University of Piraeus

School of Maritime and Industrial Studies

Department of Industrial Management and Technology

Laboratory of Simulation of Industrial Processes

PhD Thesis

Title:

«Industrial processes for the valorization of medical waste fractions»

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Prologue

The present dissertation is the result of an experimental and theoretical study that started on March 2017 at the Laboratory of Simulation of Industrial Processes, Department of Industrial Management and Technology, School of Maritime and Industrial Studies, University of Piraeus. The title of the dissertation is «Industrial processes for the valorization of medical waste fractions»[1]. The advising committee consists of Professor Dimitrios Karalekas, Professor Dimitrios Sidiras (supervisor) and Associate Professor Christina Siontorou (department board decision March 7, 2017).

The subject of this study deals with certain aspects of renewable materials sources and energy saving. This work intended to contribute to the field of valorization and recycling of medical waste fractions, putting emphasis on cellulosic and lignocellulosic medical waste fractions and especially the effect of thermochemical pretreatments on their behavior.

I would like to thank my supervising Professor Dr. Dimitrios Sidiras for supporting me and assigning me to the specific subject. I would also like to thank all the members of the advisor committee for their support and insights. I would also like to thank Professor Evangelos Topakas (head of laboratory) and Assistant Professor Anthi Karnaouri (Laboratory of General Agricultural Microbiology, Faculty of Crop Science, Agricultural University of Athens) who gave me access to the Laboratory of Biotechnology in the Chemical Engineering Department of National Technical University of Athens and its resources in order to study the effect of acid hydrolysis pretreatment on the enzymatic hydrolysis of medical waste cotton and paper substitute. Finally, I would like to thank my family for their support.

[1] («Βιομηχανικές διεργασίες για την αξιοποίηση κλασμάτων νοσοκομειακών αποβλήτων»)

Περίληψη

Η παρούσα διατριβή καινοτομεί στην έρευνα για την αξιοποίηση κυτταρινούχων/λιγνοκυτταρινούχων κλασμάτων νοσοκομειακών αποβλήτων, με σκοπό την παραγωγή ενέργειας, καυσίμων και υλικών, στο πλαίσιο της κυκλική οικονομίας μηδενικών αποβλήτων. Αρχικά, πραγματοποιήθηκε εκτεταμένη βιβλιογραφική έρευνα με σκοπό τη συλλογή δεδομένων σχετικά με την παραγωγή των νοσοκομειακών αποβλήτων, τις μεθόδους συλλογής και διαχωρισμού αυτών και τις τεχνολογίες που χρησιμοποιούνται για την αξιοποίηση ή την τελική διάθεσή τους. Βάσει των δεδομένων που συλλέχθηκαν, σχεδιάσθηκε η πειραματική μελέτη, η οποία πραγματοποιήθηκε με σκοπό να αναδείξει την δυνατότητα του βαμβακιού και χαρτιού νοσοκομειακής προέλευσης για την παραγωγή ενέργειας μέσω αύξησης της θερμογόνου δύναμής του καθώς και τη δυνατότητα χρήσης αυτού ως προσροφητικό μέσο για την απορρύπανση υδάτων. Μελετήθηκε, επίσης, η επεξεργασία του νοσοκομειακού βαμβακιού και του χαρτιού με ενζυμική υδρόλυση .

Ειδικότερα, για την εξέταση της προσροφητικότητας καθώς και της ανώτερης θερμογόνου δύναμης του βαμβακιού των νοσοκομειακών αποβλήτων πραγματοποιήθηκε φρύξη (κοιν. καψάλισμα, torrefaction). Η προκατεργασία αυτή πραγματοποιήθηκε σε συγκεκριμένο εύρος θερμοκρασίας με μέγιστη τους 340 ^{o}C και διαφορετικούς χρόνους παραμονής, προκειμένου να μελετηθούν οι παράμετροι που επηρεάζουν την απόδοση της διαδικασίας. Πραγματοποιήθηκαν 14 πειράματα σε υψικάμινο. Για τη μέτρηση της θερμογόνου δύναμης στα δείγματα χρησιμοποιήθηκε θερμιδόμετρο Parr 1341 Plain Jacket Bomb και έγιναν 14 μετρήσεις. Στα ίδια δείγματα ελέγχθηκε και η προσροφητικότητα. Για την προσομοίωση των ρυπασμένων υδάτων δημιουργήθηκε διάλυμα που περιείχε μπλε του μεθυλενίου (Methylene Blue, $C_{16}H_{18}ClN_3S.xH_2O$), ενώ οι μετρήσεις των δειγμάτων έγιναν σε φασματοφωτόμετρο HACH DR6000 UV-VIS (λ=664 nm). Για την προσομοίωση των πειραματικών δεδομένων χρησιμοποιήθηκαν

κατάλληλα κινητικά μοντέλα. Αξιοποιήθηκε ο συνδυαστικός παράγοντας σοβαρότητας (Combined Severity Factor, R_0) που συνδυάζει σε μία μεταβλητή την επίδραση του χρόνου αντίδρασης και της θερμοκρασίας της φρύξης.

Στη συνέχεια πραγματοποιήθηκε μέσω του προγράμματος Design Expert ο πειραματικός σχεδιασμός (Design of Experiments, DoE) κατά Box-Behnken για την εφαρμογή της μεθοδολογίας επιφανειακής απόκρισης (Response surface methodology, RSM) με σκοπό τη μελέτη της επίδρασης της όξινης υδρόλυσης(με χρήση θειικού οξέος) στο κλάσμα βαμβακιού και χαρτιού των νοσοκομειακών αποβλήτων, ώστε να συσχετιστεί με το R_0 ως προς τα πειραματικά αποτελέσματα. Ο πειραματικός σχεδιασμός αποτελείτο από 15 πειράματα για το βαμβάκι και 15 για το χαρτί. Στη συγκεκριμένη περίπτωση το R_0, εκτός του χρόνου αντίδρασης και της θερμοκρασίας, εμπεριέχει και τη συγκέντρωση του οξέος που χρησιμοποιήθηκε. Τα προϊόντα που προέκυψαν από την κατεργασία του βαμβακιού μελετήθηκαν ως προς την προσροφητικότητα τους με 15 μετρήσεις, καθώς και ως προς την ανώτερη θερμογόνο δύναμη με 15 μετρήσεις. Τα πειράματα εκτελέστηκαν σε αντιδραστήρα διαλείποντος έργου (τύπου αυτοκλείστου) 3,75 L Parr 4553. Όλα τα παραπάνω πειράματα πραγματοποιήθηκαν στο Εργαστήριο Προσομοίωσης Βιομηχανικών Διεργασιών του τμήματος Βιομηχανικής Διοίκησης και Τεχνολογίας του Πανεπιστημίου Πειραιά.

Για την ανάλυση της σύστασης των δειγμάτων της στερεής φάσης, χρησιμοποιήθηκε το σύστημα υγρής χρωματογραφίας υψηλής απόδοσης (HPLC) 1260 Infinity II LC System, της Agilent με χρήση στήλης Aminex HPX-87H στους 50 ^{o}C, μετά από ποσοτική σακχαροποίηση αυτών με την πραγματοποίηση 30 μετρήσεων για κάθε ένα κλάσμα. Η ίδια διαδικασία χρησιμοποιήθηκε και στην ανάλυση της υγρής φάσης, με σκοπό τον προσδιορισμό της ποσότητας και του είδους των συνολικών σακχάρων και τον έλεγχο για προϊόντα αποικοδόμησης αυτών. Πραγματοποιήθηκαν 30 μετρήσεις για την κάθε μία στερεή φάση (βαμβάκι και χαρτί) και 30 μετρήσεις για την κάθε μία υγρή.

Τα στερεά δείγματα χρησιμοποιήθηκαν για την παραγωγή ζυμώσιμης γλυκόζης μέσω ενζυμικής υδρόλυσης. Το ενζυμικό μείγμα Cellic® CTec2 της Novozymes A/S χρησιμοποιήθηκε για την υδρόλυση των δειγμάτων η οποία πραγματοποιήθηκε στους 50 ^{o}C. Δείγματα ελήφθησαν μετά από 24 και 48 ώρες και στη συνέχεια αναλύθηκαν με τη μέθοδο DNS (δινιτροσαλικυλικού οξέος) και της μεθόδου glucotest με χρήση φασματοφωτόμετρου (30 μετρήσεις στις 24 και 30 στις 48 ώρες για κάθε μέθοδο και κάθε υλικό). Αυτά τα πειράματα πραγματοποιήθηκαν στο Εργαστήριο Βιοτεχνολογίας της Σχολής Χημικών Μηχανικών του Μετσόβειου Πολυτεχνείου.

