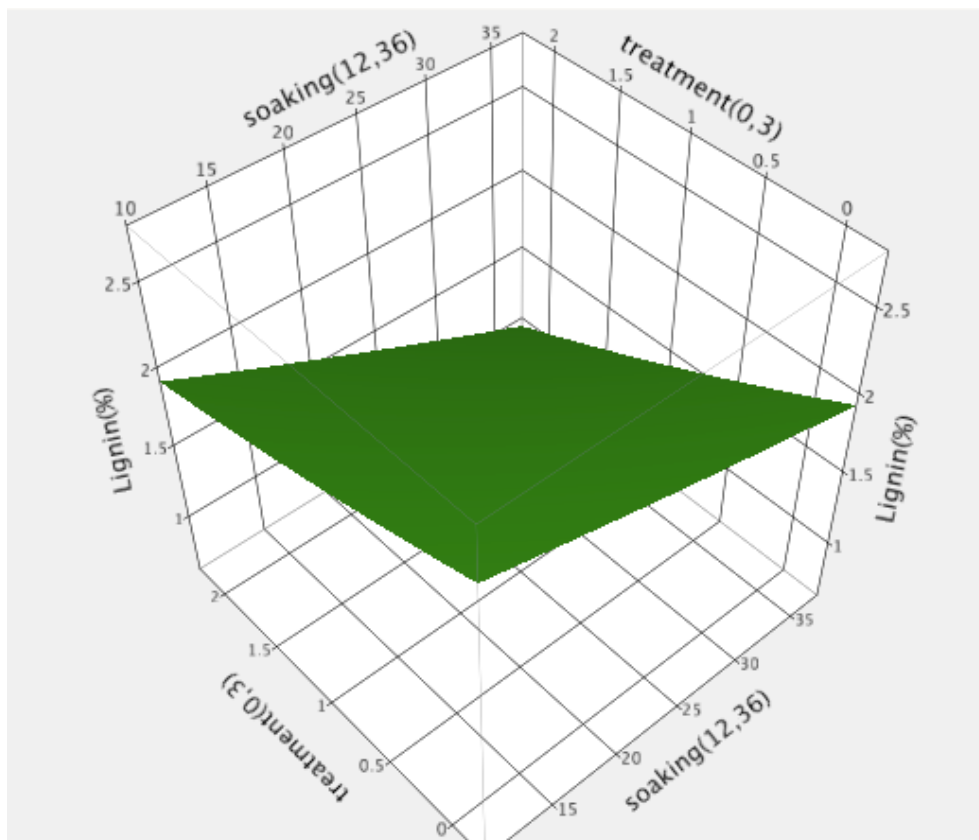


Figure 6.7 Response surface curve of lignin percentage in flax fibers

Lignin concentration was decreased with increase in soaking time and microwave power used in the treatments. The lignin concentration is expressed as the following polynomial equation having an R^2 value of 0.93 with a p value < 0.0001 and an RMSE value of 0.1066. A comparison between the actual and the predicted values of lignin concentration for various levels of treatments is tabulated in Table 6.1.

Predicted percentage of lignin was calculated by the following equation:

$$\begin{aligned} \text{Lignin (\%)} = & 1.733 - 0.4325(\text{Soaking}) - 0.3029(\text{Treatment}) \\ & - 0.6438(\text{Soaking} * \text{Treatment}) + 0.7767(\text{Soaking})^2 \\ & + 0.6142(\text{Treatment})^2 \end{aligned} \quad (6.3)$$

6.4.4 Pectin Concentration

Pectin amounts are often low in flax fibers, but they are strategically located within the plant tissues like cement for bricks. Pectin, along with hemicelluloses, are called matrix polysaccharides in flax plants and hold tissues, including fibers together (Sakai, Sakamoto et al. 1993). The efficiency of retting could be explained on the basis of the pectin present in the flax fiber. From Figure 6.8, there was a significant difference between microwave and hot water retting at soaking level of 24 and 36 hours. But at 12 hours soaking, there was no significant difference in the pectin concentration. This may be because for 12 hours of soaking, microwave energy couldn't break the strong pectin bonds since the effect of soaking was not prominent at 12 hours. But in 24 and 36 hours of soaked samples, there was a significant difference between hot water and microwave treated flax fiber's pectin concentration, which proved the effect of microwave assisted retting. The probable reason for the degradation of pectin bonds at higher soaking duration was because of the combined effect of thermal and non-thermal properties of microwave. Soaking brought down the glass transition temperature of pectin that allowed its degradation at lower temperature. When the flax stem exposed to microwave radiation contained polar molecules and ions, then the radiation could initiate chemical, biological and physical processes (Tsubaki and Azuma 2011).

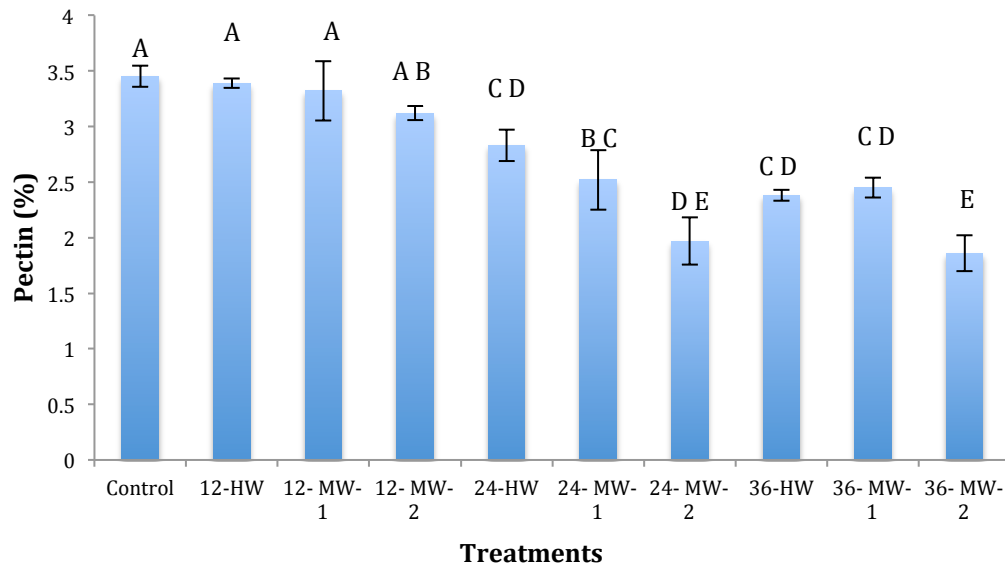


Figure 6.8 Pectin percentage in flax fibers after various treatments

The vibration of polar molecules and the movement of ions resulted in the generation of heat and extensive collisions in the plant cell within the cell wall, which helped in the breaking of strong pectin bonds (Sridar 1998).

The response surface curve of pectin concentration changes is presented in Figure 6.9. As per the response surface, the pectin content was decreasing with increase in soaking as well as the treatments. The percentage of pectin was predicted by a polynomial equation with an R^2 value of 0.76 with a p value < 0.001 and RMSE value of 0.268 as shown below.

$$\begin{aligned}
 \text{Pectin (\%)} = & 2.663 - 0.48(\text{soaking}) - 0.24(\text{Treatment}) \\
 & - 0.2769(\text{Treatment})^2
 \end{aligned}
 \tag{6.4}$$

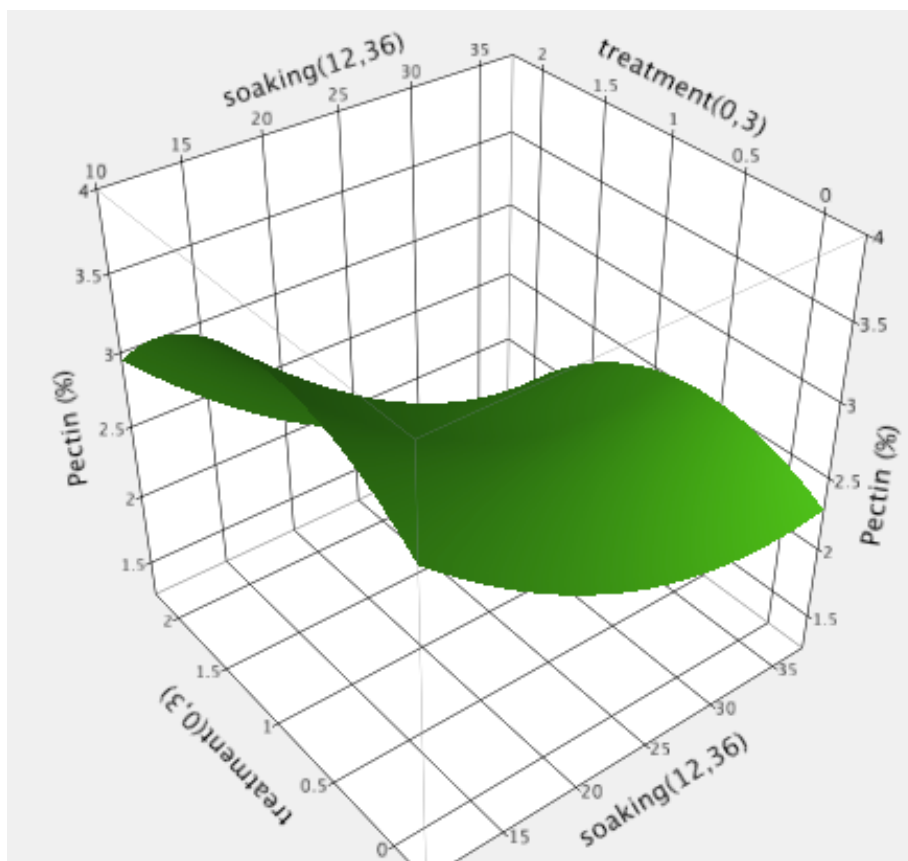


Figure 6.9 Response surface curve of pectin percentage in flax fibers

Predicted and actual values of pectin content at various levels of experiments are tabulated in Table 6.1.

6.4.5 Sugar Content in the Solution

Flax stems were immersed in water for soaking and the microwave assisted retting was conducted in the same solution. The solution was subjected to analysis of sugar content and the results are shown in Figure 6.10. According to Figure 6.10, there was an increase in sugar content with respect to the treatments at each soaking level. Maximum sugar release was observed for the samples with 24 hours soaking and 2 W/g microwave treatment and there was a significant difference in the release of sugar between hot water treated sample and microwave treated samples.

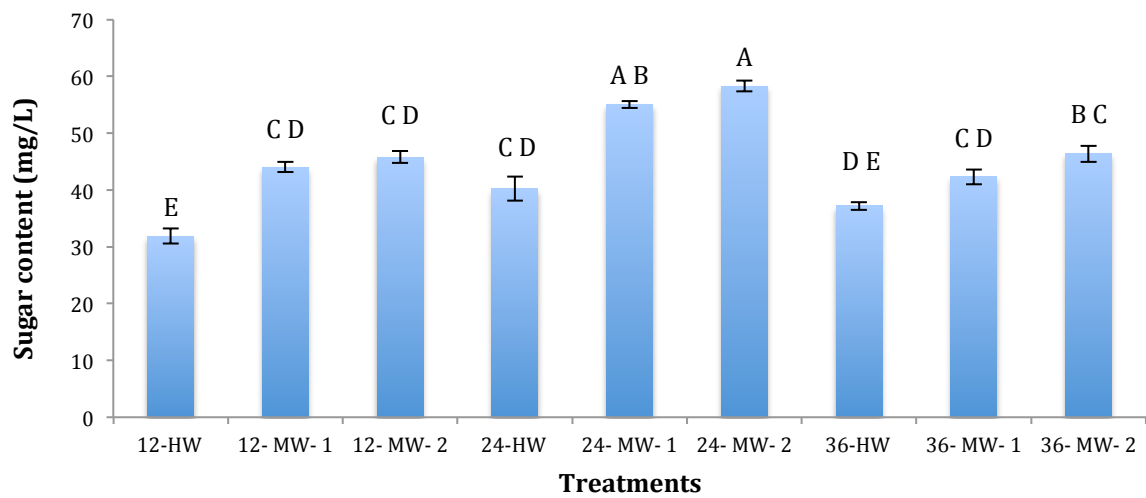


Figure 6.10 Sugar release in the solution after various treatments

Response surface curve for sugar release at various levels of experiment is shown in Figure 6.11.

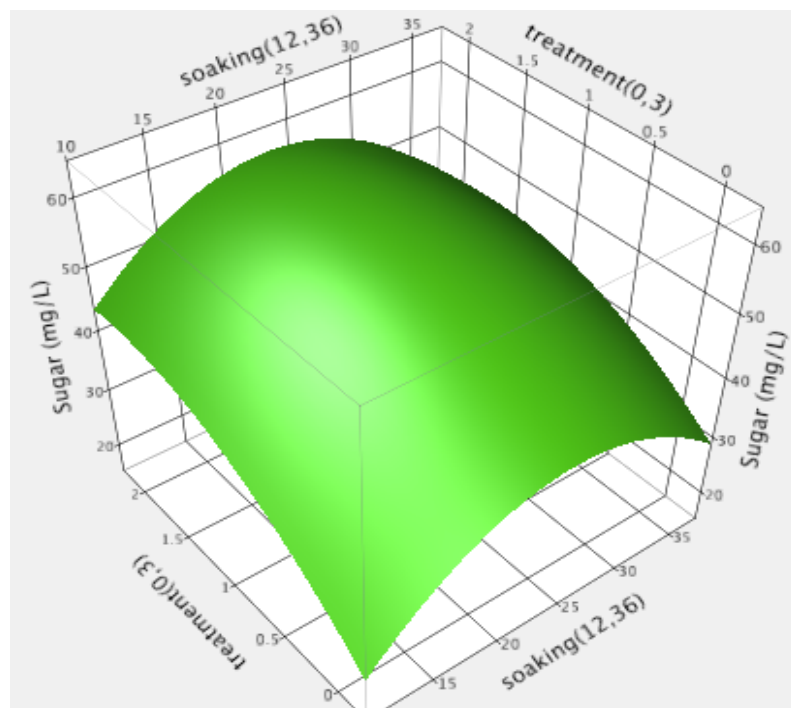


Figure 6.11 Response surface curve of sugar release in flax fibers

The response surface showed a trend of change in sugar content which is expressed as a polynomial equation with R^2 value of 0.94 and a p value <0.0001 and RMSE value of 2.0802. The actual and predicted values of sugar content were tabulated in Table 6.1.

The sugar content with respect to various treatment levels were calculated by the following equation:

$$\begin{aligned}
 \text{Sugar content } \left(\frac{mg}{L} \right) &= 54.382 + 1.3(\text{Soaking}) + 6.0788(\text{Treatment}) \\
 &\quad - 1.1969(\text{Soaking} \times \text{Treatment}) - 10.0963(\text{Soaking})^2 \\
 &\quad - 3.58(\text{Treatment})^2
 \end{aligned} \tag{6.5}$$

6.4.6 Visual Analysis of Flax Fibers

Flax fibers obtained by various retting processes were analyzed by using a Leica DM 2000 (Leica microsystems, Germany) optical microscope equipped with a digital camera with a scale of 1:1000. The results are shown in Fig 6.12. It is clear from Fig 6.12 that the control fiber samples were thick and dark which indicated the presence of impurities like wax, pectin, hemicellulose and shives. The soaked fibers were thinner than the control sample that showed the removal of wax and peripheral impurities. Among the soaked fibers, 36 hours soaked fibers were found to be the thinnest, but they were not separated. Analysis of microwave-assisted retted samples proved the fiber separation when compared with hot water treated samples, because the fibers were separated in microwave-assisted retted fiber samples. Among the microwave-assisted retted fibers, 12 hours soaked fibers were not separated as compared to the 24 and 36 hours soaked and microwave retted fibers as shown in Figure 6.12, which clearly proved the effectiveness of microwave-assisted retting.

Table 6.1 Central composite design for compound release in various retting treatments of flax stems

Soaking (hrs)	Treatment	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
		Cellulose (%)	Cellulose%	Hemicellulose (%)	Hemicellulose (%)	lignin (%)	lignin (%)	pectin (%)	pectin (%)	sugar (mg/L)	sugar (mg/L)
36(+1)	1 (0)	83.1	81.92	21.23	22.28	1.29	1.06	2.12	2.10	42.9	42.59
24 (0)	1 (0)	70.77	71.92	20.54	22.05	1.76	1.73	2.83	2.72	55.05	54.38
24 (0)	2 (+1)	79.98	78.24	21.11	19.80	1.37	1.46	2.1	2.31	56.8	60.41
36(+1)	2 (+1)	80.89	85.23	17.52	20.92	1.15	0.72	1.86	1.69	46.37	46.90
36(+1)	0 (-1)	81.04	78.61	20.66	22.00	1.87	1.41	2.38	2.04	37.19	35.16
24 (0)	0 (-1)	66.12	65.61	23.12	22.68	2.11	2.01	2.45	2.67	41.23	45.24
12(-1)	1 (0)	65.03	61.92	28.27	32.18	2.01	2.15	3.32	3.34	44.04	39.60
36(+1)	1 (0)	81.05	81.92	22.42	22.28	1.34	1.06	2.45	2.10	42.3	42.59
12(-1)	2 (+1)	70.91	71.25	21.45	29.02	1.96	1.96	3.12	2.93	45.8	47.34
12(-1)	1 (0)	64.21	61.92	29.12	32.18	2.37	2.15	3.22	3.34	43.8	39.60
12(-1)	0 (-1)	62.47	52.60	29.42	33.70	2.54	2.35	3.39	3.29	31.9	28.75
12(-1)	2 (+1)	69.2	71.25	23.1	29.02	2.21	1.96	3.24	2.93	44.3	47.34
12(-1)	0 (-1)	60.21	52.60	28.23	33.70	2.34	2.35	3.42	3.29	32.1	28.75
36(+1)	2 (+1)	82.1	85.23	17.23	20.92	1.09	0.72	1.84	1.69	47.12	46.90
12(-1)	2 (+1)	68.67	71.25	24.1	29.02	1.98	1.96	3.19	2.93	45.01	47.34
24 (0)	2 (+1)	78.92	78.24	19.88	19.80	1.32	1.46	1.97	2.31	58.3	60.41
36(+1)	1 (0)	84.2	81.92	23.43	22.28	1.21	1.06	2.19	2.10	42.3	42.59
24 (0)	0 (-1)	65.73	65.61	22.04	22.68	2.05	2.01	2.52	2.67	40.23	45.24
24 (0)	1 (0)	71.87	71.92	21.54	22.05	1.86	1.73	2.83	2.72	55.05	54.38
36(+1)	2 (+1)	84.2	85.23	18.12	20.92	1.05	0.72	1.84	1.69	46.98	46.90
24 (0)	1 (0)	72.12	71.92	20.12	22.05	1.81	1.73	2.98	2.72	56.22	54.38
36(+1)	0 (-1)	79.22	78.61	21.01	22.00	1.79	1.41	2.29	2.04	40.1	35.16
36(+1)	0 (-1)	80.11	78.61	19.921	22.00	1.85	1.41	2.35	2.04	40.12	35.16
24 (0)	1 (0)	73.2	71.92	22.745	22.05	1.83	1.73	2.75	2.72	53.9	54.38
24 (0)	1 (0)	72.55	71.92	21.34	22.05	1.69	1.73	2.81	2.72	57.43	54.38
12(-1)	0 (-1)	61.34	52.60	30.12	33.70	2.67	2.35	3.35	3.29	33.1	28.75
24 (0)	3 (+1)	80.01	78.24	18.45	19.80	1.53	1.46	1.93	2.31	57.4	60.41
36(+1)	3 (+1)	82.34	85.23	18.01	20.92	1.18	0.72	1.85	1.69	48.3	46.90
36(+1)	0 (-1)	80.23	78.61	20.13	22.00	1.79	1.41	2.19	2.04	40.5	35.16
24 (0)	1 (0)	73.12	71.92	23.1	22.05	1.75	1.73	2.69	2.72	56.33	54.38
24 (0)	1 (0)	70.12	71.92	20.23	22.05	1.79	1.73	2.98	2.72	55.2	54.38
12(-1)	1 (0)	63.23	61.92	27.54	32.18	2.11	2.15	2.78	3.34	43.21	39.60
36(+1)	1 (0)	82.1	81.92	20.91	22.28	1.42	1.06	2.23	2.10	44.2	42.59
12(-1)	1 (0)	64.22	61.92	28.76	32.18	2.4	2.15	2.84	3.34	43.5	39.60
12(-1)	2 (+1)	71.01	71.25	23.49	29.02	2.21	1.96	1.89	2.93	46.21	47.34
24 (0)	0 (-1)	64.22	65.61	23.02	22.68	2.1	2.01	2.45	2.67	42.12	45.24
24 (0)	0 (-1)	65.32	65.61	22.76	22.68	2.07	2.01	2.51	2.67	43.1	45.24
24 (0)	2 (+1)	78.93	78.24	19.1	19.80	1.47	1.46	1.92	2.31	59.2	60.41
12(-1)	0 (-1)	60.11	52.60	28.97	33.70	2.61	2.35	3.38	3.29	34.21	28.75
24 (0)	1 (0)	70.12	71.92	21.23	22.05	1.71	1.73	2.67	2.72	53.9	54.38