Σύμφωνα με τα αποτελέσματα, το βαμβάκι στα νοσοκομειακά απόβλητα είχε καλύτερη απόδοση από το χαρτί ως πηγή θερμότητας. Ομοίως, απεδείχθη καλύτερο προσροφητικό υλικό, ιδίως μετά από την επεξεργασία της του με όξινη υδρόλυση. Επίσης, παρουσίασε μεγαλύτερη απόδοση μετατροπής σε ζυμώσιμη γλυκόζη από το χαρτί στα νοσοκομειακά απόβλητα, κάτι που το καθιστά μία πολλά υποσχόμενη πηγή ενέργειας και υλικών στα πλαίσια της κυκλικής οικονομίας μηδενικών αποβλήτων.

Summary

The present dissertation innovates as regards the research for the valorization of cellulosic and lignocellulosic fractions of medical wastes (MW), aiming to production of energy, fuels, and materials, within the framework of zero waste circular economy. Initially, an extensive literature review was conducted to collect data on MW production, collection and segregation methods, and technologies used for their utilization or final disposal. The design of the experimental study was based on the collected data with a view to highlighting the capabilities of medical cotton and paper waste in energy production by increasing its higher heating value, as well as their use as adsorbents for the decontamination of wastewater. The enzymatic digestion capacity of medical cotton waste and medical paper waste were also studied.

More specifically, the adsorption and the higher heating value of medical cotton waste have been studied with torrefaction. Pretreatment was performed on a specific temperature range with a maximum at 340^{o}C. Different reaction times have been used in each experiment in order to elucidate the parameters that affect process efficiency. 14 experiments were performed in a blast furnace. A Parr 1341 Plain Jacket Bomb calorimeter was used to measure the calorific value of the samples, whereas adsorption was tested for all samples. The simulated wastewater used herein was Methylene Blue solution ($C_{16}H_{18}ClN_3S.xH_2O$), whereas the samples were analyzed with a HACH DR6000 UV-VIS spectrophotometer (λ = 664 nm).

Kinetic modeling was used, along with the Combined Severity Factor (R_0), which unifies in one variable the effect of reaction time and temperature.

Box-Behnken's Design of Experiments (DoE) was carried out through the Design Expert program using the Surface Response methodology (RSM) to study the effect of acid hydrolysis on the medical cotton and paper waste fractions to correlate with

R_0 in terms of experimental results. In this case R_0, apart from reaction time and temperature, incorporate the acid concentration used herein. DoE consists of 15 experiments The products obtained from the treatment were studied for their adsorption capacity and their higher heating value (HHV). The experiments were performed in a 3.75 L Parr 4553 batch reactor (autoclave). All the above experiments were conducted at the Industrial Processes Simulation Laboratory, Industrial Management and Technology department, University of Piraeus.

The Agilent 1260 Infinity II LC System high performance liquid chromatography (HPLC) system was used to analyze the solid phase samples composition after quantitative saccharification. 30 measurements were made for each material. An Aminex HPX-87H column at 50^{o}C was used. The same procedure was performed in the liquid phase to check for degradation products as well as to determine the kind and the amount of the total sugars. 30 measurements were conducted for the liquid phase and 30 for the solid phase of each material.

These solid samples were then used to produce fermentable glucose by enzymatic hydrolysis. Novozymes A / S Cellic® CTec2 enzyme mixture was used to hydrolyze the samples at 50°C. Liquid samples were taken at 24 and 48 hours and then measured using the DNS (Dinitrosalicylic acid) method and Glucotest spectrophotometric method (30 measurements were made for each method and each material at 24 and 48 hours). These experiments were made at the Biotechnology Laboratory, Chemical Engineer Department of National Technology University of Athens.

According to the results, the medical cotton waste treated by acid hydrolysis had a better performance as a heat source than paper, Similarly, the hydrolyzed samples proved better adsorbents than the torrefied ones. It also presented a higher conversion efficiency to fermentable glucose than medical paper waste, rendering it more appropriate for bioethanol production. In conclusion, medical cotton waste (MCW) has been

proven a suitable and promising source of energy and materials in the context of the zero-waste circular economy.

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Introduction

The progress of medicine and technology gives access to people to a better-quality life. Medical consumables and equipment are evolving and multiplying to serve this cause. As a result, medical waste (MW) generation (MWG) is growing annually. MW are of great danger to human health and environment because of the hazardous and infectious substances that are attached to them. Researchers have been recording the evolution of MW and their generation the last decades. Their interest has been risen intensely the recent years because of the need to find ways of valorizing MW fractions (MWF). There are many MW treatment (MWT) technologies (MWTT) that are used to treat MW but all of them have limitations and flaws. Following the trend of zero waste circular economy many attempts have been made on MW recycling to produce energy, fuels, and materials.

The purpose of this dissertation is to contribute on this venture of huge interest to valorize MWF. The first step was the choice of the suitable MWF. MW was bibliographically examined to fully understand their generation, their classification, the treatment methods applied on each fraction and the potential products of these treatments. There were many articles read and among them there were 188 chosen to be used for an in-depth review paper with title: "Medical Waste Treatment Technologies for Energy, Fuels, and Materials Production: A Review", by Giakoumakis, G.; Politi, D.; Sidiras, D, published in Energies 14, 8065 (2021). This review paper combined information about MWG, MW classification (MWC), MW disposal (MWD), MWT. MWTT, and the possible products of these treatments mostly from the up-to-date articles. This is the first review paper on the MW sector that provides combined all this information focusing on energy, fuels, and materials production.

The theoretical study of MW lead in choosing MCW and medical paper waste (MPW) as fractions to be further examined owing to their potential as recycled materials. Both are included on the MWF called MPW and is about 25% w/w of the total MW. The effect of several pretreatments on MCW was studied to valorize certain aspects, such as heating value, adsorbance and fermentable glucose production capabilities. Fermentable glucose production capabilities were studied at MPW as well. The pretreatment methods applied were acid hydrolysis, consequential acid/enzymatic hydrolysis, and torrefaction. This experimental investigation lead in publishing the article entitled: "Simulation and optimization of combined acid pretreatment and enzymatic saccharification of medical cotton waste", by Giakoumakis, G., Karnaouri, A., Topakas, E. and Sidiras, D., in Biomass Conversion and Biorefinery 11, 515–526 (2020). This was an innovative work using MCW as a source of glucose production, a raw material appropriate for the bioethanol industry within the biorefinery concept.

Below there is a short explanation of each chapter that follows:

The first chapter of the theoretical part refers to the MWG and MWC and the practices used globally to treat MW.

The second chapter focuses on MW handling, collection, separation, treatment, and transport. The chapter presents a thorough review of treatment methods, including technologies employed, their efficacy, and their performance. The third chapter discusses the potential applications of the resultant products in the energy sector and in sorptive material sector. The optimization process limitations and the economic feasibility of the commonly employed treatment methods are discussed in the fourth chapter provides information about.

The experimental part is introduced in the fifth chapter that states the materials and methods employed, the equipment and the analyzers used.

The results of the experimental studies are presented and extensively discussed in chapter six, ie., MCW adsorbance, gross heat of combustion, and MCW and MPW enzymatic digestibility, including a full-scape optimization and modeling.

Chapter 7 is a concluding chapter that provides information about the results of each set of experiments. It also informs about the suitability of the selected methodology and the kinetic models used alongside with some proposals for future research.

Alongside with the preparation of this dissertation the following papers were published.

- Sidiras, D., Politi, D., Giakoumakis, G. and Salapa, I. (2022). Simulation and optimization of organosolv based lignocellulosic biomass refinery: A review. Bioresource Technology, 343, p.126158.
- Sidiras, D.K.; Nazos, A.G.; Giakoumakis, G.E.; Politi, D.V. Simulating the Effect of Torrefaction on the Heating Value of Barley Straw. Energies 2020, 13, 736.

Chapter 1. Medical Waste generation and classification

MW is produced from healthcare units, medical laboratories, bio-medical research centers and dental clinics. Their generation rate is continuously rising. COVID-19 pandemic had a huge impact on this phenomenon. MW is classified based on the nature of each waste and its usage. This chapter gives an in-depth bibliographical examination of MW generation (MWG) sources and rates and simultaneously provides thorough information about the MWC methods used globally. Researchers around the world have focused on providing constantly, relative to the above, information, through their work. This has leaded on a massive volume of articles that explain how MWG and MWC occurs, and their impact on human health and environment. Our work is summed up below.

According to Khan et al. (2019) and Das et al. (2021), if MW is handled in inappropriate way, there exists a serious risk of disease transmission, especially to the MW handlers, the health care personnel and the patients, whereas a risk to the public cannot be easily overruled. The need for appropriate and efficient MW management (MWM) has increased during the COVID-19 outbreak mainly due to the increase of MW volume (Barua et al 2021, Alrawi et al 2021 COVID-19 pandemic increased MWG, in many countries by 350–500%, especially medical plastic waste in developing and developed countries, showing the fluctuation of MW recycling efficiency among many countries. (Fadaei 2021).

Healthcare is a fast-developing industry due to the demand for more sophisticated/demanding medical treatments, resulting in an increasing need for MWT and MWD (Kenny et al. 2021). Life cycle assessment (LCA) and circular economy (CE) methods have been applied in the biomedical sector and proved suitable to handle the medical, pharmaceutical, and dental waste sector within `1qa framework of ‘green circulation’ (Antoniadou et al. 2021).

A meta-analysis of MWM practices in 78 countries was conducted by Singh et al. (2021) and identified impediments and challenges facing the integration of MWM in the CE concept, on the basis of statistical correlations with healthcare expenditure per capita of GDP (HCECGDP), human development index, life expectancy, and environmental performance index. Only 38.9% of MW was separated for proper management, while only 41% of workers were well trained for MWD. Capoor and Parida (2021) investigated the problems from COVID-19 MW and national and international authorities’ guidelines on MWM during the pandemic. According to all the guidelines, the COVID-19 MWM follows environment friendly principles/practices of MWM to work safely and minimize the possibility of infection. Separation at source of COVID-

19 MW, and safety measures during the MW-cycle provide the safest and shortest possible path that leads out of this crisis.

Chisholm et al. (2021) studied the sustainability aspects of MWM in Africa as regards flexible solutions for environmental protection and human health safety. They concluded that improper MWH is of great risk for human health and environment. The MWD method should be decided based on MW type, cost, and pollution and contamination during transport.

Careful planning, use of large capacity mobile recycling facilities, and established guidelines for disposal of MW could reduce the risk of COVID-19 spread in developing countries (El-Ramady et al, 2021). Lofti et al. (2021), developed a sustainable MWM system for collection and transportation of MW in pandemics; they designed numerous practical illustrations at various scales, solved the problem using CPLEX solver, and compared the results for a diverse set of conditions. They also investigated the practical implications. Moreover, He et al. (2021) optimized the problem of the automated MW sorting system by considering the operational flow of MW. They developed a mixed-integer programming model for the optimization of the MW assignment, presorting stations, and automated guided vehicles.

In this work, the existing MW treatment/disposal technologies are reviewed as regards to their capability to produce energy, fuels, and materials. The MWG data derived from 188 papers, mainly in web of science database, covering the period from 1990 to 2021, giving most attention at the recent years, and divided into gross MW and hazardous MW. The capability of the examined MWTT to produce energy, fuels, and materials is very promising, expected to materialize in the near future, eliminating, at the same time, the MW management problem (Giakoumakis et al. 2021b).

1.1. Medical Waste generation

According to Song et al. (2021), COVID-19 and produces a large amount of MW dangerous for the human health and environment. In Hubei Province during COVID-19, the MW production rate has been estimated using a neural network model; when related to the environmental impact, scenarios emerged resulting in four scenarios for the estimation of the environmental impact of new MW generated during the pandemic with a volume of about 3367 tons when treated with four different MWTT (incineration etc.). Kalantary et al. (2021) estimated that the COVID-19 pandemic increased MW generation (MWG) by 102 % in private and public hospitals in Iran. Moreover, the fraction of infectious waste increased by 9 % in MW composition and 121 % compared to pre COVID-19 era. Maalouf and Maalouf (2021) analyzed the infectious MWG rates

(MWGRs) and MWM practices in Lebanon during the COVID-19 pandemic, estimating 39 tons per month of infectious MW, COVID-19-related generated, i.e., 5% - 20% of total infectious MW. Mekonnen et al. (2021) assessed the MWG in Ethiopia during the COVID-19 pandemic and estimated about 493 kg/day MWGR in all hospital service units. 62% of the total MW production was general waste (GW) and 38% was hazardous MW (HMW). In Peshawar, Pakistan, Khalid et al. (2021) studied the MWM procedures in teaching hospitals and found that government teaching hospitals produced 900 kg/day MW, government non-teaching hospitals 167 kg/day and private teaching hospitals 79 kg/day, without any separation at generation point. In Vietnam, Nguyen et al. (2021) estimated the MWGR and MW composition during the COVID-19 pandemic considering the resources/equipment supply and found 1486 tons per year MW produced from the isolated COVID-19 patients' treatment (4.6 kg/bed/day), quarantine in medical facilities (3.9 kg/bed/day), centralized quarantine (46.4 g/bed/day), testing (50 g/test) and vaccination (10.5 g/shot), where plastic was 76.7%. Tsai (2021) in Taiwan analyzed the MWG and the impact of COVID-19 on MWGR and quantity which increased from 35,747 tons in 2016 to 40,407 tons in 2019, i.e., increase by 4.17%.

In Dar es Salaam city, Tanzania, Anicetus et al. (2020), estimated the quantity of MWG in 4 healthcare units and found the generation rate per healthcare ranging from 299 kg/day to 1554 kg/day. According to Borowy (2020), health facilities have an increasing MWGR, while 15% of MW is infectious, radioactive, or toxic. Khan et al. (2019) mentioned the significant fluctuation in the MWG from various regions. In Bench Maji Zone, Ethiopia, Meleko et al. (2018) assessed the MWGR in different health facilities and found that MWs were sharps, infectious, pathological, and pharmaceutical, and the MWGR was 0.267 (23.3%), 0.2695 (23.6%), 0.441 (38.6%) and 0.166 (14.5%) kg/day, respectively. Minoglou et al. (2017) examined the influence of several socioeconomic and environmental parameters on the MWGR. They found correlations between the quantities of MW, in kg/bed/day, versus economic indices like HCECGDP, social indices like Human Development Index, mean years of schooling, life expectancy, under-five mortality rates, HIV prevalence, deaths due to tuberculosis and malaria, and total CO2 emissions as environmental sustainability index, from 42 countries. Maamari et al. (2015), analyzed infectious MWGRs and patterns in Lebanon for 5 years for 57 out of a total of 163 hospitals in the country. They reported that the large private hospitals showed a high MWGR of 2.45 kg/bed/day, while the other categories showed 0.94

kg/bed/day. Moreover, infectious MWG was 1.42 kg/capita/year. Debere et al. (2013), reported for Addis Ababa, Ethiopia, year 2011, MWG 0.361- 0.669 kg/patient/day, consist of 58.7% non-HMW and 41.3% HMW. Public hospitals generated 59.2% of total MW in comparison to 40.5% of private hospitals.

In Greece, Komilis et al. (2009), calculated the hazardous MWGRs, based on 132 healthcare facilities data, especially in Athens, for a period of 22 months, i.e., the years 2009-2010. These facilities were public and private, categorized into general, birth, pediatric, cancer treatment, military, psychiatric and university hospitals. The MWGR was 0.012 kg/bed/d, for the public psychiatric hospitals, and 0.72 kg/bed/d, for the public university hospitals. Moreover, MWGR was 0.0012 kg/bed/d, for the psychiatric clinics, and 0.49 kg/bed/d, for the birth clinics considering the private healthcare facilities. In Athens, the public and private health care facilities include general, birth, pediatric, cancer, psychiatric military, and university hospitals (Komilis et al. 2011, Komilis et al. 2012).

Hamoda et al. (2005), studied the HMW and non-HMW MWGRs for two large public hospitals in Kuwait and correlated to the patients' number, the beds' number, and the conducted activity type in different hospitals sections. The MWGR was sufficiently corelated with the patients' number and not with the beds number. The MWGRs were 4.89 - 5.4 kg/patient/day, and 3.65 - 3.97 kg/bed/day. In Sivas, Turkey, Altin et al. (2003) evaluated the physical and elemental composition of MW in 4 hospitals and estimated that the daily MWGR was 985 kg/day. Additionally, the moisture content was 14,2 % and the MW was 92% combustible MW and 8% noncombustible MW. The combustible MW was 41,2% plastics, 16% paper, 4% cardboard, 10,2% textiles, and 17% food waste.

The MWG data are given in Table 1 for various countries according to numerous re-searchers, divided in total MW and HMW.

Table 1. MW generation data

Country	Total MW (kg/bed/day)	Hazardous MW (kg/bed/day)	References
Algeria	1.0		Singh et al. 2021
Belgium	1.4		Delmonico et al. 2017
Brazil	4.4	2.3	Hossain et al. 2011
Bolivia	0.5		Singh et al. 2021
Bulgaria	2.0		Singh et al. 2021
Canada	8.2		Tesfahun et al. 2015
China	0.6		Singh et al. 2021
Ecuador	0.4		Singh et al. 2021
Egypt	1.2		Singh et al. 2021
Ethiopia	1.1	0.6	Ansari et al. 2019
Ethiopia	6.03		Sanida et al. 2010
France	3.3		Singh et al. 2021
Germany	3.6	1.4	Sanida et al. 2010
Greece		0.26-0.89	Zamparas et al. 2017
Greece	1.4		Zamparas et al. 2019
Greece	1.5		Munir et al. 2014
Greece		0.33	Komilis et al. 2011
Greece		0.4	Komilis et al. 2012
India	0.5		Munir et al. 2014
Iran	3.5	1.039	Taghipour et al. 2009
Ireland	7.7		EPA 2021
Italy	1.0		Delmonico et al. 2017
Japan	2.3		Singh et al. 2021
Kazakhstan	5.34	1.2	Sawalem et al. 2009
Kuwait	3.8		Hamoda et al. 2005
Latvia	1.18		Sawalem et al. 2009

1.2. Medical Waste classification

The types of MW or healthcare waste according to the World Health Organization (WHO) (2018) are: (i) Infectious MW (blood/bodily fluids/ cultures/ infectious agents /autopsies/ infected animals/ swabs/ bandages/ medical devices), (ii) Pathological MW (human tissues/ organs/ fluids/ body parts/ animal carcasses), Sharps MW(syringes/ needles/ disposable scalpels/ blades), (iii) Chemical MW (solvents /reagents/ disinfectants/ sterilant/ heavy metals/ mercury/ batteries), (iv) Pharmaceutical MW (drugs/ vaccines), (v) Cytotoxic MW (genotoxic /highly HMW/mutagenic/ teratogenic/ carcinogenic/ cancer treatment cytotoxic drugs/ metabolites), (vi) Radioactive MW (radionuclides /radioactive diagnostic and radiotherapeutic materials), and (vii) non-HMW or general MW (waste with no physical/ chemical/ biological/ radioactive hazard).