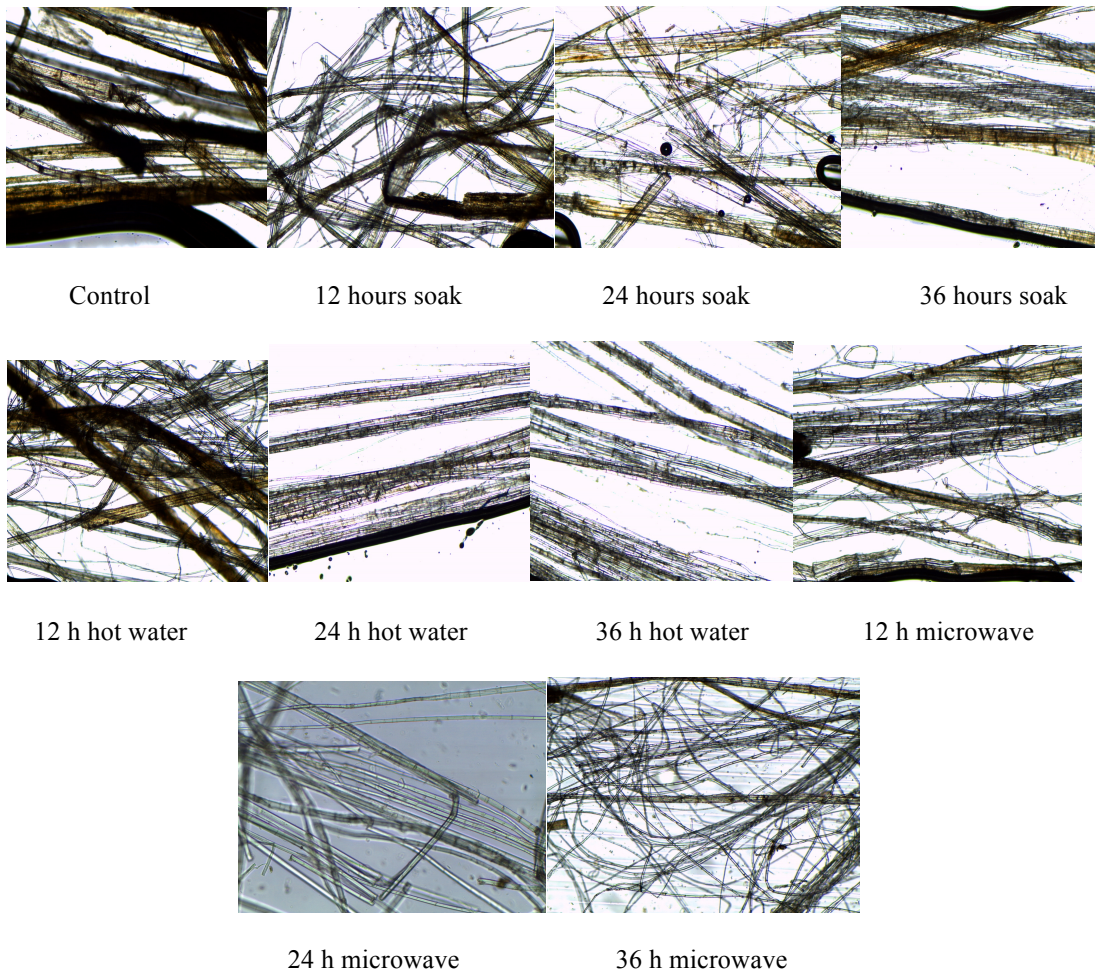


Figure. 6.12 Optical microscopic images of the flax fibers

6.4.7 Process Optimization

The main factors affecting microwave-assisted retting process were pre-soaking, microwave power, temperature and time of the process. In the earlier experiments to establish the microwave-assisted retting process, the temperature of the sample in the soaking water was $98\pm 2^{\circ}\text{C}$ and it was monitored throughout the experiment. The treatment time for the microwave-assisted retting process was optimized to 20 minutes. At the above temperature and processing time, it was experimentally proven that there were no physical and visual changes in the flax fiber. The remaining factors were soaking time and microwave power. In order to optimize the soaking time and the microwave power, a central composite design was developed as shown in Table 6.1. The highest average cellulose percentage of 81.34% was in 36 h- 2W microwave-assisted retted flax fiber samples, but in 24 h- 2 W samples, the cellulose percentage was 79.01% with a significant difference between them. The cellulose concentration in 36 hours soaked 1 W/g microwave treated samples did not show any significant difference with 36 h- 2W samples in terms of cellulose content. In case of hemicellulose removal, the minimum hemicellulose was present in 36 h- 3W sample (17.57%) followed by 24 h- 2W samples (19.88%) with a significant difference. The minimum lignin percentage was found in 36 h- 2 W samples (1.12%) followed by 24h- 2 W samples (1.32%) with a significant difference between them. The maximum pectin removal was found in the 36 h- 3W samples (1.86%) and pectin removal in that of 24 h- 2 W samples was 1.97% without any significant difference between them. The maximum sugar content was observed in the 24 h- 2W sample solution (58.3 mg/L) followed by 24 h- 1 W sample solution (55.05 mg/L). In retting, pectin removal was the most important factor to be considered. Even though the 36 hours soaked 2 W/g treatment gave the best results, the 24 hour soaked 2 W/g microwave treatment was optimum when all the factors are considered.

6.5 Conclusion

Microwave-assisted retting was established by analyzing the chemical composition of flax fibers. Since pectin was responsible for the cementing effect of fibers inside the stems, the process was optimized on the basis of the presence of pectin in the fibers after retting. In microwave-assisted retting, electromagnetic radiation penetrates into the soaked plant stem to

excite the molecules inside the plant cell. This excitation leads to the breaking of already weaker bonds due to the tension created by water. At the same time, the thermal effect of electromagnetic radiation helps in increasing the heat inside the samples by bipolar rotation and ionic migration mechanisms which helps in the structural degradation of non-cellulosic polysaccharides at reduced temperatures.

CONNECTING TEXT

Microwave- assisted retting of flax and hemp was introduced and the process was optimized by the chemical analysis of compounds like pectin, hemicellulose, lignin and pectin. The change of chemical compositions of flax and hemp were observed during microwave- assisted retting, which showed a trend at various treatment levels. In the next chapter, a kinetic model was developed for the rate of change of compounds like lignin, hemicellulose and cellulose during microwave- assisted retting of flax stems and the model was validated by analyzing the compositional changes of hemp fibers with microwave- assisted retting.

CHAPTER 7

MATHEMATICAL ANALYSIS OF COMPOUND RELEASE DURING MICROWAVE ASSISTED RETTING OF FLAX STEMS

7.1 Abstract

Microwave- assisted retting was conducted at various power levels (1 W/g, 1.5 W/g and 2 W/g) on pre- soaked flax stems (12 h, 24 h and 36 h). The retted stems were dried and the fibers were separated. The percentage of cellulose, hemicellulose and lignin presented in the flax fibers were found out by NIR (near infrared) spectroscopy. Based on the rate of change of cellulose, hemicellulose and lignin at various levels of treatments, a kinetic model was developed and the model was validated by analyzing the compositions of hemp fibers obtained from pre- soaked hemp stems at various microwave power levels. The rate of change of cellulose percentage in the model fitted with the observed values of cellulose percentage with an average R^2 value of 0.87 and an average RMSE value of 0.0130. But in hemicellulose, the R^2 value was 0.936 and average RMSE value was 0.0135, and for lignin, R^2 value was 0.92 and RMSE value of 0.0181. The rate coefficient for all the treatments was increasing within the treatment limit, which indicated the increased reaction rate with an increase in microwave power. The validation of model was successfully conducted by analyzing the components of hemp fibers at various levels of microwave powers.

7.2 Introduction

Flax (*Linum usitatissimum*) is a fibrous plant and the fibers are extracted from the stalk of the plant. Separation of fibers from the plant stems is usually a laborious process because of the adhesive nature of fiber bundles inside the stems with strong chemical bonds. Retting is the process of loosening of fibers from plant stems either by chemical or mechanical means (Akin, 2013). Various retting methods include water retting, dew retting, enzyme retting, steam explosion retting, microwave assisted retting etc. Fibers attached to the stems with a close matrix contain hemicellulose, pectin and lignin (Akin, et al., 2005). In water retting, aerobic bacteria attack the plant stems by eating down the soft part of plant stem and to break down the strong chemical bonds and release the cellulosic fibers from the plant- fiber matrix (Day et al.,

2005). The breaking of bonds leads to the release of compounds like hemicellulose, lignin and increase in cellulose content in the fibers. The fiber bundles are embedded within the plant cell and they are attached to each other strongly with various layers. A fiber bundle consists of 10-40 single fibers of length from 25 to 150 mm, which varies with variety. These fibers are loosened due to retting. The main components that hold the fibers together inside the flax stem are waxes on the cell wall, pectin substances with traces of lignin inside the primary cell wall, while secondary cell wall consists of cellulose. The cambium cells separate fibers from shives (Kadla et al., 2000). The hemicellulose branches help to bind the microfibrils to one another and to other matrix components, particularly pectin. This cross links the cellulose microfibrils into a network of tough, fibrous molecules and is responsible for the mechanical strength of plant cell walls. Pectin amounts are often low in flax fibers, but they are strategically located within the plant tissues like cement for bricks (Akin et al., 1996). Lignin is another non-cellulosic component of flax plant with a complex polyphenyl propanoid structure, which helps to oppose microbial degradation of plant carbohydrates tissues. The decomposition of the complex chemical bonds formed by these compounds results in the loosening of fiber bundles and hence further processing to achieve separation of fibers will be easier. Analysis of compounds present in fibers before and after retting is used as a way to explain the effect of retting. Microwave assisted retting of pre-soaked flax stem was conducted at Bioresource Engineering department, McGill University, and the compounds were analyzed by NIR method. The change in the composition of compounds showed a trend with respect to microwave power, soaking and treatment time. An attempt was made to develop a mathematical model, which relates the rate of change of composition in the fiber with retting and the factors like microwave energy, treatment time and pre- soaking status. There have been several studies conducted on the modeling of the bioconversion of lignocellulosic materials.

Kinetic modeling is studied widely to investigate the compound analysis of biomaterials, while some of the researchers used non-kinetic or fuzzy inference models in complex systems like conversion of cellulosic biomass. Sun and Cheng (2002) and Mosier et al. (2005) have summarized the modes of actions, and the advantages and disadvantages associated with different biomass pretreatment methods to release lignin and hemicellulose (Mosier et al., 2005; Sun & Cheng, 2002). The objective of our study is to model the effect of microwave assisted

retting on the relative changes in the components like cellulose, hemicellulose and lignin.

7.3 Materials and Method

The materials used and the methods adopted for the study are discussed in this section.

7.3.1 Microwave-Assisted Retting

Non- retted flax stems were supplied by Lanaupôle Fibers, Montreal. Flax stem samples were prepared by cutting them in equal length of 8 cm. For experimental similarity, only middle portions of the stems were used. Flax stems were water- soaked for 12 h, 24 h and 36 h intervals. Microwave assisted retting were performed on the pre-soaked flax stems at various time intervals from 5 min to 20 min with a varying power levels of 1 W/g, 1.5 W/g and 2 W/g. The stems after retting were dried and fibers were separated manually. The experiments were repeated 3 times at each level. The experimental design is as shown in Table 7.1.

The flax stems after retting were dried and the fibers were separated manually using a hackling comb and were used for further compositional analysis.

Table 7.1 Experimental design for microwave assisted retting of flax stems

Factors	Levels	Description
Pre-soaking time	1	12 h
	2	24 h
	3	36 h
Microwave retting power	1	1.0 Wg ⁻¹
	2	1.5 Wg ⁻¹
	3	2.0 Wg ⁻¹
Microwave retting time	1	0 min
	2	5 min
	3	10 min
	4	15 min
	5	20 min

7.3.2 Near Infrared (NIR) Analysis

The Flax fibers were subjected to compositional analysis using near Infrared spectrometer (NIR). The model used was Nicloet Antaris FT-NIR analyzer located at BRI, Montreal, Canada. NIR results were used to analyze the changes in the composition of lignin, hemicelluloses (impurities) and cellulose (to analyze strength).

7.3.3 Kinetic Model Studies

The general form of kinetic model used in our study is adopted from the work done by Dang and Nguyen in 2006, who proposed a kinetic model to describe delignification and carbohydrate losses of lignocellulosic materials (Bamford and Tipper, 1980), Dang and Nguyen (2006, 2007) expressed the amount of a component (X) in lignocellulosic biomaterial to a time dependent rate coefficient via a first-order-differential equation (Dang & Nguyen, 2007; Dang & Nguyen, 2006):

$$X = X_i \exp(-kt^n) \quad (7.1)$$

where X is the percentage of compound present in the fiber, X_i is the percentage of compound present in the untreated flax fiber, t is the time, k and n are the constants dependent on the heterogeneity of the material and nature of the reaction. By taking the derivative of Eqn. 7.1, we get a first order differential equation as shown below (Brown, 1980.).

$$\frac{-dX}{dt} = knt^{(n-1)}X \quad (7.2)$$

In our study, pre soaked flax stems were subjected to various microwave treatments and the experiments were repeated 3 times. Hence, effects of microwave power have to be introduced in to this equation. In this instance, a dimensionless dielectric loss tangent of the reagent (water), which is represented as D , is introduced in to the Eqn. 7.2.

$$\frac{-dX}{dt} = knt^{(n-1)}.D^b.X \quad (7.3)$$

It is to be assumed that the dielectric loss tangent of reagent remains constant during the microwave assisted retting time (Keshwani & Cheng, 2010). If the dielectric loss tangent is

constant throughout the microwave assisted retting process, the Eqn. 7.3 can be rewritten by integrating them to determine the parameters k , n and b of the kinetic model. The new form of the equation is:

$$\ln \left[\ln \left(\frac{x}{x_i} \right) \right] = \ln (k) + b \cdot \ln (D) + n \cdot \ln (t) \quad (7.4)$$

7.3.4 Validation of the Model

The model performance was evaluated by conducting microwave- assisted retting (1 W/g, 1.5 W/g and 2 W/g) on 12 h pre- soaked hemp stems and using R^2 values from the model and experimental values, and root mean square errors (RMSE) associated with the observed and the predicted values of cellulose, hemicellulose and lignin. MATLAB 2013 (The MathWorks Inc., USA) was used for the analysis and validation

7.4 Results and Discussion

Flax fibers were separated from the stems and the percentage of cellulose, hemicellulose and lignin were obtained using NIR analysis and the model was analyzed with respect to the observed results.

7.4.1 Rate of Change of Cellulose Content

The values of parameters k , n and b and R^2 and RMSE values of the model associated with the cellulose release are tabulated in Table 7.2. The observed and predicted values of the model for the rate of change of cellulose with respect to time are tabulated in Table 7.3.

The k values were kept constant for each soaking level, because the parameter k was associated with the behavior of flax stem under soaking conditions. Parameter b was dependent on the dielectric loss factor of the reagent associated with the microwave treatment; in this experiment, water was used as a reagent for the soaking and microwave assisted retting which had a dielectric loss tangent of 0.123 (Lidström et al., 2001). Parameter n was dependent on the reaction involved in the microwave- assisted retting of flax stems. For the rate of change of cellulose release in all treatments, values of n were greater than 1, which was responsible for the increase of rate coefficient ($k \cdot n \cdot t^{(n-1)}$) with respect to time.

Table 7.2 Model parameters, R^2 and RMSE values associated with release of cellulose rate at various microwave-assisted treatment of flax stems

Soaking time (h)	MW power (W/g)	k value	n value	b value	R^2	RMSE
12	1	0.333	1.103	1.281	0.906	0.007
12	1.5	0.333	1.116	0.848	0.875	0.016
12	2	0.333	1.109	0.705	0.852	0.017
24	1	0.421	1.400	1.799	0.977	0.003
24	1.5	0.421	1.279	0.884	0.884	0.031
24	2	0.421	1.126	0.531	0.981	0.013
36	1	0.547	1.250	1.078	0.971	0.012
36	1.5	0.547	1.154	0.716	0.985	0.012
36	2	0.547	1.152	0.547	0.986	0.015

In 12 h pre- soaked and microwave- assisted retted samples, the R^2 values 0.9059, 0.8753 and 0.8516 are associated with power levels of 1 W/g 1.5 W/g and 2 W/g respectively. But in 24 h and 36 h pre- soaked samples, which had higher R^2 values and lower RMSE values showed a closer fit with the observed rate of change of composition of cellulose. The average R^2 value of model fit for cellulose was 0.92 and average RMSE value was 0.0181. The closeness of fit in the cellulose release rate in various treatments is shown in Figure 7.1.

Table 7.3 Observed and predicted values of cellulose rate changes with respect to microwave – assisted retting.

Soaking time (h)	MW retting time(min)	Rate of change of cellulose					
		MW power levels (W/g)					
		Observed (1 W/g)	Predicted (1 W/g)	Observed (1.5 W/g)	Predicted (1.5 W/g)	Observed (2 W/g)	Predicted (2 W/g)
12	0	0	0	0	0	0	0
12	5	0.031	0.039	0.072	0.060	0.088	0.080
12	10	0.033	0.030	0.078	0.089	0.093	0.083
12	15	0.035	0.033	0.082	0.080	0.070	0.055
12	20	0.036	0.035	0.084	0.079	0.065	0.038
24	0	0	0	0	0	0	0
24	5	0.031	0.030	0.127	0.100	0.166	0.160
24	10	0.041	0.040	0.154	0.190	0.167	0.190
24	15	0.048	0.053	0.172	0.187	0.167	0.207
24	20	0.054	0.050	0.186	0.160	0.167	0.185
36	0	0	0	0	0	0	0
36	5	0.107	0.120	0.166	0.160	0.224	0.220
36	10	0.127	0.120	0.184	0.180	0.249	0.210
36	15	0.141	0.150	0.196	0.210	0.264	0.250
36	20	0.151	0.140	0.205	0.190	0.276	0.265

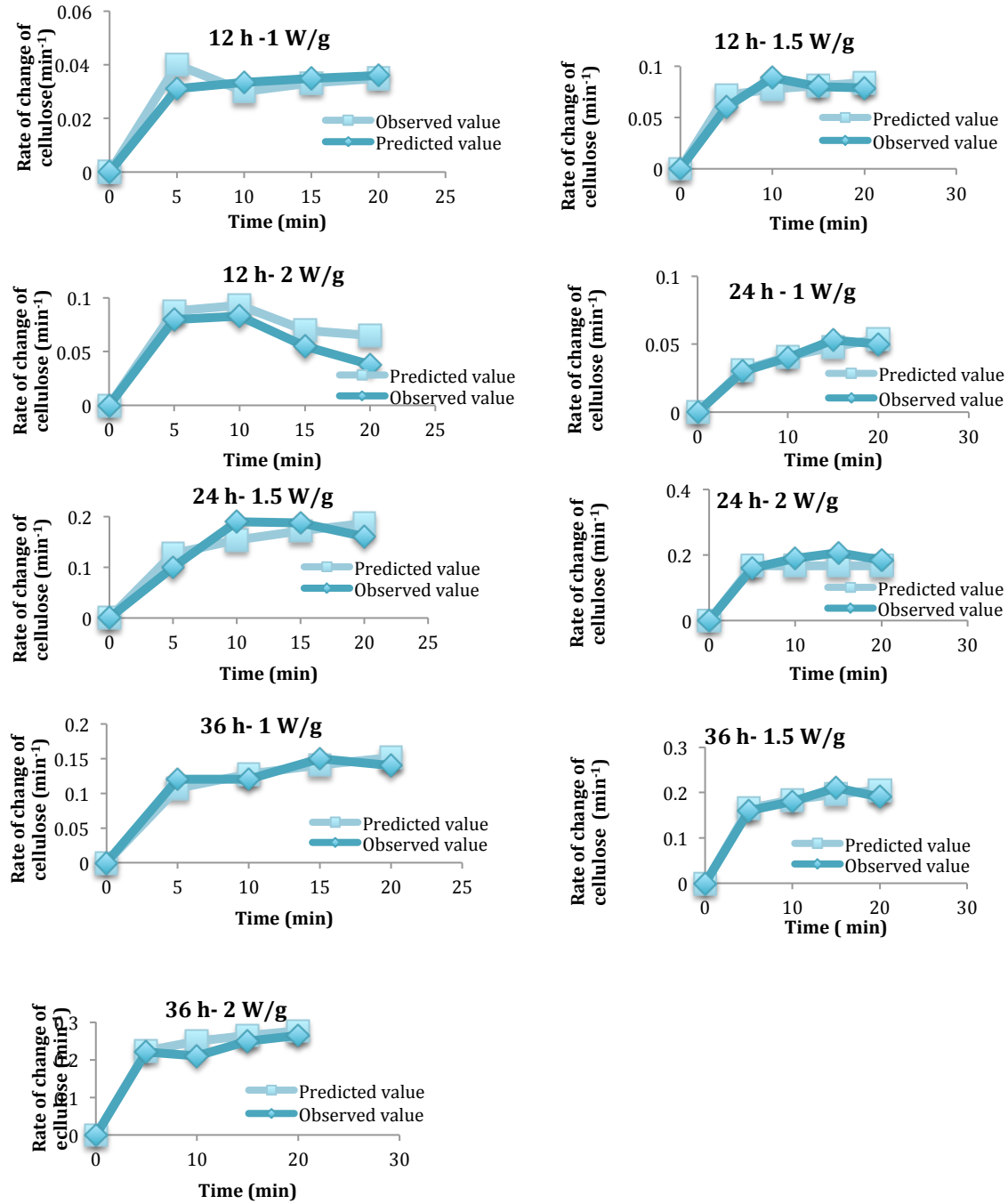


Figure 7.1 Observed and predicted values of rate of change of cellulose percentage in flax fiber.

In this model, the k value increased with pre- soaking time, which resulted in an increase in the rate of change of cellulose with respect to soaking. Parameter n , which is related to the reaction

involved with the retting process, did not show any specific change with treatments at different soaking times and microwave power levels that explained the similarity in the reaction occurring in all the treatments.

The parameter b showed a decreasing trend with an increase in soaking level from 12 h, up to 36 h, where b was associated with the dielectric loss factor of the solvent used (water) pre-soaking and microwave- assisted retting. The value of dielectric loss tangent of water was taken as 0.123 at 2450 MHz with a temperature of 99° C and assumed to be constant throughout the process (Zahn et al., 1986). Since the parameter b decreased, the value of D^b increased which in turn resulted in an increase in cellulose rate. Parameter b was decreased with an increase in the rate change of cellulose and rate of change of cellulose composition was increased due to microwave treatment (Wang, & Wen, 2008; Keshwani & Cheng, 2010).

7.4.1.1 Rate coefficient

The rates coefficients ($k.n.t^{(n-1)}$) for cellulose release at various treatment levels are shown in Figure 7.2.

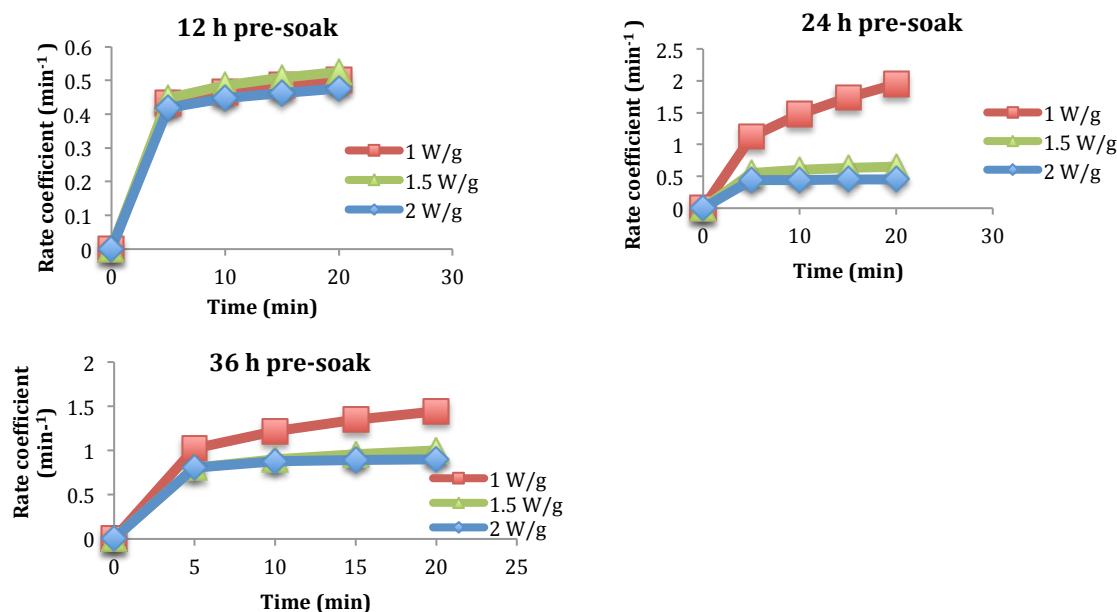


Figure 7.2 Rate coefficients for cellulose release for various treatments

The rate coefficient was found to be increasing with respect to the time. At 12 hour soaking, the rate coefficient was overlapping each other at various power levels of 1 W/g, 1.5 W/g and 2 w/g. But in the case of 24 h and 36 h pre-soak, the rate coefficient showed an increasing trend; with 1 W/g samples had the maximum value of rate coefficient, followed by 1.5 W/g and 2 W/g. Here in these experiments, the parameter k was kept constant at 12 h pre- soak (0.3331), 24 h pre-soak (0.4208) and 36 h pre- soak (0.5469). At a pre-soaking time, the value of rate coefficient was dependent on the parameter n , which was dependent on the reaction involved in the retting process. Because the value of rate coefficient increased with an increase in time of microwave retting within the treatment limits. Rate coefficient values of cellulose were less than that of hemicellulose and lignin, because cellulose is a homopolymer which contains only glucose, hence it did not permit a higher rate of release of the compound (Montane, 1994).

7.4.2 Rate of Change of Hemicellulose Content

Rate of change of hemicellulose content of the flax fibers at various treatments were calculated and compared with the predicted model as shown in Table 7.4.

The observed and predicted values of the rate of change of hemicellulose with respect to microwave- assisted retting were found to be similar as shown in Table 7.4. This similarity was explained by the R^2 values and RMSE values of the models for the prediction of the components. The observed and predicted values of hemicellulose rate showed high levels of similarity at all the treatments. The values of parameters k , n and b with corresponding R^2 and RMSE values are tabulated in Table 7.5.

The R^2 values for all the models were more than 0.92 except that of 12h- 2 W/g treated samples. The RMSE values corresponding to the model were very low, which also proved the closeness of fit. The closeness of fits of the models for hemicellulose is shown in Figure 7.3. Parameter k , which was dependent on the nature of material with respect to soaking, was kept constant for 12 h (0.335), 24 h (0.9898) and 36 h (3.586) soaking. The parameter k increased with an increase in soaking time.

Table 7.4 Observed and predicted values of hemicellulose rate changes with respect to microwave – assisted retting.

Soaking time (h)	MW retting time (min)	Rate of change of hemicellulose					
		MW power levels (W/g)					
		Observed (1 W/g)	Predicted (1 W/g)	Observed (1.5 W/g)	Predicted (1.5 W/g)	Observed (2 W/g)	Predicted (2 W/g)
12	0	0	0	0	0	0	0
12	5	0.017	0.020	0.027	0.020	0.051	0.068
12	10	0.027	0.020	0.037	0.030	0.079	0.080
12	15	0.035	0.040	0.045	0.050	0.103	0.110
12	20	0.042	0.040	0.052	0.055	0.123	0.110
24	0	0	0	0	0	0	0
24	5	0.079	0.080	0.128	0.140	0.166	0.180
24	10	0.125	0.140	0.169	0.190	0.193	0.200
24	15	0.163	0.190	0.199	0.220	0.210	0.230
24	20	0.198	0.170	0.224	0.190	0.223	0.200
36	0	0	0	0	0	0	0
36	5	0.163	0.140	0.208	0.200	0.248	0.220
36	10	0.218	0.250	0.245	0.280	0.280	0.300
36	15	0.259	0.290	0.270	0.300	0.301	0.310
36	20	0.292	0.270	0.289	0.270	0.316	0.300

The rate of change of hemicellulose is directly proportional to the parameter k , and that's why an increase in k value resulted in an increase in reaction rate. The parameter n (reaction dependent) for hemicellulose release was between 1.174 and 1.67 for all the treatment levels,

which is responsible for the increasing rate of change of hemicellulose with respect to an increase in the treatment time.

Table 7.5 Model parameters, R^2 and RMSE values associated with release of hemicellulose rate at various microwave- assisted treatment of flax stems

Soaking time (h)	MW power (W/g)	k value	n value	b value	R^2	RMSE
12	1	0.335	1.638	1.281	0.924	0.005
12	1.5	0.335	1.480	0.848	0.936	0.006
12	2	0.335	1.644	0.705	0.864	0.017
24	1	0.990	1.666	1.799	0.927	0.024
24	1.5	0.990	1.404	0.586	0.930	0.033
24	2	0.990	1.211	0.110	0.966	0.020
36	1	3.586	1.420	1.078	0.951	0.038
36	1.5	3.586	1.239	0.716	0.964	0.033
36	2	3.586	1.174	0.534	0.966	0.034

The parameter b (dielectric factor dependent) for the hemicellulose release showed a decreasing trend for 12 h, 24 h and 36 h soaked samples. As the dielectric loss tangent (D) value was 0.123 for the treatment, D^b increased with a decrease in b , which in turn responsible for an increase in the rate of change of hemicellulose release.

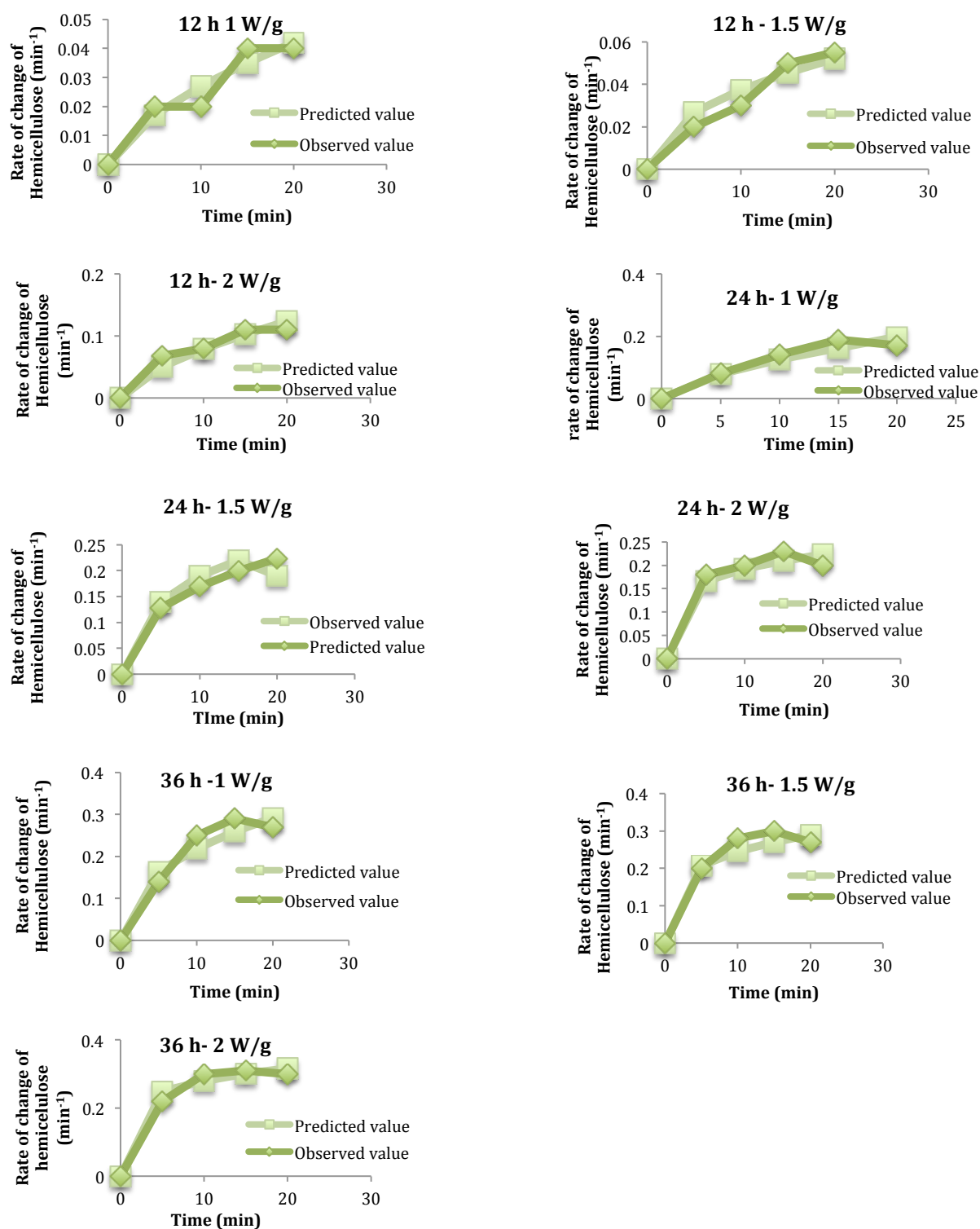


Figure 7.3 Observed and predicted values of rate of change of hemicellulose percentage in flax fibers

7.4.2.1 Rate Coefficients

Coefficients for the rate of change of hemicellulose in all the treatments showed an increasing trend with respect to time (Figure 7.4).

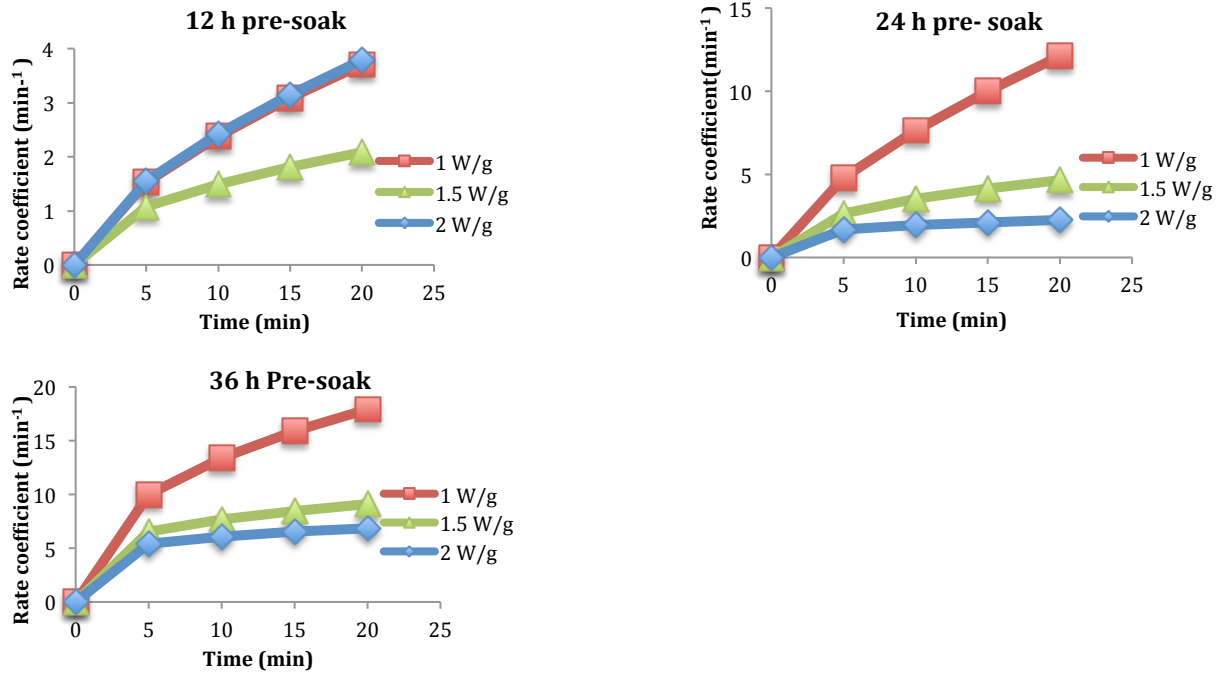


Figure 7.4 Rate coefficient for hemicellulose release for various treatments

For 12 h pre-soaked flax fibers, the rate coefficient of 1 W/g and 2 W/g samples overlapped and 1.5 W/g MW treatments showed the minimum rate coefficient. But in the case of 24 h and 36 h pre-soaked samples, the rate coefficients showed a similar trend as of cellulose, with a maximum for 1 W/g, followed by 1.5 W/g and 2 W/g. For hemicellulose, rate coefficient found to be increasing with respect to time within the treatment time.

7.4.3 Rate of Change of Lignin Content

The rate of change in the lignin composition with respect to various levels of pre-soaking and microwave assisted retting was calculated and compared with the model predicted values in table 7.6. The closeness of fit between model and observed values are shown in Figure 7.5. The validity of model was established by analyzing the R^2 and RMSE values of various treatment levels which is shown in Table 7.7.

Table 7.6 Observed and predicted values of lignin rate changes with respect to microwave – assisted retting time

Soaking time (h)	MW retting time (min)	Rate of change of lignin					
		MW power levels (W/g)					
		Observed (1 W/g)	Predicted (1 W/g)	Observed (1.5 W/g)	Predicted (1.5 W/g)	Observed (2 W/g)	Predicted (2 W/g)
12	0	0	0	0	0	0	0
12	5	0.044	0.040	0.094	0.100	0.126	0.140
12	10	0.062	0.050	0.108	0.110	0.140	0.160
12	15	0.077	0.073	0.117	0.120	0.150	0.160
12	20	0.089	0.095	0.124	0.115	0.157	0.125
24	0	0	0	0	0	0	0
24	5	0.051	0.080	0.111	0.120	0.160	0.160
24	10	0.076	0.050	0.126	0.130	0.168	0.160
24	15	0.096	0.100	0.135	0.140	0.172	0.190
24	20	0.113	0.115	0.142	0.130	0.175	0.155
36	0	0	0	0	0	0	0
36	5	0.128	0.100	0.165	0.160	0.193	0.200
36	10	0.159	0.190	0.182	0.200	0.205	0.230
36	15	0.181	0.210	0.193	0.210	0.212	0.220
36	20	0.198	0.165	0.201	0.175	0.217	0.197

R^2 values of all the treatments except for all the 1 W/g (12 h- 1W/g, 24 h- 1 W/g and 36 h- 1W/g) treatments was above 0.93, and all the treatments showed a low RMSE value which explained the closeness of fit. The values of parameters k, n and b corresponding to various treatments are given in Table 7.7.