In the United States, the Environmental Protection Agency (EPA 2021), defines the following solid MW categories: (i) HMW (not infectious but dangerous, e.g., chemical waste, discarded equipment and sharps), (ii) General Waste (bulk of office waste, mostly typical household, and most MW), (iii) Radioactive Waste (waste generated by radioactive treatments, from medical equipment for nuclear elements and from cancer therapies) and (iv) Infectious Waste (waste that could lead to an infection in humans, anything related to bodily fluids and blood).

According to Das et al. (2021), MW can be categorized as (i) hazardous, (ii) nonhazardous, and (iii) other waste. The hazardous fraction can be classified into (a) chemical, (b) infectious, (c) pathological, (d) radioactive, (e) sharps, and (f) pharmaceutical.

According to Korkut (2018) the UK government has promoted the differentiation of MW into the following categories: (i) Domestic/Municipal (concerns the other general non- MW, (ii) Offensive Waste (concerns all non-infectious and especially nappy and sanitary waste), (iii) Anatomical Waste (all waste from an animal or human including in this way organs, blood bags, and body parts), (iv) Cytotoxic/ Cytostatic

Waste (drugs and medicines with cytotoxic/cytostatic character, or items related to toxic or carcinogenic medicine), (v) Medicine Waste (creams, pills, and medicine, that are not cytotoxic/cytostatic), and (vi) Infectious Waste (contaminated with infectious bodily fluids from individuals treatment).

According to Eker and Bilgili (2011), the Western world including the USA and most European countries adopt a classification model that separates MW as follows: radioactive, hazardous, infectious, general. According to Windfeld and Brooks (2015), MW mainly consists of radioactive, infectious, and toxic materials that are associated with environmental pollution and health risks unless they are properly managed, treated and finally disposed of. Johannessen (1997) reports that laboratories, research facilities, and healthcare establishments waste is MW.

According to Kagonji and Manyele (2011), various classifications of MW have been proposed so far, with the most accepted one being that the main component of MW is hazardous and non-hazardous fractions. When reporting MWGR, emphasis is given to the effort to identify if the non-HMW stream is included, because this fraction, in many cases, represents 80% of the overall MW stream. Various factors that contribute to the presence of the significant variability of the reported MWGR, such as the presence of different hospital facilities, doubt if the non- HMW fraction can be presented in the MWGR quantification, financial factors, or even the units of expressing MWGR further complicate the comparison of MWGR among countries with different financial status and different legislation. As an example, Minoglou et al (2017) report that the following parameters are implicated in the gross differences noticed among countries: illegal dumping, MW management systems, differences in the operation of healthcare services, and different legal frameworks.

According to the recent literature, MW is classified according to materials use and the waste disposal practices (Minoglou et al. 2017). According to Reinhardt and Gordon (1991), infectious waste, which is suspected in many cases to contain a sufficient concentration of pathogens that cause sickness in vulnerable hosts, constitutes

another class that contains various materials or instruments that have been related to infected people or animals, infected animals essentially from laboratories, MW that has been related to infected patients, in many cases undergoing hemodialysis, infected patients MW in isolation districts, MW from autopsies and surgery on patients with the presence of infectious diseases, and stocks and cultures of infectious agents from laboratory work. According to Thakur and Anbanandam (2016), various interchangeable terms depending on every country's legislation have been proposed for the same kind of MW. A common assumption in the literature is that MW can be considered as any MW that is produced as a byproduct of healthcare activity at laboratories, hospitals, dentists, and surgeries.

On a global level, a constant international growth in MWG is observed. In low-income countries, MWG, although lower than in the developed countries, is sharply increasing because of the enhanced access to healthcare facilities. In rich countries, the increase in MWGR is assigned to the ageing population, leading in this way to an increasing health care waste volume (Kagonji and Manyele 2011).

Liberti et al. (1996) reported that MWG by healthcare facilities concerns used syringes and needles, radioactive materials, medical devices, pharmaceuticals, chemicals, blood and body fluids, diagnostic samples, body parts, and soiled dressings. Rehabilitation services account for 52% of total infectious MWG, analytical laboratories account for 23%, and surgeries (14%), dialysis units (7%) and first aid account for the remaining 4%. The false management of health care waste potentially exposes risks of toxic injuries to the environment and affects not only patients but also the community as well as waste handlers and health care workers.

Table 2 was constructed considering the categorization of MW in the international literature, indicating the numerous differences between the approaches of the various researchers. In Figure 1, an explanatory schematic diagram on MW catego-

ries/types is shown, considering all these opinions. The various MW fraction is presented in Table 3 as percentages. In Figure 2, the average values, the upper limits, and the lower limits of the main MW fractions percentages are presented.

Table 2. MW categories/types.

General	Recyclable	Hazardous	Radioactive	Plastics/ sharps	Pharmaceuti-cal	Toxic	Chemical	Infectious	Pathological	References
Yes	Yes	Yes	Yes					Yes		Alagöz and Kocasou 2007
			Yes	Yes	Yes	Yes	Yes	Yes		Capoor and Bromwick 2017
	Yes	Yes				Yes		Yes		Chen et al. 2021)
				Yes	Yes		Yes	Yes		Chen et al. 2013
			Yes	Yes	Yes	Yes		Yes		Nwachukwu et al 2013
Yes	Yes	Yes		Yes			Yes			Eker and Bilgili 2011
Yes						Yes		Yes		Graikos et al. 2010
Yes				Yes	Yes			Yes	Yes	Hama et al. 2021
Yes		Yes	Yes			Yes		Yes		Hamoda et al. 2005
Yes				Yes			Yes	Yes	Yes	Hasan and Rahman 2018
Yes				Yes	Yes					Hong et al. 2018
			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Insa et al. 2010
				Yes				Yes	Yes	Jang et al. 2011
				Yes				Yes	Yes	Jang et al. 2006
Yes			Yes	Yes	Yes		Yes	Yes	Yes	Kagonji and Manyele 2011
Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Kenny and Pri-yadarshini 2021
			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Ghasemi et al. 2016
Yes			Yes	Yes	Yes			Yes		Kwikiriza et al. 2019
Yes			Yes	Yes			Yes	Yes	Yes	Lee et al. 2004
Yes				Yes				Yes	Yes	Li and Jeng 1993
Yes			Yes	Yes	Yes		Yes	Yes	Yes	Mathure et al. 2016
Yes	Yes	Yes						Yes	Yes	Mentzelou et al. 2009
Yes	Yes	Yes		Yes				Yes		Anath et al. 2010
Yes		Yes		Yes					Yes	Sawalem et al. 2009
Yes	Yes	Yes		Yes	Yes		Yes			Saxena et al. 2021

Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Singh et al. 2021
Yes			Yes		Yes	Yes		Zamparas and Kalavrouziotis 2017
Yes	Yes			Yes	Yes	Yes	Yes	Zamparas et al. 2019
			Yes		Yes	Yes	Yes	He et al. 2021

Table 3. MW fractions' percentages

Country	Source	Source No	Gen-eral	Plastic	Tex-tile	Glass	Metal	Paper	Or-ganic	References
Canada	NA			14%		3%	2%	45%	17%	Phinney …
China	MSWAC	1		45%	30%	2,50%	2,50%	10%		Zhao et al. 2008
China	NA	-	56%	36%		4%	4%			Singh et al. 2021
Egypt	H	8		19%	17%	9%	1%	24%	28%	Abd El-Salam 2010
Greece	H	29		18%		8%	9%	47%	16%	Zamparas and Kalavrouziotis 2017
Greece	HF	1	82%			4%	6%			Graikos et al. 2010
India	GH/AH	2/1	54%	10%	15%	4%	1%	15%		Mandal et al. 2009
Iran	EH	12		29%	16%	8%	2%	14%	31%	Dehghani et al. 2008
Iran	EH/UH/ MH/PH/ GoH	10		23%	11%	4%	1%	13%	31%	Taghipour and Mosaferi 2009
Iran	H	3		30%	14%	4%	1%	19%	18%	Rabeie et al. 2012
Iran	H	14		41%	17%	4%	5%	8%	21%	Bazrafshan and Mostafa-poor 2010
Italy	NA			47%		7%	2%	33%		Wajs et al. 2019
Jordan	H	21		27%	11%	10%	5%	38%		Abdulla et al. 2008
Korea	HF	478		47%			6%	37%		Jang et al. 2006
Kuwait	PH	2		18%	11%	10%	9%	32%	12%	Hamoda et al. 2005

Libya	UH/PC/ HC/PrH/ GH	2/2/2/4	24%	9%	8%	1%	20%	38%	Sawalem et al. 2009
Mauri-tius	NH/GH/ PrC	1/1/1	24%	8%	3%		24,00 %	13%	Mohee 2005
Pakistan	CH	1	57%		11,00%		3,00 %		Munir et al. 2014
Pales-tine	GH	3	30%	2%	8%	2%	33%	25%	Al-Khatib et al. 2019
Taiwan	UH	1	50%	10%			16%	22%	Li and Jeng 1993

EH=educational hospital, GH=General Hospital, AH=Anticancer Hospital, MSWAC=Medical Solid Waste Average Composition, HF=Healthcare facilities, MH=Maternity Hospital, CH=Children's Hospital, PH=Public Hospital, PC=Private clinic, PrH=Private Hospital, HC=Health Center, NH=National hospital, NA=not available, UH=University Hospital, M.H.=Military Hospital, GoH=Governmental Hospital.