Table 7.7 Model parameters, R^2 and RMSE values associated with release rate of lignin at various microwave- assisted treatment of flax

Soaking time (h)	MW power (W/g)	k value	n value	b value	R^2	RMSE
12	1	2.979	1.517	1.281	0.829	0.018
12	1.5	6.061	1.200	0.848	0.987	0.007
12	2	6.906	1.158	0.709	0.906	0.024
24	1	8.106	1.569	1.799	0.816	0.023
24	1.5	8.106	1.177	0.884	0.981	0.009
24	2	8.106	1.063	0.531	0.948	0.020
36	1	9.520	1.317	1.078	0.873	0.035
36	1.5	9.520	1.145	0.716	0.955	0.021
36	2	9.520	1.084	0.547	0.951	0.024

The parameter k increased with an increase in soaking time with 6.061 for 12 h soaking, 8.106 for 24 h soaking and 9.52 for 36 h soaking. This increase resulted in the increase of rate of change of composition of lignin at higher levels of soaking. The value of parameter n lied between 1.063 and 1.5769 for the entire treatments without showing a proper trend. The values of n were greater than 1 for all the treatments, which was due to the increase in the rate of change of composition of lignin with an increase in microwave energy. As in the case of cellulose and hemicellulose, b value showed a decreasing trend with an increase in the microwave energy for all the 3 soaking levels.

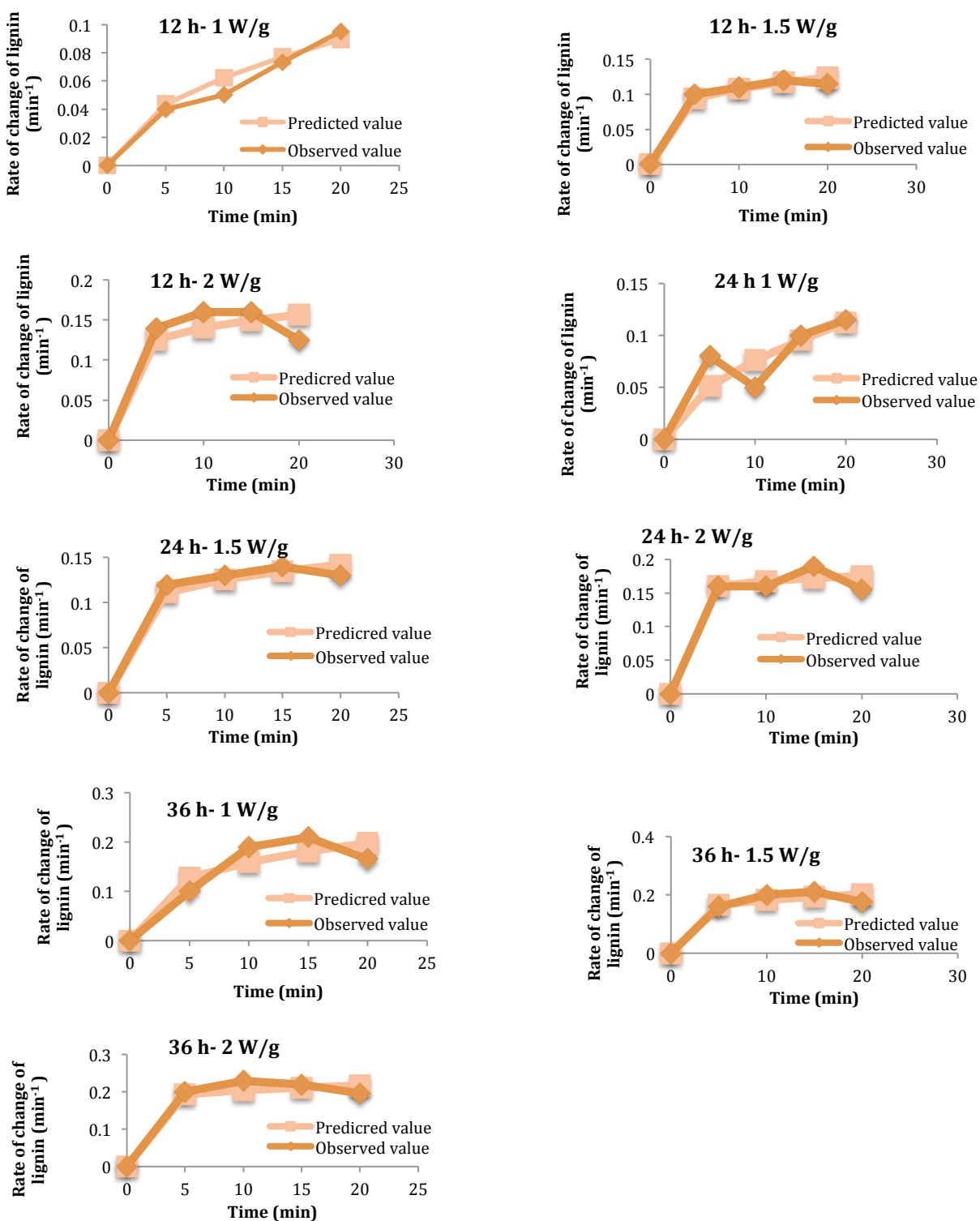


Figure 7.5 Observed and predicted values of rate of change of lignin percentage in flax fibers.

7.4.3.1 Rate Coefficient

The change of rate coefficients corresponding to various treatments with respect to time are shown in Figure 7.6.

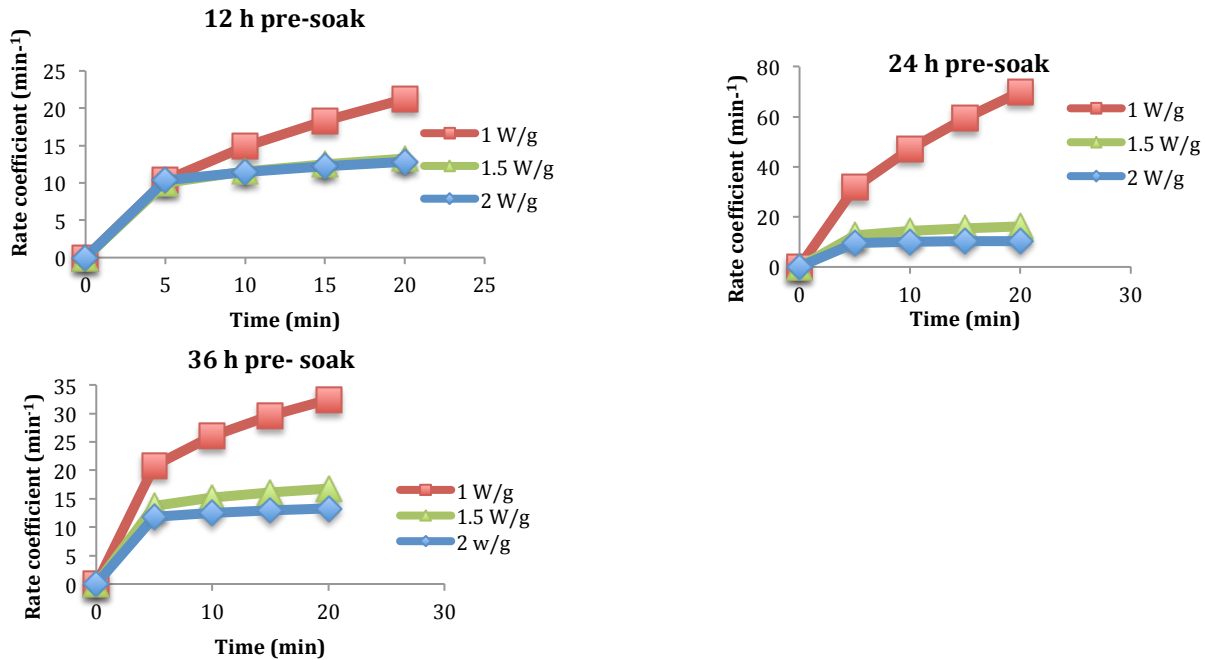


Figure 7.6 Rate coefficients for lignin release for various treatments

For all the 3 pre-soaking conditions, 1 W/g treated samples showed maximum increase in rate coefficient with respect to time. But for 1.5 and 2 W/g treatments, the rate coefficients showed a steady trend after 5 minutes of treatment time. Within the treatment time, there was no decrease in the rate coefficient for the release of lignin in microwave assisted retting of flax stems.

7.4.4 Validation of the Model

The kinetic model developed was validated using the data obtained from the analysis of 12 h water pre-soaked hemp fiber retted by microwave energy. Since coefficients n , and b are dependant on the nature of reaction and dielectric property of solvent, those values were kept the same as for the flax stems at 12 h soaking. Only k is different for hemp compared to flax which is dependent on the nature of the material to be treated. The values of parameters and corresponding R^2 and RMSE values are presented in Table 7.8.

Table 7.8 Model validation using microwave- retted hemp fibers

MW power (W/g)	Component	<i>k</i> value	<i>n</i> value	<i>b</i> value	R ²	RMSE
1	Cellulose	1.892	1.103	1.281	0.971	0.014
1	Hemicellulose	0.2879	1.638	1.281	0.99	0.0001
1	lignin	0.7125	1.517	1.281	0.37	0.011
1.5	Cellulose	1.126	1.116	0.8479	0.85	0.048
1.5	Hemicellulose	0.2879	1.48	0.8479	0.76	0.01009
1.5	lignin	0.1459	1.2	0.8479	0.88	0.01075
2	Cellulose	1.106	1.09	0.7046	0.87	0.0541
2	Hemicellulose	0.1515	1.644	0.7046	0.69	0.01751
2	lignin	2.433	1.158	0.7046	0.87	0.0165

The R² values of the model ranged from 0.34 to 0.99 for all the experiments. The average R² value for all the validation was 0.81. All the treatments showed low RMSE values corresponding to their R² values showed closeness of the model. The diverse nature of plants made it difficult to have a high level of closeness between predicted and observed values.

Kinetic model introduced to study the rate of change of cellulose, hemicellulose and lignin showed good results for most of the treatment levels with high R² values and low RMSE values. The diverse nature of the biological materials was the probable reason for lower R² values at certain treatment levels. Microwave assisted retting increased the rate of change of cellulose hemicellulose and lignin within the treatment times of 0-20 min. Further increase in the microwave treatments time could lead to evaporation of entire water and over heating of stems which in turn could result in low quality fiber.

7.5 Conclusion

The kinetic model for the compositional changes in microwave assisted retting of flax stem was established and validated. The variables subjected for the model study were microwave energy, pre-soaking time and the microwave treatment time and the nature of the material. The R^2 values of the model ranged from a minimum of 0.829 to a maximum of 0.998 which was due to the diverse nature of the biomaterials towards physico-chemical reactions. The observed and predicted values of release of cellulose, hemicellulose and lignin was found to be close enough with relatively high R^2 values and low RMSE values. The rate coefficient for all the treatments were increasing within the treatment limit, which indicated the increased reaction rate due to microwave energy.

CONNECTING TEXT

Microwave- assisted retting of flax and hemp, optimization of microwave- assisted retting and development of a kinetic model were discussed in the previous chapters. The flax stems obtained after microwave- assisted retting were fully soaked and needed to be dried before further processing. Dried stems were transferred to a decortication facility, which has multiple rollers and combs. The rollers crush the stems and fibers are loosened due to the crushing action and then they are combed/scutched to remove the impurities present in the fiber. Drying of flax stems usually conducted by hot air drying and the desirable moisture content for decortication process is 10% (w.b.) and 4% for storage prior to decortication. Proper drying of flax stems is an essential step in order to separate high quality clean fiber from it. The conventional heating methods utilize more energy and time to reduce the moisture content from 65% to 10 %. To minimize these problems associated with drying of flax stems after retting, a pre- drying process was developed for dewatering flax stems after microwave- assisted retting. Electro- osmotic dewatering was introduced to dewater high moisture flax stems using a bench type roller press, which is discussed in the next chapter.

CHAPTER 8

ELECTRO- OSMOTIC DEWATERING OF HIGH MOISTURE FLAX STEMS

8.1 Abstract

Retted flax stems contained high amount of water due to the pre- soaking and retting process. As a pre- drying process, electro- osmotic dewatering was conducted on high- moisture flax stems by bench type electro- osmotic roller press dewatering. Various parameters affecting electro- osmotic dewatering were cylinder pressure (1000 kPa - 3000 kPa), applied voltage (12 V- 36 V) and pre- soaking time of the flax stem (12 h- 36 h). The experiment was designed using central composite design with the help of JMP[®] software. From the experiments, a maximum of 38.34% of the total water contained in the stem was removed from 12 h soaked using 1000-kPa-cylinder pressure and 36 V applied voltage during the electro- osmotic treatment. At a given soaking time, 36 V with 3000-kPa-cylinder pressure will give a maximum water removal for flax stems. The electro- osmotic permeability of the stems at various conditions was studied. In all the treatments, electro- osmotic permeability ranged between $3.32 \times 10^{-5} \text{ m}^2/\text{V.s}$ and $1.22 \times 10^{-4} \text{ m}^2/\text{V.s}$. Electro- osmotic permeability was found to be increasing with increase in water removal and decreased with an increase in applied voltage.

8.2 Introduction

Flax fibers are widely used to make several products termed biocomposites, high quality papers, apparels etc. and flax fibers are processed from flax stems. Retting is the most important process in the processing of flax stems, which is the loosening of fibers from their stems (Akin 2013). There are various ways of conducting retting such as water retting, dew retting, enzyme assisted retting, steam explosion retting, microwave assisted retting etc. The flax stems after retting process contain high amount of moisture. For further processing of decorticating the stems into fibers, the flax stems have to be dried to reduce the moisture content significantly. Usual drying methods are hot air drying, solar drying, microwave assisted drying etc. (Nair et al. 2012). The time and energy required in reducing the moisture of completely wet flax stems to a low level of 4-5% (wet basis) moisture content by conventional methods like hot air drying will be really

high. In this scenario, there is a possibility of a lower energy consuming pre-treatment where most of the surface water can be removed prior to drying.

Pressing by using mechanical energy is one of the most appropriate ways of dewatering the flax stems. The energy required for pressing induced dewatering is much smaller than the energy required for heat induced water removal. As an example, 7 kJ/kg is needed to remove water at an average pressure of 7kPa whereas about 2320 kJ/kg for heat-induced water removal (Schwartzberg, Rosenau et al. 1977, Chen, Mujumdar et al. 1996). In pressing, water plasticizes the solids and prevents compression-induced fragmentation of the solid and the resistance to flow of water to be removed increases with cake formation on the filter medium. Later, these limitations have been overcome by the addition of combined fields to expression such as electro-osmotic dewatering (Orsat, Raghavan et al. 1993, Yoshida 1993, Orsat, Raghavan et al. 1999). Kondoh et al. in 1990 conducted a successful study of a combined electric and mechanical dewatering. They incorporated electrical field as an addition to a pressure dehydrator, the water content of activated sludge was reduced to 50- 60% when compared to 75- 85% achieved with mechanical force. When a solid particle travels within liquid medium under the influence of an applied electric field, a plane of shear is formed around that solid particle. The electrical potential difference between the plane of shear and the bulk solution is called the zeta potential (ζ). The zeta potential is an important factor determining the electro- osmotic flow rate. According to the Helmholtz- Smoluchowski theory, the electro- osmotic flow rate is directly proportional to the zeta potential. For a biomass, zeta potential is directly proportional to electro osmotic water removal (Chen, Mujumdar et al. 1996). The main factors affecting zeta potential are ion concentration, pH of the fluid and the sludge conductivity. If the ion concentration is too high, the zeta potential is reduced so that the electro- osmotic flow rate decreases (Lockhart 1992). The electro- osmotic flow could be modified by the addition of ionic solutions (Orsat, Raghavan et al. 1999). Changes in pH cause a change in the zeta potential which in turn affects the rate of change of electro- osmotic water removal (Rabie, Mujumdar et al. 1994). An increase in electrical conductivity of biomass reduces the zeta potential at the surface of the solid phase of the biomass (Gazbar, Abadie et al. 1994).

Flax stems obtained after retting contain high moisture content, possibility of uneven drying due to conventional methods of drying also cannot be ruled out. To overcome the difficulties

associated with energy, time and quality, we introduced a dewatering process, electro- osmosis as a pre- treatment before the stems are subjected to drying. The objective of this study is to investigate the effect of electro- osmotic dewatering as a pre-drying method of the retted flax stem and to optimize the process by analyzing the variables like cylinder pressure, voltage and soaking duration.

8.3 Materials and Methods

The materials used and the methods followed for the electro- osmotic dewatering of flax stems is discussed in this section.

8.3.1 Flax Stems

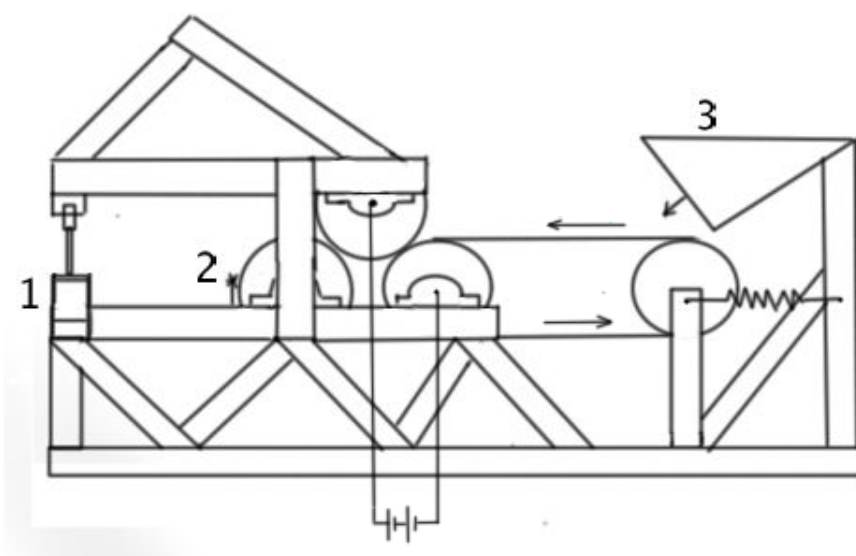
Flax stems of variety Evelin fiber flax were kindly given by Lanaupôle fiber, Montreal, and they were cut in to 15 cm of length. The initial moisture content of the flax stem samples was found to be 3.9 % (wet basis) by oven dry method.

8.3.2 Electro- Osmotic Dewatering Apparatus

Roller press electro-osmotic dewatering apparatus is as shown in Figure 8.1 (Orsat et al. 1999). The main component of the apparatus was four carbon rollers arranged in an aluminum frame as shown in Figure 8.1. The flax stems were fed from the feeding chute at the right side. The bottom cylinder acted as the cathode and top cylinder as the anode. A belt made from a cotton cloth acted as a membrane between the anode and cathode. A hydraulic pump is attached to the top cylinder to vary the pressure between the rollers. The DC voltage was generated using 12 V DC batteries. The voltage was monitored throughout the experiments and found to be constant during the dewatering process.

8.3.3 Experimental Design

Response surface statistical design was used for this study with JMP[®] 10 software. The variables were voltage (12 V-36V), roller pressure (1000 kPa – 3000 kPa) and soaking time of flax stems (12 h- 36 h). Experiments were conducted with different variables, and the % of water removed in liquid form from each experiments were noted. The experimental design is shown in Table 8.1.