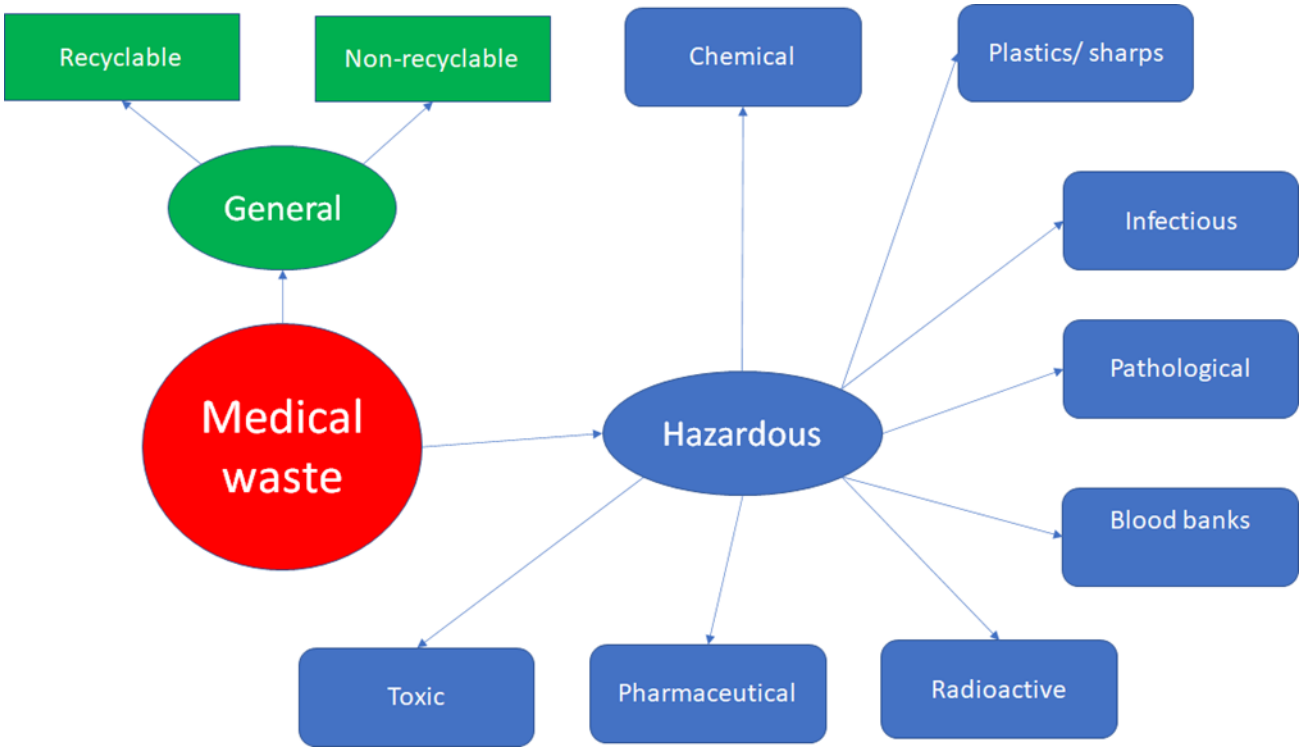


Figure 1. A schematic diagram on MW categories/types.

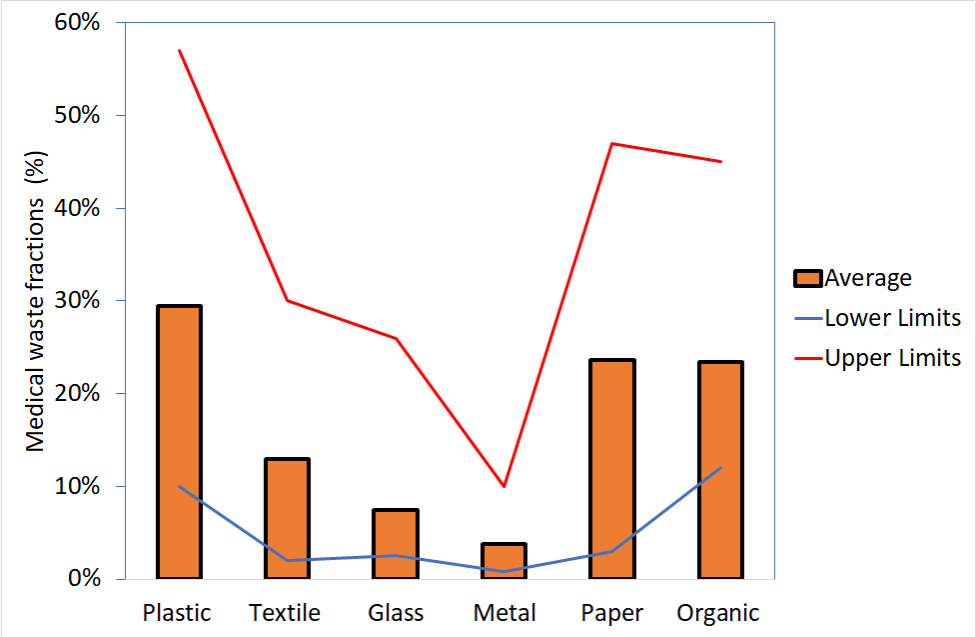


Figure 2. verage values, upper limits, and lower limits of the main MW fractions.

Chapter 2. Medical Waste treatment technologies

2.1. MW handling

According to Liu et al. (2021), MWM is significant for the medical practitioners who handle various MWTT, such as incineration, chemical disinfection, microwave, autoclaving and reverse polymerization. These MWTT need to consider health hazards, social acceptance, environmental impact, and economical cost. To select the most suitable technology, a multi-criteria decision-making framework is needed, involving several factors. Consequently, a new Pythagorean fuzzy-based decision-making methodology was developed to provide a fuzzy combined solution framework to rank the alternatives.

According to Zhao et al. (2021), MW has increased due to the COVID-19 pandemic and has stimulated high interest in MW treatment/disposal. Additionally, the recovery of MW energy is mandatory in order to achieve higher heating value (HHV). The use of sustainable, economical, and environmentally friendly MWTTs, achieving higher energy recovery, is essential for the harmless disposal of MW.

Kenny and Priyadarshini (2021) examined the current MWD methods and their environmental and public health effects, finding that MWTTs have a high dependence on basic, low-tech MWTTs while there is lack of use of 'greener' MWTTs due to cost, access, and feasibility. Moreover, MWTTs depends on the development level of the country. Bucătaru et al. (2021), found a correlation between the different forms of MWM in different countries, which effects the processes for the collection, storage, and destruction of the HMW. Letho et al. (2021), found that understanding and practice of MWM by the healthcare workers decreases the lack of proper application of the National guidelines.

The main target of healthcare facilities is to decrease health associated problems caused by improper MWM as well as to prevent these potential consequences for the health of the community. Healthcare services create waste with a higher potential for injury and infection than any other form of waste. MWM is presented as an integral part of healthcare services, since inadequate MWM can be harmful and thus counteract the benefits offered by these services (Ndejjo et al. 2015).

MWM has provoked an intense scientific dialogue on MWG because of the healthcare activities of which the inappropriate management affects animals and plants, the community, and the environment. This concern is growing based on the development of healthcare facilities number, as population growth reduces, in many cases, the space for MWD. Moreover, MWG by changes in human behaviors related to lifestyle, such as the increasing use of disposables, threatens natural resources and human beings. In addition, exposure because of environmental contamination by laboratory and pharmaceutical waste leads to disease in animals and humans (Kwikiriza et al. 2019). Additionally, MW may have a long-term effect on human health and environment, through underground water sources polluted by untreated MW either buried in the ground or drained in the domestic sewer system. Many researchers emphasize that many individuals can be infected either through infected people or MW or through affected animals, surface water or air, ground water, or contamination of soil (Udin et al. 2014).