1. Hydraulic cylinder, 2. Rotating scraper, 3. Feeding chute

Figure 8.1. Roller press electro- osmotic dewatering apparatus (Orsat et al., 1999)

Table 8.1. Experimental design of electro- osmotic dewatering of flax stems

Pattern	Voltage (V)	Cylinder Pressure (kPa)	Soaking time (h)	% Of total water removed	Volume of water removed (cm ³)
---	12	1000	12	30.76	5.24
---	12	3000	36	31.94	5.44
+++	36	3000	36	30.34	5.17
+-	12	3000	12	36.59	6.23
---	12	1000	36	29.01	4.94
+++	36	3000	36	30.34	5.17
+++	36	3000	36	30.43	5.19
A00	36	2000	24	36.24	6.18
0	24	2000	24	35.84	6.11
---	12	3000	36	31.94	5.44
0	24	2000	24	35.84	6.11
00A	24	2000	36	30.68	5.23
00a	24	2000	12	34.68	5.91
0	24	2000	24	35.84	6.11

Pattern	Voltage (V)	Cylinder Pressure (kPa)	Soaking time (h)	% Of total water removed	Volume of water removed (cm ³)
---	12	1000	12	30.76	5.24
+++	36	1000	36	29.85	5.09
0	24	2000	24	35.84	6.11
+-	36	1000	12	37.96	6.47
++-	36	3000	12	37.45	6.38
0a0	24	1000	24	34.45	5.87
0A0	24	3000	24	35.01	5.97
+-	36	1000	12	38.34	6.53
0a0	24	1000	24	34.2	5.83
0A0	24	3000	24	35.01	5.97
a00	12	2000	24	34.49	5.88
0	24	2000	24	35.84	6.11
0A0	24	3000	24	35.51	6.05
++-	36	3000	12	37.45	6.38
00A	24	2000	36	30.87	5.26
00A	24	2000	36	30.84	5.26
A00	36	2000	24	36.29	6.18
++	12	1000	36	29.01	4.94
0a0	24	1000	24	34.2	5.83
++	12	1000	36	29.34	5.00
A00	36	2000	24	37.54	6.40
a00	12	2000	24	34.49	5.88
---	12	1000	12	29.98	5.11
+++	36	1000	36	29.98	5.11
+-	36	1000	12	37.4	6.37
++-	36	3000	12	38.34	6.53
0	24	2000	24	35.84	6.11
+-	12	3000	12	36.59	6.23
a00	12	2000	24	34.46	5.87
00a	24	2000	12	34.68	5.91

The roller speed was set at 0.25 cm/s and the time to pass the flax stems of 15 cm was about 64 s. The flax stems were arranged on the roller in a single layer with average thickness of 0.5 cm. The zeta potential of flax stems was found to be -15 mV at a pH of 7 by using a Laser Zee meter

(Model 501, Penkem Inc.) (Orsat et al. 1999). In this study, since the effect of apparatus voltage, soaking of flax stems and cylinder pressure were taken into consideration, pH, zeta- potential and ionic concentrations were kept constant for all the treatments.

Flax stem samples of 15 cm length were spread uniformly at a width of 5 cm and a thickness of 0.5 cm maintained on the belt of the apparatus. The initial mass of the flax stems was M_1 and final mass of the sample was M_2 , and the mass of the dry sample was m_s , so, the solid concentration of the flax sample before the treatment was,

$$SD_1 = \frac{m_s}{M_1} \quad (8.1)$$

Where SD_1 was the solid concentration before dewatering. After electro- osmosis, the sold concentration

$$SD_2 = \frac{m_s}{M_2} \quad (8.2)$$

$$SD_2 = \frac{m_s}{M_1 - M_w} \quad (8.3)$$

Where M_w is the mass of water displaced.

From Eqn (8.1), (8.2) and (8.3), the mass of water displaced due to electro- osmosis was,

$$M_w = \frac{(SD_2 - SD_1)M_1}{SD_2} \quad (8.4)$$

8.3.4 Electro- osmotic permeability

The electro-osmotic permeability, k_e depends mainly on, the pore area and is independent of the size of the individual pores, whereas hydraulic permeability is very strongly influenced by the actual pore size (Casagrande 1949, Mok 2006). The electro-osmotic permeability is not a constant and it could be determined by conducting test using the flax stem samples. Cross sectional area (A) of the flax stem sample in contact with the cylinders and thickness (L) were measured. The current (I) was kept constant throughout the experiment to calculate $i_e (I/L)$ and the volume of water extracted during the time of the process (64 sec) was noted. The measured value of current was 1.5 A, 2.5 A and 4 A at voltages 12 V, 24 V and 36 V respectively. The initial resistance $R_0 (V/I)$ was also noted. The value of electro- osmotic permeability (k_e) was calculated using the equation:

$$Q_e = k_e j_e A R_0 \quad (8.5)$$

Where Q_e is the quantity of water displaced per unit time (m^3/s). The unit of electro- osmotic permeability is $\text{m}^2/\text{V.s}$. The experiments were repeated for various parameters (voltage, cylinder pressure and soaking) to find out the electro- osmotic permeability.

8.4 Results and Discussion

Results obtained from the experiments on electro- osmotic dewatering of flax stems and its discussion is included in this section.

8.4.1 Water Removal

The percentage of water released from the total water contained in the flax stem samples with respect to various parameters such as voltage, cylinder pressure and soaking are shown in Table 8.1. The percentage of water removed by electro- osmosis was analyzed using a central composite design, the predicted versus actual plot is shown in Figure 8.2.

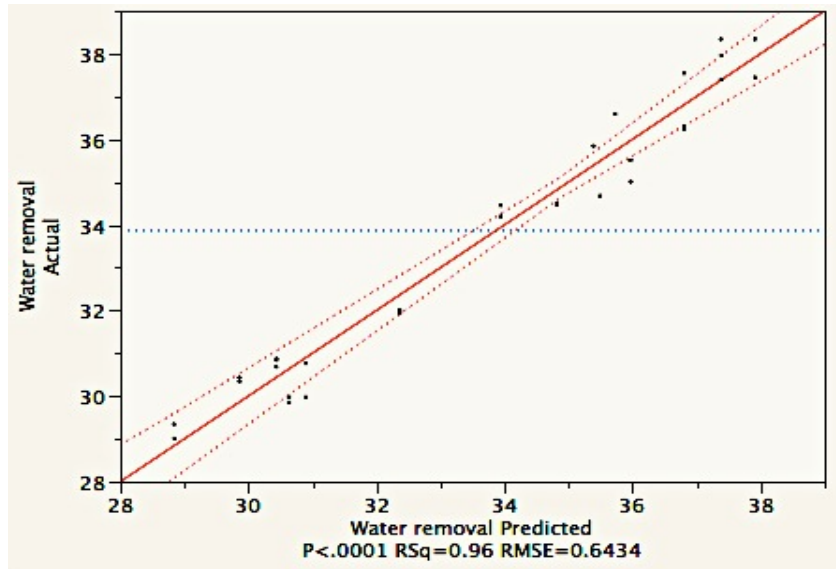


Figure 8.2 Actual versus predicted % of water removed by electro osmosis

According to the design, the R^2 value was 0.961 with an RMSE (root mean square error) value of 0.6434 with a significant level of $p < 0.0001$.

The predicted % of water removal was estimated from the following equation:

$$\begin{aligned} \text{Water removal (\%)} = & 35.3884 + 0.99 (\text{voltage}) + 1.015 (\text{cylinder pressure}) \\ & - 2.52 (\text{soaking}) - 1.07625 (\text{voltage} \times \text{cylinder pressure}) \\ & - 1.1721 (\text{voltage} \times \text{soaking}) - 0.32 (\text{cylinder pressure} \\ & \times \text{soaking}) - 2.42 (\text{soaking} \times \text{soaking}) \end{aligned} \quad (8.6)$$

Eqn. (8.6) expressed the % of total water removed from the flax stem as a function of applied voltage, cylinder pressure and soaking. Experiments were conducted without electro- osmosis with three different cylinder pressures and 3 soaking levels. The amount of water removed was 14 ± 1.5 % for all the soaking levels and cylinder pressures. But percentage of water removed due to electro- osmosis with mechanical pressure on the cylinders ranged between 27.01% and 38.34%. This proved the effect of electro- osmosis in the dewatering of flax stems when compared to mechanical dewatering treatments.

The significance of the water removal among the electro- osmotic treatments is shown in Figure 8.3.

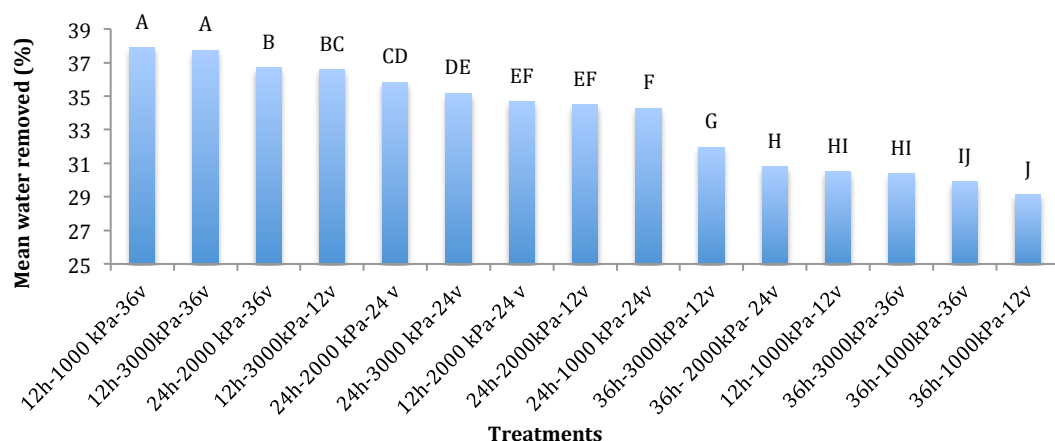


Figure 8.3. The significance of the % water removed by various electro- osmotic treatments

The treatments 36 V- 3000 kPa- 12 h soak and 36 V- 1000 kPa- 12 h did not show any significant difference between the treatments and they showed significant difference with the other treatments and those treatments showed maximum water removal. Water removal of 36 V- 2000

kPa- 24 h and 36 V- 1000 kPa- 36 h had no significant difference, but 36 V- 2000 kPa- 24 h samples showed significant difference with 24 V- 2000 kPa- 24 h but 36 V- 1000 kPa- 36 h did not show significant difference with 24 V- 2000 kPa- 24 h. The minimum water removal was obtained in the treatment (12V- 1000 kPa- 36 h) which was almost double the average water removed by mechanical expression. From the above treatments, for a given soaking, 36 volts and 2000 kPa or 3000 kPa cylinder pressure was the best for maximum removal of water.

8.4.1.1. Effect of Voltage on Electro- Osmosis

For all the levels of soaking and cylinder pressure, increases in voltage lead to an increase in water removal. As an example, treatments 12 V- 2000 kPa- 24 h, 24 V- 2000 kPa- 24 h and 36 V- 2000 kPa- 24 h showed 34.46%, 35.84% and 37.54% respectively (Table 8.1). From the surface plot of water removal with respect to voltage applied (Figure 8.4) it is evident that as the voltage increased, the % of water removed from the flax stem also increased. Water removal is directly proportional to the applied voltage, but the energy consumption is directly related to current, voltage and time of the electro- osmotic process (Larue, Mouroko-Mitoulou et al. 2001).

8.4.1.2. Effect of Cylinder Pressure on Electro- Osmosis

The effect of cylinder pressure on water removal in electro- osmotic treatment is shown in Figure 8.4. From the figure, it is proven that there was a significant increase in the water removal with respect to an increase in the cylinder pressure from 1000 kPa to 3000 kPa (Barton, Miller et al. 1999). The results showed significant difference in the % of water removed with respect to change in cylinder pressure at lower soaking levels, but the difference in the water removal was not significant at 24 and 36 h soaking which showed the presence of tightly bound water molecules inside the plant stem (Figure 8.3).

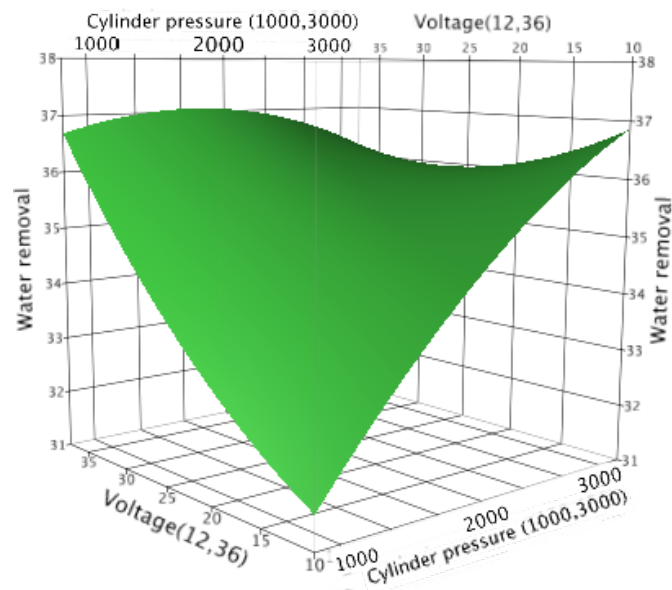


Figure 8.4. Response surface curve of % electro- osmotic water removal with respect to cylinder pressure and voltage

8.4.1.3. Effect of Soaking on Electro-Osmosis

Water removed due to electro- osmosis was inversely proportional to soaking (Figure 8.5).

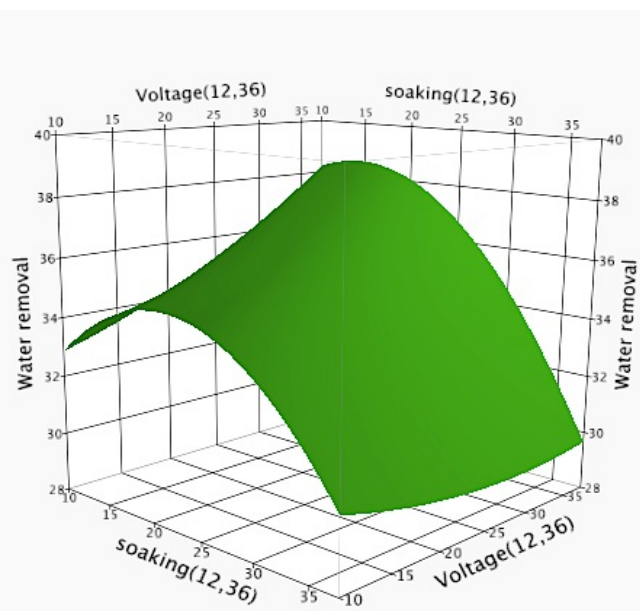


Figure 8.5. Response surface curve of % electro- osmotic water removal with respect to soaking and voltage

As the soaking time increased, the water removed decreased significantly. Pre- soaking led to the water intake through the outer skin (Akin, Morrison et al. 2003). So, due to pre- soaking, the flax stems were highly moist so that there were plenty of water molecules inside the plant cell bound to the cellulose, hemicellulose, pectin etc. of the plant fibers to form a matrix. Those water molecules were difficult to extract by mechanical pressure.

8.4.2 Electro- Osmotic Permeability

Electro- osmotic permeability ($\text{m}^2/\text{V.s}$) of a biomass found to be constant through out the process and is considered constant for the design of electro- osmotic apparatus (Mok 2006). The value of electro- osmotic permeability was directly proportional to the percentage of water removed. From the equation (8.2), it was clear that $k_e \propto Q_e$, the volume of water removed by electro- osmosis, $\propto \frac{1}{i_e}$, the current gradient and $\propto \frac{1}{R_0}$ where $R_0 = V/I$, and from Figure 8.6, it is clear that, electro-osmotic permeability decreased with an increase in voltage with significant difference in the permeability values.

In this study, voltage between the electrodes, cylinder pressure and flax stem's soaking time were taken into consideration. To find an optimized condition for maximum water removal, the desirability of the response (% of water removed) was kept at maximum and corresponding factors were analyzed (Figure 8.7). According to Fig 8.7, in order to achieve maximum water removal, 37.5 V could be applied between the electrodes; with 2225 kPa cylinder pressure and flax stems soaked for 14.42 hours could be used. Here the soaking times of flax stems were entirely dependent on the retting process and the water removal decreased with an increase in soaking time.

The percentage of water removed was associated with initial and final concentration of the material to be dewatered. Mok derived an equation for the time required to remove a desired quantity of water by electro- osmotic treatment at constant applied voltage in 2006. According to the study by Mok, the time of treatment was derived from Eqn. (8.4) and (8.5).

Eqn. (8.5) could be rewritten by,

$$\frac{M_w}{t\rho_w} = \frac{k_e IR_0}{L} \quad (8.7)$$

Where ρ_w is the density of water.

Substituting M_w (Eqn.8.4) in Eqn. 8.7, we get,

$$t = \frac{(SD_2 - SD_1)\rho_1 L^2}{SD_2 k_e IR_0 \rho_w} \quad (8.8)$$

Where t is the treatment time and ρ_1 is the initial density of the sample. But, this equation did not satisfy the values obtained by our experiment. The probable reason for that was the pressure by the rollers and the soaking time of the flax stem also to be considered. According to our study, the soaking time is directly proportional to the time of the treatment, and the roller pressure was inversely proportional to the soaking time of the sample. So the equation could be rewritten as shown below:

$$t \propto \frac{(SD_2 - SD_1)\rho_1 L^2 S}{SD_2 k_e IR_0 P} \quad (8.9)$$

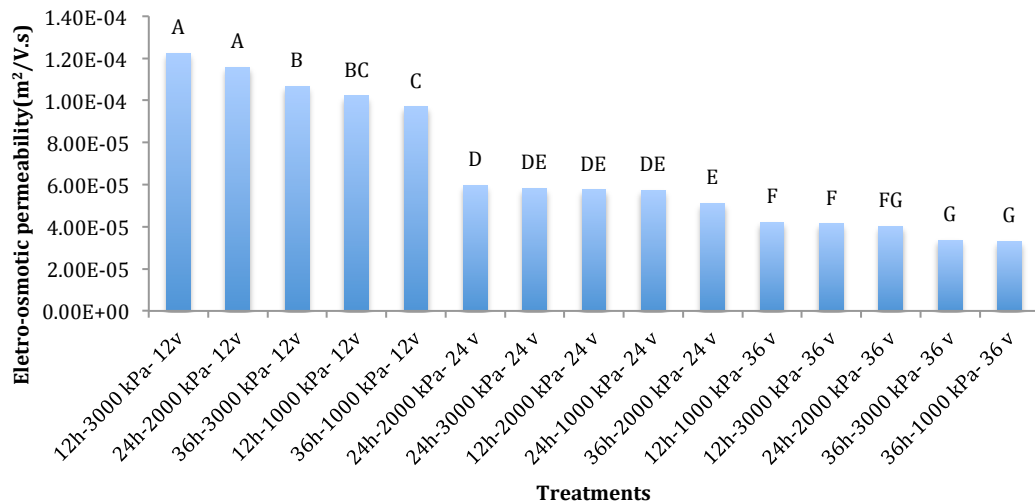


Figure 8.6 Electro- osmotic permeability with respect to various electro- osmotic dewatering of flax stem

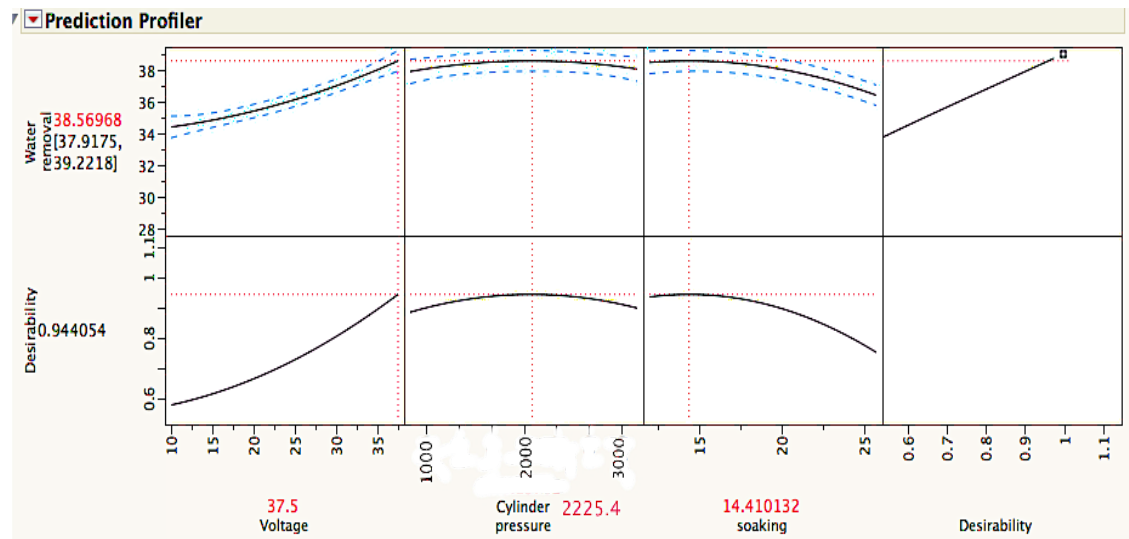


Figure 8.7 Prediction profile of the treatment for maximum desirability

Where P is the dimensionless cylinder pressure coefficient, and S is the dimensionless factor associated with the soaking of the material. In accordance with the time of treatment, the cylinder speed could be adjusted. Using multiple rollers for the electro- osmotic dewatering will also increase the treatment time. The development and validation of the model needed individual studies and those will be the part of recommended future studies.