Low-income countries usually apply poor MWM policies, because of very limited resources. Therefore, in these countries, MW is disposed of and handled as domestic waste, posing a significant threat to the waste workers' health, the public health and the environment (Ndejjo et al. 2015). Scarce data are currently available regarding a commonly accepted system for effective hospital waste management, especially in rural or privately funded hospitals in poorer countries. However, the waste generation rate in private and public hospitals in Kampala, Uganda, varies substantially based on patients' condition, giving emphasis to items carried into the ward, visitors number, and type or state of condition (Kwikiriza et al. 2019).

The WHO has emphasized the significance of acting with discretion on hospital waste handling. In an assessment conducted in 22 different developing nations and based on the outcome, it was found that 18–64% of the healthcare units included in the study did not use proper waste management practices. Mentzelou et al. (2009) reported that the most essential factors that are underestimated or neglected during the process of MWM in Greece are: assessing the required activation, human resource training, and use of proper waste collection and, in many cases, disposal of raw collection materials. The main characteristics that determine waste handling are (i) benefits and profits from shelling and recycling as well as zero incidents, (ii) cost of transportation, storage, and the process of deposit, (iii) locations and nature for waste recycling, disposal, and storage, (iv) name and registered places of companies of the recycling and disposal firms,

(iv) human resource activities, (v) date of transport, (vi) origin and nature of the waste, and (vii) weight. The lack of standardized and commonly accepted guidelines for MWM in both developed and underdeveloped countries as well as the poor data in the literature create the need for greater awareness and collaboration among research centers and authorities. The fact that only a few researchers have studied the subject of MW creates the need for greater awareness.

2.2. MW collection, separation and transportation

Govindan et al. (2021) developed a bi-objective mixed-integer linear programming software for MWM during the COVID-19 outbreak by simultaneously minimizing the total costs and risks of exposure of the population to contamination. They included the location routing problem, the vehicle scheduling/failure, the time window-based green vehicle routing problem, the split delivery, the people risk, and the load-dependent consumption of the fuel to process both infectious and non-infectious MW.

Healthcare facilities and hospitals usually provide laboratories, clinics, and surgery with color-coded bins or bags for collection and disposition of waste. Different colors (usually yellow, red, or green) denote different waste stream or types of waste. Unfortunately, no global or even local coloring system has been imposed by international or national health authorities, so that others rely on the MW source for sorting, and others use pathogenicity risk to determine the MWD stream (Mühlich et al. 2003). Lack of standardization results in ineffective MW sorting so that healthcare workers may mistakenly, dispose of objects in the infectious MW stream and cause unnecessary infectious MWG (Almuneef 2003). It is well established that most of the hospital MWG is noninfectious and could thus be treated as usual household waste in either rubbish dumps or recycling programs (Garcia 1999). Improper MW sorting has considerable consequences, as there is a substantial cost premium to dispose of infectious waste. United States authorities have estimated that the cost of disposing of infectious waste is much higher when compared to the cost of disposing of typical non-infectious waste ($0.79 /kg vs $0.12/kg) (Lee et al. 2004). Additional data from the UK confirms that the cost of disposing of typical infectious waste is comparable to that reported in the USA (£0.45/kg). Disposal of MW must also be completed in a way that ensures minimal, or ideally no, accidental exposure of workers responsible for handling such infectious items. Healthcare facilities are legally responsible for ensuring that their personnel

do not touch the infectious MW placed in the appropriate waste bin. However, even in countries with strict legal frameworks such as the UK, there are reports suggesting that not only the guidelines do not provide sufficient precautions to avoid contact with HMW, but also safe practices are often ignored (Blenkharn 2005). The legislative incompetence regarding poor MWM practices may result in infection and disease of either patients or workers, and thus legal liability for the hospital administration. The EPA has decided that the disease-causing potential of MW is grater at the point of generation. This finding further imposes the need for developing safeguards in healthcare facilities. According to the EPA suggestions, "safe-guarding of infectious MW within healthcare facilities ought to be made a top waste management priority" (Gusca et al. 2015).

Tirkolaee and Aydın (2021) applied an MWM model for collection and transportation, by (i) using heuristic and meta-heuristic algorithms, (ii) considering 'planning cycles', (iii) applying uncertainty and forecasting techniques such as robust optimization, and (iv) integrating emerging technologies.

MW is usually transported from the place it is produced to the treatment site that is located either within the healthcare facility or in a central offsite establishment. The most frequently used methods of treatment are incineration, autoclaving, and microwaving, which result in the residual ash. This final product is usually transported to the landfill for disposal (Tata and Beone 1995) by a contractor who has the responsibility of the final disposition at the appropriate waste depot (Hantoko et al. 2021). This third part collects the waste from central points and transports it safely to the final disposal facility. Unfortunately, there are several drawbacks to this procedure since there are legal gaps concerning the responsibilities of the contractors, who can earn a lot of money by skipping the legislation and inappropriately disposing of MW. The cost of disposal has been estimated at GBP 450/ton in the UK and USD 790/ton in the USA (Lee et al. 2004, Blenkharn 2005) so the third-party firms have a strong incentive to dispose of MW with minimal or no treatment in less expensive ways and not to follow the guidelines for proper transport to the final treatment facility for sterilization. A rigid MW tracking system is a prerequisite to avoid or at least minimize illegal dumping, which can otherwise become chronic and result in increased risk for public health and the environment because of pathogen release (Brichard 2002). Weak legislation can also provide third parties with another possibility of pocketing money; they can resell

items that should be disposed of, e.g., sharps on the black market for re-use. Recovered and non-sterile sharps represent significant risk for patients' infection via spread of blood-borne pathogens (Solberg 2009). Reusing or recycling of potentially infectious MW is not allowed regardless of the use of a sterilization process (Zhao et al. 2008).

2.3. Treatment and disposal technologies for MW

The quantity of used personal protective equipment, e.g., facemasks, gloves etc., and the spread of infectious MW from hospitals, healthcare facilities, and quarantined households increased due to the COVID-19 pandemic. Moreover, food and plastic waste increased. As a result, MWT facilities became overburdened, necessitating the use of alternative treatment and disposals such as co-disposal of MW in municipal solid waste incinerator, industrial furnaces, cement kilns, and deep burial, to increase handling capacity. Consequently, the operation of such facilities must be upgraded for MW handling according to the limitations as regards COVID-19 (Hantoko et al. 2021). Appropriate MWM practices improve landfill operations and prevent the spread of COVID-19, while on-site treatment and temporary storage helps to reduce the MWM problem (Das et al. 2021). The WHO official statement that 'at present, there are practically not environmentally friendly, low-cost options, for safe disposal of infectious wastes' (WHO 2020) reflects the major concern of the international community regarding the safety of disposal at a reasonable cost and with minimal environmental burden (Brichard 2002). The proper collection mechanisms for infectious MW using trained workers and specific containers, and in situ pretreatment is necessary (WHO 2020). In the western world, 50% of MW is incinerated, 30% is autoclaved, and the rest is treated by alternative processes (Zhao et al. 2008, Rutala et al. 1992). Incineration raises several concerns regarding air pollution and formation of toxic polychlorinated dibenzo-p dioxins (dioxins) and polychlorinated dibenzofurans (furans) following combustion (Lee et al. 2004). The need for alternative treatment methods that safely kill any pathogens is unquestionable and has resulted in the use of autoclaving and microwaving, among others.

2.4. Sanitary landfill technology

Ozbay et al. (2021) investigated landfills' damaging effects on the environment and public health and the necessity for appropriate MWM practices to eliminate these

effects. Insufficient landfill management causes problems regarding leachate collection and landfill gas generation, resulting in increased groundwater and air pollution. These drawbacks of using landfills as the major disposal technique lead to the effects of improper landfill management on the environment and human health. According to Hereher et al. (2020), the most appropriate way to utilize the disposal of solid MW is landfilling in developing countries. Siting the possible location for landfills signifies one of the most popular functions of Geographic Information Systems (GIS). They applied this methodology to find suitable locations for landfills in Muscat Governorate, Oman. Moreover, Nik Ab Rahim et al. (2021) reported that extensive non-engineered landfilling procedures in developing countries have increased environmental matters, while using a sanitary landfill seems unfeasible because of economic powerlessness. In Peninsular Malaysia, they investigated the viability of a sanitary landfill plan by incorporating its environmental issues into the plan assessment while at the same time using three policy-related procedures. Kareem et al. (2021) studied a landfill where MWD is a complex problem associated with several aspects and guidelines. They found that the best sanitary landfill site in the case of An-Najaf city was defined by applying a GIS using eight suitable criteria, i.e., urban area, roads, soil types, rivers, elevation, wind, slope, and religious/archaeological/historical places.

The sanitary landfill procedure is the oldest method for MWD that is still used in several low-income countries. It is based on the decomposition of waste into harmless substances through long-term storage in the landfill's ground. Unfortunately, this way of disposal is accompanied by the infiltration of various toxic substances such as pathogens and radioactive materials so that these substances will seriously affect the environment and humans. An effective way of overcoming this issue is to select the sanitary landfill and to ensure that the anti-seepage system is covered with a layer of clay, high-density polyethylene, and other materials as well as with the appropriate landfill gas collection system and output pipelines. Moreover, local authorities must take into consideration the nature of the MW, the geological conditions, the climate, and the distance from the nearest civil landscape to license the construction of such facilities. The sanitary landfill method is cheap, easy to install, but there are several limitations to its use, such as the need for disinfection and reduction in the waste before landfilling, the necessity to inhabit a large terrestrial area, and the production of lots of harmful gases as well as the production of O2 and H2. In addition, periodic and long-

term monitoring of soil and groundwater is required Abd El-Salam, 2010, Diaz et al. 2005).

2.5. High temperature incineration technology

Ilyas et al. (2020) investigated numerous disinfection technologies for COVID-19 MW handling, separation, and collection, following several physical and chemical treatment stages. Additionally, policy guidelines on the international initiatives for COVID-19 MWM with the use of various disinfection processes were examined and some examples were successfully applied to decrease health and environmental consequences.

Incineration of MW is a universal method of disposition for all kinds of waste that is suitable for all kinds of infectious waste. Incineration employs a high-temperature combustion range (800–1200 ◦C), which completely kills the pathogen while also burning 90% of the organics (Data et al. 2018, Wang et al. 2020). Moreover, deep oxidation of the waste under high temperature flame results in the drying and incineration of the substances and their conversion into a residue mass that can be treated as a harmless material and gas. The application of this method is effective since the waste mainly consists of hydrocarbons with a high calorific value that can be easily destroyed during incineration (Windfeld and Brooks 2015).

There are some restrictions in the use of this approach, such as the requirement for constant high furnace temperature, high oxygen mixing, appropriate turbulence and mixing degree of the equipment, maintenance of moisture content, sufficient gas residence time, periodical maintenance of the equipment, and finally, sufficient gas residence time and control of the final flue gas. The volume and weight of the final product are significantly reduced, the waste is destroyed, the method can be effectively applied to all types of waste regardless of waste volume, it is stable, standardized, does not need specific expertise, the produced heat energy is recyclable, the MW is well disinfected/sterilized, and the pollutants are removed. No method is ideal, so there are also several disadvantages in incineration such as air pollution, production of toxic and carcinogenic substances (dioxins, polychlorinated biphenyls, polycyclic aromatic compounds) and harmful gases (HCl, HF, SO2) (Jang 2011, Karagiannidis et al. 2010, Voudrias 2016).

According to the Greek regulations, incineration is appropriate for the treatment of HMW, and substantially decreases their weight and volume. The degree of automation and flexibility is high, while the community acceptance of an incineration facility is reduced compared to alternative treatment technologies (Voudrias 2016, Voudrias and Graikos 2014). Incineration that is performed by burning at very high temperature ensures sterilization and produces a residual ash with minimal volume that is buried in a landfill facility (Lee and Huffman 1996). The main disadvantage of incineration process is the release of toxic gas into the atmosphere. The main toxins that are released during incineration are dioxins, furans, and mercury (Insa et al. 2010). Dioxins are organic compounds that consist of two benzene rings connected by two oxygen atoms, containing 4–8 chlorines that substitute hydrogen atoms of the. Their half-life is 7 to 11 years which makes them very persistent, and they accumulate in the environment. Moreover, they are well known to be carcinogenic and are also associated with reproductive harm in humans (Schecter et al. 2006). The chemical structure of furans is similar to that of dioxins, with the only difference of one oxygen atom between the two benzene rings. Their toxic properties are significant. Mercury emissions that come from MW incineration account for 3–9% of total Hg emissions (Pacyna et al. 2006). The impact of atmospheric Hg emissions is serious for public health and the environment since Hg can accumulate in fatty tissue when inhaled. Additionally, they cause harm to the nervous, reproductive, and excretory systems (Wolfe et al. 1998). It is widely acknowledged that reducing dioxin emissions through fabric filters and complete combustion at temperatures above 800 ◦C are the most effective methods (Kilgroe 1996).

2.6. High temperature pyrolysis technology

A more technologically advanced technology for MWT is pyrolysis which operates at 540–830 °C, including plasma/ laser-based/oxidation and induction-based pyrolysis (Datta et al. 2018). High-temperature pyrolysis technology heats the organic components of MW under oxygen-free or -depleted conditions and breaks their chemical bonds, so that the organic compounds with high molecular weight are transformed into combustible liquid and gases. The pyrolysis gas contains H2, CH4, CO, CO2 and other hydrocarbons and volatile organic substances. The temperature and time of pyrolysis are substantial while the MW humidity and particle size have a significant impact on the procedure efficiency. The molecular structure of the MW defines the pyrolysis procedure. The high temperature pyrolysis technology of MW burns cracked gas and coke. The combustible gas can be used as fuel for the pyrolysis, decreasing its operating cost compared to common incineration. Pyrolysis requires a reduced air coefficient, the flue gas is reduced, and the flue gas purification apparatus is reduced, resulting in a lower overall cost compared the usual incineration. During incineration, dioxins are easily produced because of the high oxygen combustion. Pyrolysis can have lack of oxygen and removal of acid gas, which decreases the dioxins creation comparing to the conventional incineration. High-temperature pyrolysis MW can directly feed the furnace (Xu et al. 2020).

In combination with harmless municipal solid waste, pyrolysis treatment technology of MW offers a different approach for the diversification of MWT. Pyrolysis technology has a high energy recovery rate, minimal secondary pollution, and sufficient economics. An equipment set for MW pyrolysis process with simultaneous gas retrieval, almost fully automated, needs little area, conventional equipment's control, industrial function, little market changes, and strong marketing. As mentioned above, pyrolysis technology can use the created gas by the MW treatment to achieve energy circulation, decrease energy consumption, reduce processing costs, and achieve economic viability (Ilyas et al. 2020, Xu et al. 2020, Dharmaraj et al. 2021, Czajczynska et al. 2017, Khaskhachikh et al. 2021)

2.7. Medium temperature microwave technology

Microwave technology uses 177–540 ◦C for reverse polymerization due to high-energy microwaves for degradation of organic substances. Electromagnetic waves (wavelength 1 mm–1 m, frequency 300–3000 MHz) increase the internal energy by vibration/rubbing of molecules' bonds. N2 atmosphere prevents the combustion with

oxygen in contrast with high-temperature disinfection. The lower energy and temperature used herein reduce heat losses and avoid environmental pollution because of the nontoxic residue after the disinfection procedure. Specially designed microwave apparatus can inactivate SARSCoV-2 (Wang et al. 2020) and are appropriate for the on-site disinfection of COVID-19 MW. On-site disinfection prevents the risks of time consuming COVID-19 MW transportation. The microwave technology can be combined with autoclaving, with sterilization steam at 93–177 ◦C (Ilyas et al. 2020).

Microwaves (2450 MHz, 12.24 cm) destroy most of the microorganisms. MW water is quickly warmed, and the contagious elements are destroyed because of high temperature. The MW is fed into a shredder and smashed to little pieces. Then, it is moistened, moved to the microwave generators equipped irradiation chamber, and irradiated for 20 min. Finally, the pretreated MW is compacted in containers and joined with the municipal solid waste. The high costs, in combination with operation/maintenance costs eliminates the applicability in emerging nations. The development of comparable methods is occurring now. The cost of a system including a microwave treatment device with the ability to accept 250 kg/h of MW, and all its necessary equipment might cost around USD 500.000 (Diaz et al. 2005, Voudrias 2016, Zimmermann 2017).

2.8. Pressure steam sterilization technology

The technique is based on the processing of crushed MW at 121 ◦C for 20 min under 100 kPa. The steam that is generated at these conditions penetrates the waste and subsequently denatures and inactivates microbial proteins. The residual waste can then be either incinerated or sent to a landfill. Although this method can be used for the processing of contaminated clothing, syringes, and microbial culture equipment it is not applicable to tissues and carcasses. The effectiveness of this cheap/low operating cost technique depends on the temperature, time, and quantity of the MW. The main limitation of the technique is the volume of the product is comparable to that of the initial waste. There are toxic emissions and several toxic chemicals, such as formaldehyde, phenol, and mercury cannot be processed (Windfeld and Brooks 2015, Jang et al. 2006, Karagiannidis et al. 2010, Voudrias 2016). The pressure steam sterilization technology public acceptance in Greece is higher compared to that of the incineration technology (Mantzaras and Voudrias 2017).