8.5 Conclusion

Electro- osmotic dewatering of flax stems was conducted on a bench type roller press apparatus by varying applied voltage, cylinder pressure and pre-soaking duration of flax stems. Percentage of water removed due to electro- osmosis was increased with an increase in voltage and cylinder pressure. The most desirable treatment condition for a given soaking time was 36 V of voltage with 2000 kPa or 3000 kPa, since there was no significant difference between two cylinder pressures. The electro- osmotic permeabilities of the flax stem samples were studied at various treatment levels and found to be increasing with an increase in water removal and decreased with an increase in applied voltage. This dewatering technique removed about 38% of total water contained in the stems with a treatment time of 64 seconds. The duration and energy requirement of further drying process will be reduced significantly due to this pre- drying step. In order to increase the efficiency of the system, multiple rollers (electrodes) could be introduced to increase the process duration for the maximum water removal by electro- osmosis.

CONNECTING TEXT

Electro- osmotic dewatering of flax stem was studied and discussed in the previous chapter. Microwave- assisted retted hemp contains 70- 80 % moisture (w.b.) after the retting process. Hemp stem have an average diameter of 1 cm, but the diameter of flax stems are 0.1-0.2 cm only. Unlike flax, hemp stems have a hollow core at the middle of the stem through which free water easily penetrates into the stem. The diameter and structural difference of the hemp stems with flax stems leads to the requirement of a separate study on the electro- osmotic dewatering of hemp stems, which is explained in the next chapter.

CHAPTER 9

ELECTRO- OSMOTIC DEWATERING OF PRE-SOAKED HEMP STEMS

9.1 Abstract

Retted hemp stems containing high amount of moisture were subjected to electro- osmotic dewatering by using bench type roller press. Variables like applied voltage (12V, 24 V and 36 V), cylinder pressure (1000 kPa, 2000 kPa and 3000 kPa) and soaking duration of hemp stems (12 h, 24 h and 36 h) were subjected to investigation and the factor to be considered was percentage of total water expelled due to electro- osmotic dewatering. Maximum percentage of water was removed from the 24 h soaked hemp stem at 36 V applied voltage with a cylinder pressure of 2000 kPa. The water removal was increased with increase in applied voltage and cylinder pressure. Soaking up to 32 h lead to an increase in water removal and then it started decreasing. The probable reason for that was the penetration of surface water in to micro-pores and its adhesion to the lignocellulosic bonds. Electro- osmotic permeability of hemp stems at various levels of voltage, cylinder pressures and soaking levels were studied and the result proved that electro- osmotic permeability was inversely proportional to applied voltage and it had no relation with applied pressure. The maximum water removal was predicted at 36 V applied pressure, 3000 kPa applied cylinder pressure and a pre-soaking duration of 32.84 h samples.

9.2 Introduction

Hemp (*Cannabis Sativa*) is a fibrous plant cultivated by over 30 countries with China as a leading producer followed by France, Chile, Russia, India etc. Biofibers produced from the stems of hemp plant have a large potential in various industries like composite, apparel, automotive, paper etc. and industrial hemp is one of the strongest natural fiber (Pickering et al. 2005; Pickering et al. 2007; Akin 1989; Dupeyre and Vignon 1998; Akin et al. 2001). After retting process, the hemp stems are totally wet and those stems have to be dried to a low moisture content of about 10 % moisture content (wet basis) (Booth et al. 2004). To overcome the excess energy utilization problem while removing the water from a very high level of 65-

70% (w.b.) to 10% by conventional drying method, it is necessary to introduce a pre- drying process prior to drying.

In light of this scenario, the objective of this study is to develop an electro- osmotic dewatering system for high moisture hemp stems by using roller type mechanical press apparatus. Experiments were conducted at various levels of voltage between rollers (electrodes), roller pressures and durations of soaking and the corresponding water removal was noted at various levels of treatments.

9.3 Materials and Methods

The materials used and the methods followed for the electro- osmotic dewatering of hemp stems are discussed in this section.

9.3.1 Hemp Stems

Dried hemp stems of Pointe-3 variety were kindly received from Natural Research Council, Montreal, Canada for the electro- osmotic drying test. The initial moisture content of the hemp stems was 4.2% (wet basis). The stems were cut in to 15 cm length pieces and the stems were chosen for the experiments in such a way that, the diameter was almost same (around 1 cm) to ensure the uniformity of the result.

9.3.2 Electro- Osmotic Dewatering Apparatus

The apparatus used for electro- osmotic dewatering of hemp stems was the same set up used for electro- osmotic dewatering of flax stems. The details were discussed in section 8.3.2.

9.3.3 Experimental procedure

The experimental procedure was similar to that of electro- osmotic dewatering of flax stems. The experimental design and the % of total water removed are shown in Table 9.1.

9.4 Results and Discussion

Results obtained from the experiments on electro- osmotic dewatering of hemp stems and its discussion are included in this section.

9.4.1 Water Removal

Pre-soaked (12 h, 24 h and 36 h) hemp stems were subjected to electro-osmotic dewatering at various applied voltages (12 V, 24 V and 36 V) and cylinder pressure (1000 kPa, 2000 kPa and 3000 kPa). The percentage of total water removed from the hemp stems and its initial and final moisture content (wet basis) are shown in Table 9.1. Maximum % of water removed (48.82%) was observed in the treatment 36 V-1000 kPa- 24 h hemp stem samples and a minimum of 26.39% of total water was removed from 24 V- 2000 kPa- 12 h hemp stems sample. Actual water removed by dewatering versus predicted values are plotted in Fig 9.1. Actual and predicted values of water removal showed a linear relationship with R^2 value of 0.94 and root mean square error value of 2.6501 with a significant level, $p = 0.0061$. According to the central composite design by using JMP[®] 10 software, the equation of the model is as shown below:

$$\begin{aligned} \% \text{ Water removed} = & 40.077 + 1.81 (\text{Voltage}) + 6.1 (\text{Soaking}) \\ & - 0.341 (\text{Voltage} \times \text{Pressure}) - 6.27 (\text{Soaking}^2) \end{aligned} \quad (9.1)$$

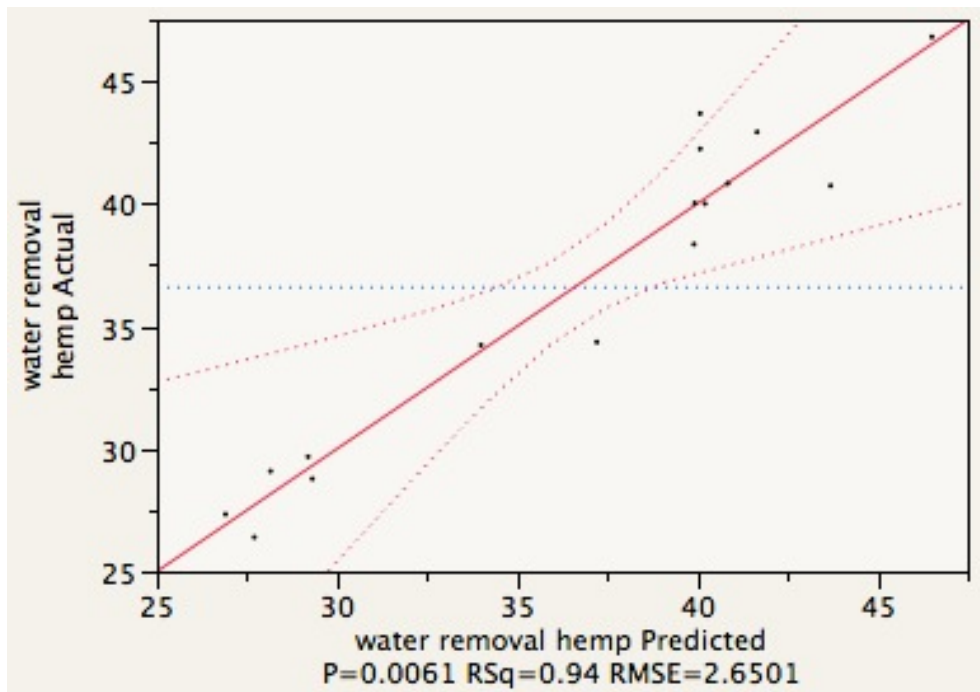


Figure 9.1 Actual versus predicted plot of % of water removed from the hemp stems by electro osmosis

Table 9.1 Experimental design of electro- osmotic dewatering of hemp stems and water release due to electro- osmosis

Pattern	Voltage (V)	Pressure (kPa)	Soaking (h)	% Of total water	Initial MC (%)	Final MC (%)	Change in MC (%)
+++	36	1000	36	36.99	70.40	44.36	26.04
---	12	1000	12	31.71	65.19	44.52	20.67
+++	36	3000	36	29.65	69.09	48.61	20.48
00A	24	2000	36	28.84	69.77	49.65	20.12
--+	12	1000	36	40.81	69.28	41.00	28.27
00a	24	2000	12	26.39	64.97	47.82	17.15
++-	36	3000	12	36.68	63.37	40.13	23.24
0	24	2000	24	43.68	65.80	37.06	28.74
0a0	24	1000	24	39.82	69.38	41.62	27.77
0	24	2000	24	42.24	69.80	40.32	29.48
a00	12	2000	24	34.36	68.07	44.68	23.39
+++	12	3000	36	42.92	72.83	41.58	31.26
A00	36	2000	24	48.82	66.86	34.22	32.64
+-	12	3000	12	36.76	65.77	41.59	24.18
+--	36	1000	12	28.78	63.74	45.40	18.34

Dewatering was performed without applying the electricity on pre- soaked hemp stems (12 h, 24 h and 36 h) at a cylinder pressure of 3000 kPa and the % of total water removed was found to be 12.1%, 19.7 % and 21.3% respectively. Those samples were considered as Control1 (12h) Control 2 (24 h) and Control 3 (36 h) for the analysis of significance (Figure 9.2).

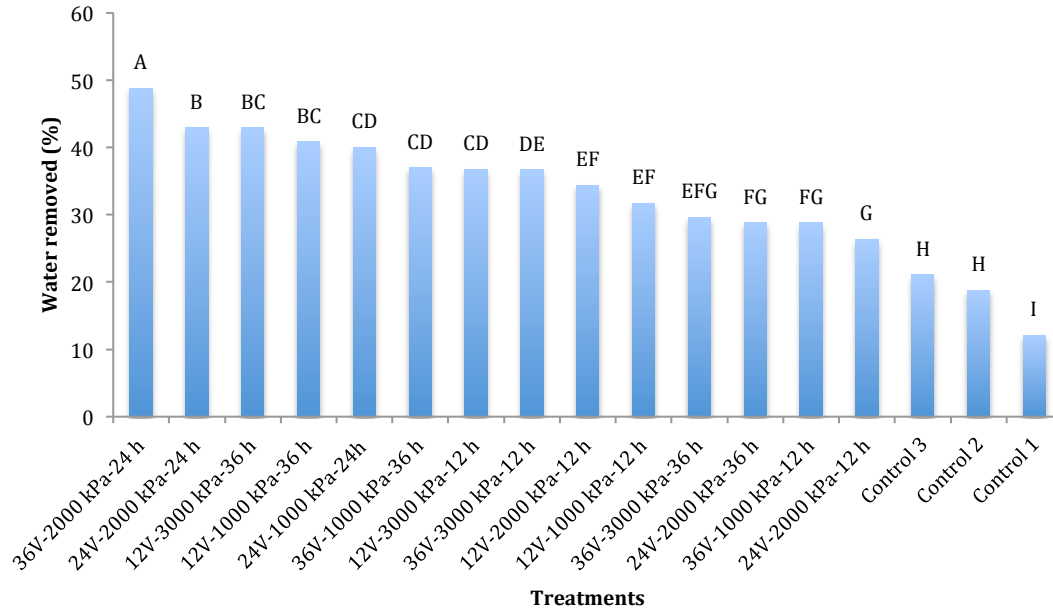


Figure 9.2 % of total water removed by various electro- osmotic treatments on hemp stems

There was significant difference in the water removal among the hemp stem samples. There was significant difference between 36V- 2000 kPa- 24 h sample and the rest of the samples. The combined effect of cylinder pressure, voltage and soaking made the explanation difficult with respect to Fig. 9.2. To analyze the effect of cylinder pressure, consider treatments 24V-2000 kPa- 24 h and 24V- 1000 kPa- 24 h with a water removal percentage of 42.24 % and 39.82% respectively. So, percentage of water removed increased with the cylinder pressure and there was a significant difference between the two values. Whereas to analyze the effect of applied voltage, % water removed in treatments 36V- 2000 kPa- 24 h and 24 V- 2000 kPa- 24 h was 48.82% and 43.68% respectively with a significant difference in the value. Significant difference was shown between control samples and electro- osmotic dewatered samples and that difference experimentally proved the effect of electro- osmosis in dewatering of hemp stems.

9.4.1.1. Effect of Voltage on Electro- Osmosis

The effect of applied voltage between the electrodes on electro- osmotic dewatering is explained in Fig. 9.3.

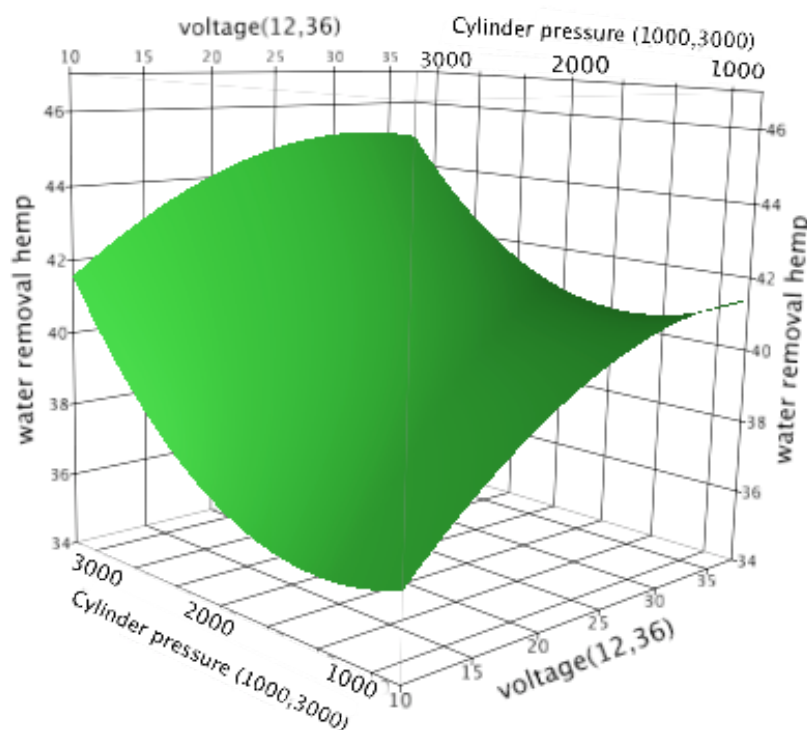


Figure 9.3 Response surface curve of % total water removal with respect to cylinder pressure and voltage

As shown in Fig 9.4, at a particular cylinder pressure, the percentage of total water from the hemp stem samples removed was increased with an increase in applied voltage within the range of 12 V to 36 V. When DC voltage was applied to a material like hemp stems, the free water of the double layer ($+^{ve}$ charge) was attracted towards the cathode and initiated the water towards the cathode (Lo et al. 1994). According to Darcy's equation of water flow, applied voltage between the electrodes is directly proportional to the volume of water removed in an electro-osmotic dewatering system (Mok 2006). Increase in water removal in electro- osmosis was obtained either by increasing the electric field strength or by increasing the zeta potential. The zeta potential of this experiment was set to be constant throughout the process and hence the water removal was affected by increase in voltage gradient. The zeta potential of flax stems was found to be -12 mV at a pH of 7 using a Laser Zee meter (Model 501, Penkem Inc.) (Orsat et al., 1999). In this study, since the effect of apparatus voltage, soaking of flax stems and cylinder pressure were taken into consideration, pH, zeta- potential and ionic concentrations were kept constant for all the treatments.

9.4.1.2 Effect of Cylinder Pressure on Electro- Osmosis

The effect of cylinder pressure on electro- osmotic dewatering of hemp stems is as shown in Fig. 9.4. As from the figure, the rate of water removed due to electro- osmosis initially reduced with an increase in cylinder pressure from 1000 kPa to 1500 kPa, and then it was increased with an increase in cylinder pressure up to the maximum pressure of 3000 kPa. According to the theory, the applied pressure on the samples is directly proportional to the rate of water removed. But the possible reason for the slight decrease in the percentage of water removed with increase in pressure could be the heterogeneous nature of biomaterials towards its physical and structural changes even within the same variety.

9.4.1.3 Effect of Soaking on Electro-Osmosis

Effect of soaking on electro- osmotic dewatering is shown in Figure 9.4.

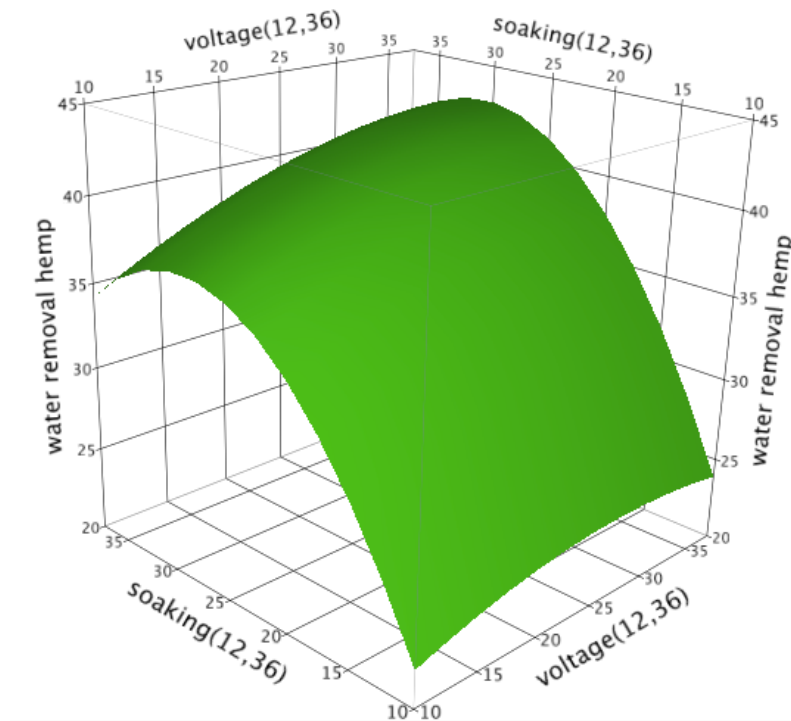


Figure 9.4 Response surface curve of % electro- osmotic water removal with respect to soaking and voltage

The water removal was directly proportional to the pre- soaking of hemp stems up to 32 h and

after that the water removal showed a decreasing trend. As per the structure, hemp stems have a hollow core, which can hold water while soaking. The free water inside and around the hollow core increased with soaking, and made it easy to remove due to electro- osmotic dewatering (Benhaim, 1999). But the possible reason for a decrease in water removal after 32 h soaking would be after a saturation level, the water penetrated more into the micro pores of the plant cell and bonded with the lignocellulosic structures. Removal of this water was difficult to perform with electro- osmotic dewatering process.

9.4.2 Electro- Osmotic Permeability

Electro- osmotic permeability, k_e ($\text{m}^2/\text{V.s}$) of soaked hemp stems was constant throughout the electro- osmotic dewatering process (Fig 9.5) (Mok 2006).

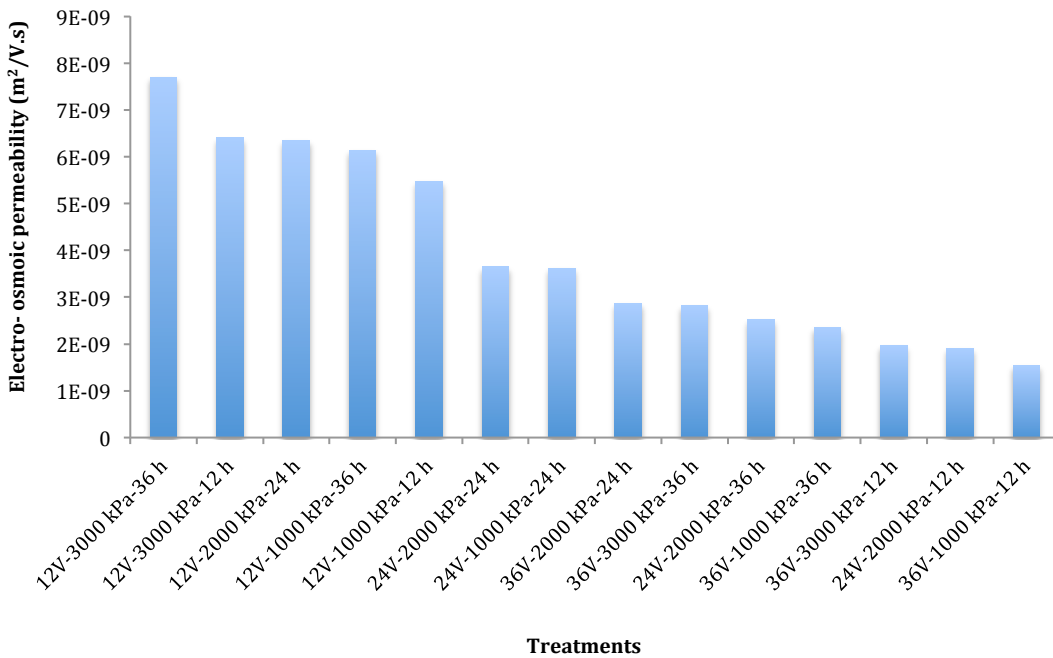


Figure 9.5 Electro- osmotic permeability with respect to various electro- osmotic dewatering of flax stems

Maximum electro- osmotic permeability was found in treatment 12 V- 3000 kPa- 36 h and the minimum was found in 36 V- 1000 kPa- 12 h. The value of electro- osmotic permeability is directly proportional to the percentage of water removed. From the Fig 9.5, it was clear that electro-osmotic permeability (k_e) decreased with an increase in voltage but there was no

significant difference in the electro- osmotic permeability among various treatments. Electro- osmotic permeability $k_e = \frac{Q_e}{iAR}$ where Q_e is the quantity of water displaced per unit time (m^3/s), i is the current gradient, A is the area of the material to be dewatered and R is the initial resistance of the material. In this study, electro- osmotic permeability was only dependent on the voltage applied and the resistance offered by the material. From Fig 9.5, it is observed that the value of k_e was high at 12 V treatments and was minimum at 36 V treatments.

The value of parameters (applied voltage, cylinder pressure and soaking) at maximum percentage of total water removed by electro- osmotic dewatering is explained by the prediction profile generated by JMP[®] 10 and is shown in Fig 9.6.

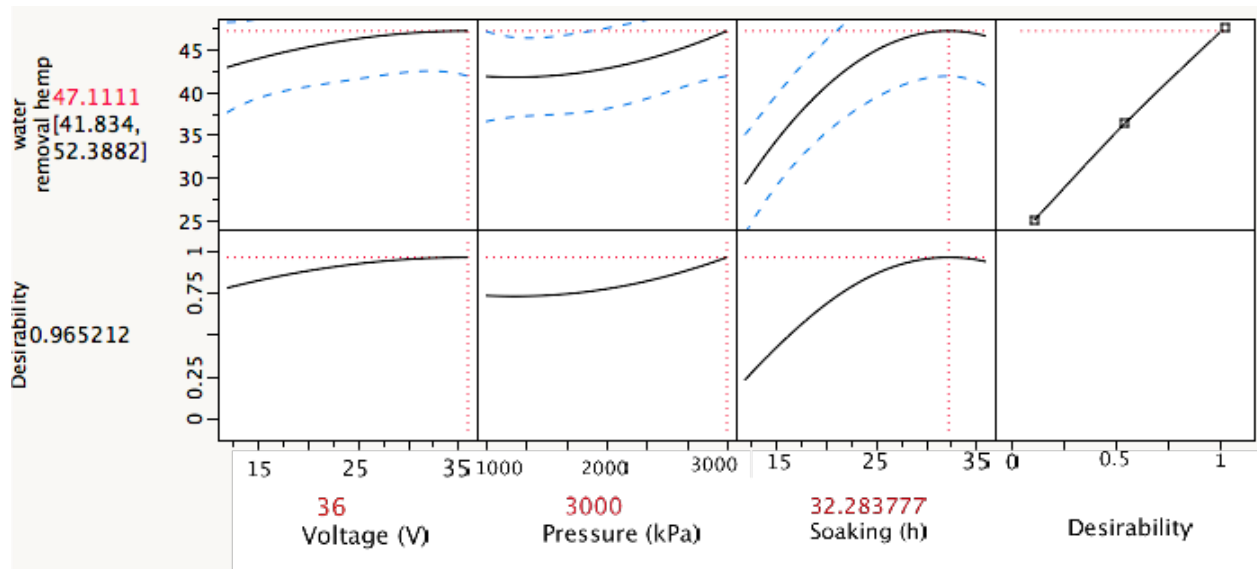


Figure 9.6 Prediction profile of the treatment for maximum desirability

According to the prediction, maximum desired water removed was 47.11% of the total water present in the hemp stems at 36 V applied voltage, 3000 kPa cylinder pressure and at a pre-soaking duration of 32.28 h. Since soaking was entirely dependent on retting, the factor to be considered was voltage and cylinder pressure. The maximum water removal is obtained at 36 V applied voltage and 3000 kPa cylinder pressure.

9.5 Conclusion

Electro- osmotic dewatering of soaked hemp stems was conducted using a bench type roller press. Cylinder pressure, applied voltage and pre- soaking duration of hemp stems were investigated. Maximum water removal was predicted with a cylinder pressure of 3000 kPa, 36 V of applied voltage and at a soaking duration of 32.28 h. By electro- osmotic dewatering using bench type apparatus, around 29% to 49% of the total available water was found to be removed from hemp stems. This proved the efficiency of electro- osmotic dewatering system, which will save the time and energy needed for total drying process. During the dewatering process, the hemp stems were dewatered and crushed, which will further improve the decortication process for the separation of fibers from the hemp stems.

CHAPTER 10

GENERAL SUMMARY AND CONCLUSION

A new retting method for flax and hemp stems with the application of microwave power was developed and the process was optimized. Water retting of flax stems was conducted as an initial study to understand the retting process and the physical properties were compared with non- retted flax fibers. From the analysis of physical qualities of retted and non- retted flax fibers, it was concluded that retting is the most important step in the processing of flax fiber in terms of its physical and structural qualities.

After conducting initial studies on water retting of flax stems, a novel microwave- assisted retting/ degumming of flax and hemp stems was established and the extent of retting was determined by analyzing the compositional changes of the fibers. Fried test was conducted to analyze the retting efficiency of flax stems. 24 hours soaked flax stem samples treated at 2 W/g power for 20 minutes showed the maximum retting efficiency of 100%. The combined thermal and non- thermal effects of microwaves were subjected to analysis in the retting of flax and hemp stems. Since the introduction of electromagnetic energy in retting of flax and hemp is in its beginning stage, there are many future studies to be done for further improvement of the process. 36 h soaked hemp stems, treated in the microwave- chamber at 2 W/g power for 20 min showed maximum retting efficiency in terms of changes in cellulose, hemicellulose and lignin with microwave- assisted retting. Loosening of fibers occurred due to combined thermal and non- thermal effects of microwave energy on pre- soaked hemp stems. Pre- soaking of flax and hemp stems lead to weakening of the strong polysaccharide bonds, which cemented fibers to the stems. With the application of microwave energy, the water inside the plant stems increases the pressure, and with the energy dissipated by microwave together lead to the breaking of already weakened bonds and hence release the fibers from the stems.

Chemical analysis of changes of cellulose, hemicellulose, lignin and pectin was conducted on microwave- assisted retted flax fibers. Pectin was one of the major components, which is responsible for the strong attachment of the fibers in the stems. The effect of microwave was explained on the basis of change in pectin content in the fibers with microwave retting. In microwave-assisted retting, electromagnetic radiation penetrates into the soaked plant stem to

excite the molecules inside the plant cell. This excitation leads to the breaking of already weaker bonds due to the tension created by water. At the same time, the thermal effect of electromagnetic radiation helps in increasing the heat inside the samples by bipolar rotation and ionic migration mechanisms which helps in the structural degradation of non-cellulosic polysaccharides at treduced temperatures.

A kinetic model was developed for the analysis of compositional changes in flax fibers obtained by microwave assisted retting of flax stems and the model was validated with the data obtained from the microwave- assisted retted hemp fibers. The observed and predicted values of release of cellulose, hemicellulose and lignin was found to be close enough with relatively high R^2 values and low RMSE values. The rate coefficient for all the treatments were increasing within the treatment limit, which indicated the increased reaction rate due to microwave energy.

In order to develop a system to dewater the retted, high moisture flax and hemp stems, a bench type roller press electro- osmotic dewatering apparatus was introduced. From the experiments, electro- osmotic dewatering was affected by applied voltage, cylinder pressure and pre-soaking of flax stems. Percentage of water removed due to electro- osmosis was increased with an increase in voltage and cylinder pressure. For flax stems, the most desirable treatment condition for a given soaking was 36 V of voltage with 2000 kPa or 3000 kPa, since there was no significant difference between two cylinder pressures. For hemp, maximum water removal was predicted with a cylinder pressure of 3000 kPa, 36 V of applied voltage and at a soaking duration of 32.28 h. By electro- osmotic dewatering using bench type apparatus, around 29% to 49% of the total available water was found to be removed from hemp stems. The electro- osmotic permeability of the flax and hemp stem samples were studied at various treatment levels and found to be increasing with increase in water removal and decreased with an increase in applied voltage.

The dewatered stems are further dried by the application of microwave energy at controlled temperature before going into the decortication facility. Nair et al., in 2008 conducted studies on microwave- assisted drying of high moisture flax stems and proved it to be an effective, faster method without affecting the physical properties of the extracted fiber. Hence, a complete system for the processing of flax and hemp stems by using electro- technology from retting,

dewatering up to drying was developed and the studies proved the system to be efficient in the lab scale. This method has a very high industrial potential and further scale up studies are required to prove its industrial acceptability.

CHAPTER 11

CONTRIBUTIONS TO KNOWLEDGE AND TECHNOLOGICAL INNOVATION

The major contributions to the knowledge from the study are:

1. Microwave- assisted retting of flax and hemp stems was developed as a novel method using electromagnetic energy and the process was optimized.
2. The non-thermal effect of microwave was explained through the experiments on microwave- assisted retting of flax and hemp.
3. Microwave- assisted retting efficiency was explained on the basis of compositional analysis of processed fibers by using NIR spectroscopy. This method could be used as a standard fast method for efficiency analysis.
4. A kinetic model was developed for predicting the rate of change of cellulose, hemicellulose and lignin content of flax and hemp fibers with respect to microwave- assisted retting and the model was validated.
5. An effective method to dewater high moisture flax and hemp stems was developed using an electro- osmotic bench type roller press.
6. A complete processing line was developed for the processing of flax and hemp stems with microwave- assisted retting of pre- soaked stems, followed by electro- osmotic dewatering and microwave drying at controlled temperatures.

CHAPTER 12

RECOMMENDATIONS FOR FUTURE STUDIES

This study has explored the area of pre- processing of flax and hemp stems. However this technology is new and there are still some future studies to be conducted. Some of the recommendations are given below:

1. Introducing a pressurized chamber for microwave- assisted retting of flax and hemp stems is a recommendation for future studies. The combined effect of pressure inside the chamber and the non- thermal effect of microwave will increase the efficiency of the process.
2. Radio frequency and ultra sound can be used as an alternative source of energy for retting of flax and hemp.
3. Detailed study on the acceptability of the process in terms of economic and energy factors could be performed for the scaling up of the existing lab scale retting method.
4. Microwave- assisted retting efficiency could be increased by using alkaline solvent for pre- soaking of flax and hemp stems instead of water.
5. In electro- osmotic dewatering, the zeta potential of flax and hemp stems can be improved by increasing the pH of the soaked stems.
6. Adding multiple rollers in the electro- osmotic dewatering system increases the treatment time and hence decrease the water content of the final sample.
7. Scaling up of the existing lab based batch system and to build a production line from the field to the pre- soaking chamber, and then transfer to microwave- assisted retting chamber. After retting process, samples are moved to electro- osmotic dewatering chamber and then to microwave drying chamber at a set controlled temperature.

REFERENCES

- Adamsen, A. P., D. E. Akin, and L. L. Rigsby. 2002. Chemical Retting of Flax Straw Under Alkaline Conditions. *Textile Research Journal*, 2002b. 72: 789-794.
- Adamsen, A.P., Akin, D.E., and Rigsby, L.L. 2002. Chelating agents and enzyme retting of flax, *Textile Res. J.* 2002 (72), 296–302.
- Akin, D. E. 1989. Histological and Physical Factors Affecting Digestibility of Forages. *Agron. J.* 81(1): 17-25.
- Akin D.E. 2005. Standards of Flax Fiber. ASTM Standardization News, ASTM publication, September 2005.
- Akin, D. E. 2012. Linen most useful: perspectives on structure, chemistry, and enzymes for retting flax. *ISRN Biotechnology*, 2013.
- Akin, D. E., Foulk, J. A., Dodd, R. B., & McAlister Iii, D. D. 2001. Enzyme retting of flax and characterization of processed fibers. *Journal of Biotechnology*, 89 (2–3), 193-203.
- Akin, D. E., Gamble, G. R., Morrison Iii, W. H., Rigsby, L. L., and Dodd, R. B. 1996. Chemical and Structural Analysis of Fiber and Core Tissues from Flax. *Journal of the Science of Food and Agriculture*, 72(2), 155-165.
- Akin, D. E., J. A. Foulk, R. B. Dodd and D. D. McAlister Iii. 2001. Enzyme-retting of flax and characterization of processed fibers. *Journal of Biotechnology* 89: 193-203.
- Akin, D.E. 2013. Linen Most Useful: Perspectives on Structure, Chemistry, and Enzymes for Retting Flax. *ISRN Biotechnology*. Volume 2013: 1-23.
- Akin, D.E., Dodd, R.B. and Foulk, J.A. 2005. Pilot plant for processing of flax fiber. *Industrial Crops and Products* 21(3): 369- 378.
- Akin, D. E., Henriksson, G., Evans, J. D., Adamsen, A. P. S., Foulk, J. A., & Dodd, R. B. 2004. Progress in enzyme-retting of flax. *Journal of Natural Fibers*, 1(1): 21-47.
- Akin, D.E., Morrison H. III, Rigsby, L.L., Evans J.D. and Foulk, J.A. 2003. Influence of Water Pre-soak on Enzyme-Retting of Flax. *Industrial Crops and Products* 17 (03): 149-159.
- Alix, S., S. Marais, C. Morvan and L. Lebrun. 2008. Biocomposite materials from flax plants: Preparation and properties. *Composites Part A: Appl. Sci. Manu.*, 39: 1793-1801.
- Atton, M. 1989. Flax Culture from Flower to Fabric. *The Ginger Press, Owen Sound, ON*.
- Baley, C. 2002. Analysis of the Flax Fibers Tensile Behaviour and Analysis of the Tensile Stiffness Tncrease. *Composites - Part A: Appl. Sci. Manu.*, 2002, 33, 939-948.
- Banik, S., Bandyopadhyay, S. and Ganguly, S. 2003. Bioeffects of Microwave—a brief review. *Bioresource Technology* 87 (2003):155–159.
- Barton, W., Miller, S., & Veal, C. 1999. The electrodewatering of sewage sludges. *Drying Technology*, 17(3), 498-522.
- Benhaim, P. 1998. Growing Hemp For Profit, Raw With Life. *Local Implications*. Department of

Agricultural Economics, University of Kentucky.

- Booth, I., Goodman, A., Grishanov, S., and Harwood, R. 2004. A mechanical investigation of the retting process in dew-retted hemp (*Cannabis sativa*). *Annals of applied biology*, 145(1): 51-58.
- Bourmaud, A., Morvan, C., Bouali, A., Placet, V., Perre, P and Baley, C. 2013. Relationships between micro- fibrillar angle, mechanical properties and biochemical composition of flax fibers. *Industrial crops and products* 44 (2013): 343- 351.
- Brown, A.E. 1984. *Epicoccum nigrum*, a primary saprophyte involved in the retting of flax. *Trans. Brit. Myco. Soci.*, 83: 29-35.
- Brown, M. E., David Dollimore, and Andrew Knox Galwey, eds. 1980. Reactions in the solid state. . *Access Online via Elsevier*, 22.
- Budarin, V.L., Clark , J.H., Lanigan, B.A., Shuttleworth, P. and Macquarrie, D.J. 2010. Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. *Bioresource Technology*. 101: 3776–3779.
- Casagrande, L. 1949. Electro-Osmosis in Soils. *Geotechnique* 1(3): 159-177.
- Casagrande, L. 1952. Electro-Osmotic Stabilizatiuon of Soils. *Journal of Boston Society of Civil Engineers* 39(1): 285-317.
- Charlet, K., J. P. Jernot, S. Eve, M. Gomina and J. Bréard. 2010. Multi-scale morphological characterisation of flax: From the stem to the fibrils. *Carb. Poly.*, 82: 54-61.
- Chen, H., Mujumdar, A., and Ragbaran, G. 1996. Laboratory experiments on electroosmotic dewatering of vegetable sludge and mine tailings. *Drying Technology*, 14(10): 2435-2445.
- Dang, V. and Nguyen, K. 2007. A universal Kinetic Equation for Characterising the Fractal Nature of Delignification of Lignocellulosic Materials. *Cellulose* 14(2): 153-160.
- Dang, V., and Nguyen, K. . 2006. Characterisation of the heterogeneous alkaline pulping kinetics of hemp woody core. *Bioresource Technology*, 97(12), 1353-1359.
- Day, A., Ruel, K., Neutelings, G., Crônier, D., David, H., Hawkins, S. and Chabbert, B. 2005. Lignification in the flax stem: evidence for an unusual lignin in bast fibers. *Planta*, 222(2): 234-245.
- de la Hoz A, Díaz-Ortiz A, Moreno A. 2004. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chem. Soc. Rev.*,05 (34): 164–178.
- Deschatelets, L. and Yu, E.C.1986. A simple pentose assay for biomass conversion studies. *Applied Microbiology and Biotechnology* 24(5): 379-385.
- Di Candilo, M., Ranalli, P., Bozzi, C., Focher, B. and Mastromei, G. 2000. Preliminary results of tests facing with the controlled retting of hemp. *Industrial Crops and Products*. 11(2–3): 197-203.
- Donaghy, J.A., Levett, P.N. and Haylock.R.W. 1990. Changes in microbial populations during anaerobic flax retting. *J. Appl. Micro.* (69): 634-641.

- Dupeyre, D. and Vignon, M. 1998. Fibers from semi-retted hemp bundles by steam explosion treatment. *Biomass and Bioenergy* 14(3): 251-260.
- Foulk, J. A., D. E. Akin, and R. B. Dodd. 2001. Processing Techniques for Improving Enzyme-Retting of Flax. *Industrial Crops and Products* 13: 239-248.
- Foulk, J.A., D.E. Akin, and R.B. Dodd. 2008. Processability of Flax Plant Stalks into Functional Bast Fibers. *Composite Interfaces*. 15: 147-168.
- Foulk, J., Akin, D., Dodd, R., & Ulven, C. (2011). Production of flax fibers for biocomposites. In *Cellulose Fibers: Bio-and Nano-Polymer Composites* (pp. 61-95). Springer Berlin Heidelberg.
- Foulk, J.A., Rho, D., Alcock, M. Chad A. Ulven, C. A. and Huo, S. 2011. Modifications Caused by Enzyme-Retting and Their Effect on Composite Performance. *Advances in Materials Science and Engineering* (11): 1-9.
- Galema, Saskia A. 1997. Microwave Chemistry. *Chem. Soc. Rev.* 26(3): 233-238.
- Garcia- Jaldon, C., Dupeyre, D. and Vignon, M.R. 1998. Fibers from Semi- Retted hemp Bundles by Steam Explosion Treatment. *Biomass and Bioenergy* 14 (3): 251-260.
- Gazbar, S., Abadie, J. and Colin, F. 1994. Combined action of electro-osmotic drainage and mechanical compression on sludge dewatering. *Water Science and Technology* 30(8): 169-175.
- George, D.F., Bilek, M.M., McKenzie, D.R. 2008. Non-Thermal Effects in the Microwave Induced Unfolding of Proteins Observed by Chaperone Binding. *Bioelectromagnetics*, 29: 324-330.
- Grishanov, S.A., Harwood, R.J. and Booth, I. 2006. A method of estimating the single flax fiber fineness using data from the LaserScan system. *Industrial Crops and Products* 23(3): 273-287.
- Grundl, T. and Michalski, P. 1996. Electro-osmotically driven water flow in sediments. *Water Research* 3, 0 (4): 811-818.
- Hegi, G. 1925. Illustrierte Flora von Mitteleuropa. *Lehmanns Verlag, Munich* 5(1): 3-38.
- Henriksson, G., Akin, D.E., Rigsby, L.L., Patel, N., Eriksson, K.E.L., 1997a. Influence of chelating agents and mechanical pretreatment on enzymatic retting of flax. *Tex. Res. J.* 67: 829-836.
- Henriksson, G., K. E. L. Eriksson, L. Kimmel, and D. E. Akin. 1998. Chemical/physical retting of flax using detergent and oxalic acid at high pH. *Textile Research Journal* (68): 942-947.
- Hering, E. 1964. Outlines of a Theory of the Light Sense, translated by L. M. Hurvich and D. Jameson, Harvard University Press, Cambridge, MA.
- Hessler, L.E. 1945. Chemical and Strength Difference in the Dew Retted Hemp Fiber. *Journal of the American Society of Agronomy*: 146-155.
- Hu, Z., Wang, Y., & Wen, Z. 2008. Alkali (NaOH) Pretreatment of Switchgrass by Radio Frequency-based Dielectric Heating. In W. Adney, J. McMillan, J. Mielenz & K. T. Klasson

- (Eds.), *Biotechnology for Fuels and Chemicals*, 589-599.
- Hunter, R. S. 1975. The Measurement of Appearance. *John Wiley & Sons*, NY.
- Jacobsen, S. E. and C. E. Wyman 2000. Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. *Twenty-First Symposium on Biotechnology for Fuels and Chemicals*, Springer.
- Judd, A. 1995. Flax-some historical considerations. Flaxseed in Human Nutrition, SC Cunnane and IU Thompson, Editors, AOCS Press, Champaign, IL: 1-10.
- Kadla, F., J., Gilbert, and D., R. 2000. Cellulose structure : A review. *34*(3-4).
- Kelley, S.S., Rowell, R.M., Davis, M., Jurich, C.K. and Ibach, R. 2004. Rapid analysis of the chemical composition of agricultural fiber using near infrared spectroscopy and pyrolysis molecular beam mass spectrometry, *Biomass and Bioenergy* 27: 77–88.
- Keshwani, D. R. and J. J. Cheng 2010. Microwave-based alkali pretreatment of switchgrass and coastal bermudagrass for bioethanol production. *Biotechnology Progress* 26(3): 644-652.
- Kessler, R. W., Becker, U., Kohler, R., and Goth, B. 1998. Steam explosion of flax—a superior technique for upgrading fiber value. *Biomass and Bioenergy* (14): 237-249.
- Kim, D., Choi, J., Kim, G., Kwon Seol, S. and Jung, S. 2011. Accelerated esterification of free fatty acid using pulsed microwaves, *Bioresource Technology*, 102 (14): 7229-7231.
- Kymäläinen, H.-R. 2004. Quality of *Linum usitatissimum* L. (flax and linseed) and *Cannabis sativa* L. (fiber hemp) during the production chain of fiber raw material for thermal insulations. Academic dissertation, *MMTEK Publications 17*, University of Helsinki.
- Larue, O., Mouroko-Mitoulou, T., and Vorobiev, E. 2001. Pressurized electro- osmotic dewatering in a filter cycle. *Drying Technology*, 19(9): 2363-2377.
- Lidström, P., Tierney, J., Wathey, B., and Westman, J. 2001. Microwave assisted organic synthesis—a review. *Tetrahedron*, 57(45), 9225-9283.
- Lightfoot, D.G., and Raghavan. G.S.V. 1994. Combined Fields Dewatering of Seaweed (*Nereocystis luetkeana*) *Transactions of the ASABE*. 37(3): 899-906.
- Lo, K., Shang, J., & Inculet, I. 1994. Electrical strengthening of clays by dielectrophoresis. *Canadian geotechnical journal*, 31(2): 192-203.
- Lockhart, N. C. 1992. Combined field dewatering: bridging the science-industry gap. *Drying Technology*. 10(4): 839–874.
- Lu, D., Cao, Q., Li, X., Cao, X., Luo, F., and Shao, W. 2009. Kinetics and equilibrium of Cu (II) adsorption onto chemically modified orange peel cellulose biosorbents. *Hydrometallurgy*, 95(1): 145-152.
- Lukasiewicz, M., Bogdal, D., and Pielichowska, J. 1996. *Adv. Synth. Catal.*, 2003, 345, 1269.
- Mitchell, J.K. 1991. Conducting Phenomena: from theory to geotechnical practice. *Geotechnique* 41 (3): 299-340.
- Mohanty, A.K., Misra, M and Drzal, L.T. 2001. Surface modifications of natural fibers and

- performance of resulting biocomposite *Compos Interface*, 8 :313- 343.
- Mohanty, A.K., Misra, M. and Hinrichsen, G. 2002. Biofibers, biodegradable polymers and biocomposites: An overview. *Macromo. Mater.Eng.*276-277, 2000: 1-24.
- Mohanty, A.K., Misra,M. and Drzal, L.T. 2002. Sustainable Bio-Composites from Renewable Resources: Opportunities and Challenges in the Green Materials World. *J. Poly. Env.*10: 19-26.
- Mok, C. K. 2006. Design and modelling of electroosmotic dewatering. Ph.D. thesis, *Univ. of Newcastle upon Tyne, U.K.*: 161.
- Montane, D., Salvado, J., Farriol, X., Jollez, P., and Chornet, E. 1994. Phenomenological kinetics of wood delignification - application of a time dependent rate-coefficient and a generalized severity parameter to pulping and correlation of pulp properties. *Wood Science and Technology*, 28(6), 15.
- Mooney, C., Stolle-Smits, T., Schols, H., and de Jong, E. 2001. Analysis of retted and non retted flax fibers by chemical and enzymatic means. *Journal of biotechnology*, 89(2): 205-216.
- Morrison Iii, W. H., Archibald,D.D., Sharma, H.S.S. and Akin, D.E. 2000. Chemical and physical characterization of water- and dew-retted flax fibers. *Industrial Crops and Products*. 12: 39-46.
- Morrison Iii, W. H., et al. 1999. Chemical, microscopic, and instrumental analysis of graded flax fiber and yarn. *Journal of the Science of Food and Agriculture* 79(1): 3-10.
- Morvan, C., Andeme-Onzighi, C., Girault, R., Himmelsbach, D.S., Driouich, A. and Akin, D.E. 2003. Building hemp fibers: more than one brick in the walls. *Plant Physiology and Biochemistry*, 41 (11-12): 935–944.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., and Ladisch, M. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 96(6), 673-686.
- Mujumdar, A.S. and Yoshida, H. 2008. Electro-Osmotic Dewatering (EOD) of Bio-Materials. *Electro-technologies for Extraction from Food Plants and Biomaterials. Springer New York* : 121-154.
- Mwaikambo, L. and M. Ansell 2003. Hemp fiber reinforced cashew nut shell liquid composites. *Composites science and technology* 63(9): 1297-1305.
- Nair, G. R., Liplap, P. Gariepy, Y. and Raghavan, G.S.V. 2012. Effect of microwave and hot air drying on hemp straw at controlled temperatures. *International Journal of Postharvest Technology and Innovation*, 2 (4): 355-369.
- Nair, G.R., Li, Z., Gariepy, Y. and Raghavan, G.S.V. 2011. Microwave Drying of Corn (*Zea mays* L. spp.) for the Seed Industry. *Drying Technology* 29 (11): 1291-1296.
- Nair, G.R., Liplap, P., Gariepy, Y. and Raghavan, G.S.V. 2011. Microwave drying of flax fiber at controlled temperature. *Journal of Agricultural Science and Technology* 1 (8B): 1103-1115.

- Nüchter, M, Ondruschka, B., Bonrath, W. and Gum, A. 2004. Microwave assisted synthesis – a critical technology overview *Green Chem.* 6: 128-14.
- Oliveira, M. E. C., and Franca, A. S. 2002. Microwave heating of foodstuff. *J. of Food Engineering*, 53: 347–359.
- Orsat, V., Raghavan, G. and Norris, E. 1993. Food processing waste dewatering by electro-osmosis. In *American Society of Agricultural Engineers. Meeting*.
- Orsat, V., Raghavan, G., Sotocinal, S., Lightfoot, D., and Gopalakrishnan, S. 1999. Roller press for electro-osmotic dewatering of bio-materials. *Drying Technology*, 17(3): 523-538.
- Ouajai, S., and Shanks, R. A. 2005. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polymer Degradation and Stability*, 89(2): 327-335.
- Page, M. and Page, C. 2002. Electroremediation of Contaminated Soils. *Journal of Environmental Engineering*, 128 (3), 208-219.
- Pallesen, B. E. 1996. The quality of combine-harvested fiber flax for industrials purposes depends on the degree of retting. *Industrial Crops and Products* 5(1): 65-78.
- Panigrahi, S., Kushwaha, R.L. and Rahman, A. 2012. Impact of fiber diameter on mechanical properties of hemp based composite. *ASABE Meeting Presentation, Paper Number: 12-1337664*.
- Pickering, K., Beckermann, G., Alam, S., and Foreman, N. 2007. Optimising industrial hemp fiber for composites. *Composites Part A: Applied Science and Manufacturing*, 38(2): 461-468.
- Pickering, K., Priest, M., Watts, T., Beckermann, G., and Alam, S. 2005. Feasibility study for NZ hemp fiber composites. *Journal of advanced materials*, 37(3): 15-20.
- Putnina, A. and Kukle, S. 2011. STEX Treated and Un- treated Hemp Fiber Comparative Analysis. Scientific Journal of Riga Tech University. *Textile and clothing Technology* 6: 36-42.
- Rabie, H., Mujumdar, A., and Weber, M. 1994. Interrupted electro-osmotic dewatering of clay suspensions. *Separations Technology*, 4(1), 38-46.
- Rampacek, C. 1966. Electro-osmotic and electro-phoretic dewatering as applied to solid liquid separation. In: J. B. Poole and D. Doyle (Eds.), *Solid-liquid separation-a review and a bibliography-*. Her Majesty's Stationery Office. London: 100–108.
- Reddy, N. and Yang, Y. 2005. Biofibers from agricultural byproducts for industrial applications. *Trends in Biotech.*, 23: 22-27.
- Rognes, H., Gellerstedt, G., and Henriksson, G. 2000. Optimization of flax fiber separation by leaching. *Cellulose chemistry and technology*, 34(3-4): 331-340.
- Sadasivam, S. and Manickam, A. 1996. Biochemical Methods for Agricultural Sciences. *New Age International (P) Ltd., New Delhi*: 97.
- Saeman, J. F., Bubl, J. L., and Harris, E. E. 1945. Quantitative saccharification of wood and cellulose. *Industrial & Engineering Chemistry Analytical Edition*, 17(1): 35-37.

- Sakai, T., Sakamoto, T., Hallaert, J., and Vandamme, E. J. 1993. Pectin, pectinase and protopectinase: production, properties, and applications. *Advances in applied microbiology*, 39: 213.
- Sato, S., Shibata, C., and Yazu, M. 1996. Non-thermal killing effect of microwave irradiation. *Biotechnology techniques*, 10(3): 145-150.
- Schwartzberg, H., Rosenau, J. and Richardson, G. 1977. The removal of water by expression. In *AIChE Symposium Series* (73): 177-189.
- Shamolina, I.S., Bochek, A.M., Zabivalova, N.M., Medvedeva, D.A. and Grishanov, S.A. 2003. An Investigation of Structural Changes in Short Flax Fibers in Chemical Treatment. *Fibers and Textiles in Eastern Europe*. 11 (1): 33-40.
- Shamolina, I.S., Bochek, A.M., Zabivalova, N.M., Medvedeva, D.A. and Grishanov, S.A. 2003. An Investigation of Structural Changes in Short Hemp Fibers in Chemical Treatment. *Fibers and Textiles in Eastern Europe*. 11 (1): 33-40.
- Sharma, H. S. S. 1987. Screening of polysaccharide-degrading enzymes for retting flax stem. *International biodeterioration*, 23(3), 181-186.
- Sharma, H. S. S. 1988. Chemical retting of flax using chelating compounds. *Annals of Applied Biology* 113: 159-165.
- Sharma, H. S. S., and Faughey, G. J. 1999. Comparison of subjective and objective methods to assess flax straw cultivars and fibre quality after dew-retting. *Annals of applied biology*, 135(2): 495-501.
- Shehsad, Asim. 2013. A study in physical and mechanical properties of hemp fibers. *Journal of Advances in Materials Science and Engineering* (2013): 1-9.
- Sohn, M., Barton, F.E., Akin, D.E., and Morrison, W.H. 2004. A new approach for estimating purity of processed hemp fiber by NIR spectroscopy. *Journal of Near Infrared Spectroscopy* 12 (4): 259-262, 2004.
- Springer, J. 2002. Surface Characterization of Flax, Hemp and Cellulose Fibers; Surface Properties and the Water Uptake Behavior. *Polymer Composites* 23(5): 873.
- Sridar, V. 1998. Microwave radiation as a catalyst for chemical reactions. *Current Science* 74(5): 446-450.
- Stamboulis, A., Baillie, C.A. and Peijs, T. 2001. Effects of environmental conditions on mechanical and physical properties of flax fibers. *Composites - Part A: Applied Science. Manual* (32): 1105-1115.
- Steel, B.C., Bilek, M.M., McKenzie, D.R. and dos Remedios, C.G. 2002. A technique for micro second heating and cooling of a thin biological sample. *European Biophysics Journal* (31): 78-382.
- Stuerga, D. A. C., and Gaillard, P. 1996. Microwave athermal effects in chemistry: A myth's autopsy. Part I: Historical background and fundamentals of wave-matter interaction. *Journal of microwave power and electromagnetic energy* 31(2): 87-100.

- Sun, Y., and Cheng, J. 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83(1), 1-11.
- Thomsen, A. B., Thygesen, A., Bohn, V., Nielsen, K.V., Pallesen, B and Jørgensen, M.S. 2006. Effects of chemical-physical pre-treatment processes on hemp fibers for reinforcement of composites and for textiles. *Industrial Crops and Products* (24):113-118.
- Thygsen, L.G., Bilde-Dorensen, J.B., and Hoffmeyer, P. 2006. Visualization of dislocations in hemp fibers-A comparison between scanning electron microscopy and polarized light microscopy. *Industrial Crops and Products*. 24: 181-185.
- Tsubaki, S., and Azuma, J. I. 2011. Application of microwave technology for utilization of recalcitrant biomass. *Advances in induction and microwave heating of mineral and organic materials. InTech*: 697-722.
- Turner, A. J. 1949. The Structure of Textile Fibers VII- The Structure of Flax. *Journal of the Textile Institute Proceedings*, 40(9): 857-P868.
- Uludag, S., Loha, V., Prokop, A. and Tanner, R. 1996. The effect of fermentation (retting) time and harvest time on kudzu (*Pueraria lobata*) fiber strength. *Applied Biochemistry and Biotechnology*, 57-58(1): 75-84.
- Van de Weyenberg, I., Ivens, J., De Coster, A., Kino,B., Baetens, E. and Verpoest, I. 2003. Influence of processing and chemical treatment of flax fibers on their composites. *Composites Science and Technology* (63): 1241-1246.
- Van Sumere, C. F. and Sharma., H.S.S. 1991. Analyses of fine flax fiber produced by enzymatic retting. *Aspects of Applied Biology* 28: 15-20.
- Van Sumere, C.F. 1992. Retting of Flax with special reference to enzyme retting. In: Sharma, H.S.S., Van Sumere, C.F. (Eds.) 1992. *The Biology and Processing of Flax. M Publications, Belfast, Northern Ireland*: 157–198.
- Vijh, A. K. and Novak, J. P. 1997. A new theoretical approach to electro-osmotic dewatering based on non-equilibrium thermodynamics. *Drying Technology*, 15 (2): 699-709.
- Wang, B., Panigrahi, S., Tabil, L. and Crerar, W. 2007. Pre-treatment of flax fibers for use in rotationally molded biocomposites. *Journal of reinforced plastics and composites*, 26(5): 447-463.
- Wayne, H. and Wendy, S. 2000. The THC content of cannabis in Australia: evidence and implications. *Australian and New Zealand Journal of Public Health* 24 (5): 503-508.
- Weiting, G. C. 1951. Paper Chromatography of Flax Fiber Polyuronide Hemicellulose, *Nature* 168(280): 2.
- Xu, J., Wang, Z., and Cheng, J. J. 2011. Bermuda grass as feedstock for biofuel production: A review. *Bioresource technology*, 102(17): 7613-7620.
- Yat, S. C., Berger, A., and Shonnard, D. R. 2008. Kinetic characterization for dilute sulfuric acid hydrolysis of timber varieties and switchgrass. *Bioresource technology*, 99(9): 3855-3863.

- Yin, C. 2012. Microwave-assisted pyrolysis of biomass for liquid biofuels production, *Bioresource Technology*, 120 (September 2012): 273-284.
- Yoshida, H. 1993. Practical aspects of dewatering enhanced by electro-osmosis. *Drying Technology*, 11(4): 784-814.
- Yoshida, H. and Yukawa, H. 1988. A theoretical analysis of the electro-osmotic dewatering of sludge. *Inter. Chem. Eng.* 28 (3): 477-485.
- Yoshida, H. and Yukawa, H. 1991. Analysis of dewatering processes enhanced by electro-osmosis. *Fluid/Particle Separation Journal*. 4(1):1-7.
- Yoshida, H. and Yukawa, H. 1992. Analysis of electro-osmotically enhanced sludge dewatering. In: A. S. Mujumdar (Ed.), *Advances in drying* (5): 301-323.
- Yuan, X., Jayaraman, K. and Bhattacharyya, D. 2001. Plasma treatment of sisal fibers and its effect on tensile strength and interfacial bonding, Presented at the Third International Symposium on Polymer Surface modification, Newark, New Jersey, USA, 2001.
- Zahn, M., Ohki, Y., Fenneman, D. B., Gripshover, R. J., & Gehman, V. H., Jr. 1986. Dielectric properties of water and water/ethylene glycol mixtures for use in pulsed power system design. *Proceedings of the IEEE*, 74(9), 1182-1221.
- Zhang, J., Henriksson, G., and Johansson, G. 2000. Polygalacturonase is the key component in enzymatic retting of flax. *Journal of biotechnology*, 81(1): 85-89.
- Zhang, L.L., Zhu, R.Y., Chen, J.Y., Chen, J.M. and Feng, X.X. 2008. Seawater-retting treatment of hemp and characterization of bacterial strains involved in the retting process, *Process Biochemistry*, 43 (11), 1195-1201.