High-pressure steam sterilization technology and incineration technology are appropriate for all kinds of MW. High-pressure steam sterilization technology needs a

large, dedicated autoclave, and generates volatile toxic chemicals. Chemical disinfection is frequently used to disinfect liquid waste, but it is complicated to decontaminate big amounts of waste. Incineration technology has a broad range of treatments and can efficiently wipe out contagious and toxic substances in MW. However, to generate toxic substances such as dioxins, suitable furnace types and improved flue gas purification devices must be applied. However, new technologies like microwave sterilization, dry heat treatment, plasma spray gun, radiation treatment, electrothermal deactivation, liquid alloy treatment, and glass paste curing are infrequently used in China, and they are also undeveloped technologies abroad and are hard to employ. Comparatively speaking, the high temperature pyrolysis has a broad range of functions, a great recovery ratio of pyrolysis, less toxic waste such as dioxins, and great economic advantages.

2.9. Chemical disinfection technology

The chemical disinfection technologies are appropriate for COVID-19 MW after mechanical shredding (Ilyas et al. 2020). The air is passed through a high efficiency filter to absorb shredding aerosol. The crushed MW is further mixed with chemical disinfectants and remains under negative pressure. The organics are degraded, and the infectious microbes are inactivated or destroyed. No residual hazards are left when using chemical disinfectants because they kill both microorganisms and bacterial spores (Wang et al. 2020). The chemical disinfection of COVID-19 MW can be divided into chlorine- and nonchlorine-based technologies (Duarte and Santana 2020). The chemical disinfection process relies on the use of chemical agents, such as ozone, peracetic acid, sodium hypochlorite, glutaraldehyde, etc., for disinfection of the MW. This approach is effective not only for liquid waste, but also the municipal solid waste treatment. The effectiveness of the procedure depends mainly on the type and biological characteristics of microorganisms, the level of contamination, the chemical composition, temperature, quantity, and concentration of the disinfectant as well as the exposure time, the pH, and the mixing requirements for every kind of waste. Alternatively, chemical waste can be ground prior to exposure to the disinfectant, ensuring by this method adequate exposure of the chemicals to the particles of the MW and easy disposal of the residue. Residual liquid products can be disposed of in the domestic sewer system and solid products in the landfill (Voudrias 2016).

In addition, grinding of MW with a rotary crushing apparatus can be applied before exposing it to a liquid chemical disinfectant, ensuring maximum contact and thus sufficient exposure of the chemicals to particles of the MW and aiding easy disposal of any residues. The liquids produced during the process go into the sewer system, and the solid residues are discarded in landfills. Chemical processing is a simple, cheap, and convenient process that results in rapid disinfection and good deodorization of the final product, high waste volume reduction with no production of waste liquid or gas waste. The main disadvantages of the method are the toxicity of the disinfectants for humans and the strict requirements for temperature setting and pH monitoring. The method is not recommended for radioactive MW from chemotherapy and volatiles (Diaz et al. 2005). The use of chemicals for disinfection is expected to achieve public acceptance in Greece (Voudrias 2016).

In addition, grinding of MW with a rotary crushing apparatus can be applied before exposing it to a liquid chemical disinfectant, ensuring maximum contact and thus sufficient exposure of the chemicals to particles of the MW and aiding easy disposal of any residues. The liquids produced during the process go into the sewer system, and the solid residues are discarded in landfills. Chemical processing is a simple, cheap, and convenient process that results in rapid disinfection and good deodorization of the final product, high waste volume reduction with no production of waste liquid or gas waste. The main disadvantages of the method are the toxicity of the disinfectants for humans and the strict requirements for temperature setting and pH monitoring. The method is not recommended for radioactive MW from chemotherapy therapy and volatiles (Diaz et al. 2005).

2.10. Plasma technology

Plasma technology is a relatively new method based on the use of a gas cloud that is generated by the ionization of an inert gas. This cloud mainly consists of many positively charged, negatively charged, and neutral particles. When electric current passes through this system, the gas is ionized and generates an instant glow discharge that reaches a very high temperature (up to 3000 ◦C) and results in rapid dehydration and heating of the waste. The product of this procedure is a mixture of combustible

gases such as H2, CO and alkanes. Following a second combustion, all pathogenic microorganisms in the waste are destroyed. The final product can be safely disposed of in a landfill. The effectiveness of this expensive technique depends on the power of the instrumentation since the higher energy output, facilitates the temperature conversion. This method is appropriate for all forms of MW since no harmful products are released, the end volume is significantly reduced, and the heat energy that is produced can be recycled (Cai and Du 2021, Aboughaly et al. 2020, Erdogan and Yilmazoglu 2021).

2.11 Torrefaction technology

Torrefaction is the process by which biomass is depolymerized. A considerable amount of time is demanded to achieve the degree of depolymerization of the biomass as desired. Time and temperature are the two parameters that define the degree of torrefaction. Torrefaction time applied can also be found in literature as reactor residence time (Cahyanti 2020). Reactor residence time start at the point biomass reaches (200°C). Before that, degradation of biomass has not taken place yet (Giakoumakis and Sidiras 2017, Giakoumakis et al. 2018). Torrefaction can be applied on medical cotton waste (MCW) which is a cellulose-based material structured by around 95% cellulose (Kale et al. 2018, Emam et al. 2015). There are many treatment methods used to valorize such materials. MCW is usually infected and hazardous. It should be sterilized to remove any pathogenic or infectious substances that might be harmful. To accomplish this, it is placed in an autoclave at 121 °C, 15 bar, for 15 minutes to destroy any infectious bacteria or possible viruses. This method is efficient for the sanitization of MCW (Sheriteh et al. 2010, Sajjanshetty et al. 2014). Torrefaction can work as a sterilization method to MCW.

2.11.1. Torrefaction reactors

a) Fixed bed reactor

Fixed bed reactor is the simplest and most common type that accepts all kinds of biomass. Raw biomass is consumed into the reactor. It uses its furnace for drying

and torrefaction. When the reactor cools down, biomass that has been torrefied is gathered at the end of the process. (Ribeiro et al., 2018).

b) Moving bed reactor

In this case, solid biomass particles are consumed from the peak of a vertical reactor and the particles are dried and torrefied until they reach the exit founded at the lowest position of this reactor (Dhungana et al., 2012). Produced gases and vapors, via torrefaction, are recirculated and instantly produce heat to biomass.

c) Microwave reactor

In such reactors, water included in biomass absorbs energy that is given by microwaves created from electromagnetic waves. This phenomenon concludes in the production of heat energy which benefits the achievement of torrefaction (Wang et al., 2012; Thorn et al., 2011).

d) Rotary drum reactor

Biomass flows during this process through the reactor entrance into a rotating reactor. The product leaves the reactor through its exit. Direct or indirect heat is given to achieve the demanded temperatures with superheated steam or exhaust gases created from combustion of volatile gases formed when torrefaction occurs (Rodrigues et al. 2018).

e) Fluidized bed reactor

Fluidized bed reactor has a unique way of working. Blowing of inert gases coming from the lowest point of the reactor causing pretreated (mill or pulverization) biomass to float and create fluid on a certain reactors' level, named bed height. This serves the purpose of constituting uniform temperature distribution through the bed (Li et al., 2012). To reach the demanded temperature, it is needed to achieve velocity greater than the minimum fluidization velocity.

2.11.2 Solid yield and energy yield.

These terms refer to the conversion of mass and chemical energy to biochar when biomass is pretreated. Solid yield or mass yield is identified as the portion of the initial organic component of biomass that is transformed to solid char (Nanou et al., 2016). Biomass including higher hemicellulose percentages concludes to smaller yield while biomass when hemicellulose is in low percentages yield is higher (Chew and Doshi, 2011). Hemicellulose decomposition is mainly accomplished in torrefaction where all the hemicellulose decomposes prior to 300 ^{o}C, which concludes to low mass yield.

2.11.3. Recent data

There have been numerous experimental studies through years that give access to data of torrefied biomass. HHV is usually the measured result. Table 4 provides some examples of different biomass types and the relation of their HHV in raw and torrefied form.

Table 4. Raw/torrefied biomass HHV

Biomass	Temperature (^{0}C)	Time (min)	HHV (MJ/kg)		Increase	Reference
			Raw	Torrefied		
Corncob	300	30	18.7	28.1	50%	Tian et al. 2020
Corn stalk digest	300	30	15.3	21.6	41%	Zhang et al. 2019
Eucalyptus tree residues	300	60	18.1	23.5	30%	Cardona et al. 2019
Stem wood	300	60	19.8	23.6	19%	Wang et al. 2018
Wheat straw	300	30	17.5	22.5	29%	Bai et al. 2018
Sugarcane bagasse	300	60	16.5	24	45%	Kanwal et al. 2019
Pine wood chips	300	20	19.4	23%	18%	Alvarez et al. 2018
Cotton stalk	300	60	18.2	24.7	36%	Budde et al. 2018
oil palm fronds	300	30	22.5	29.2	30%	Lau et al. 2018
Stump	300	60	19.5	23.4	20%	Wang et al. 2018
Spruce	280	50	18.3	21.5	17%	Sarker et al. 2021
Pine	280	50	18.7	22.1	18%	Sarker et al. 2021
Bark	300	60	19.5	24.3	25%	Negi et al. 2020
Energy sor-ghum	300	30	17.3	23.6	36%	Negi et al. 2020

2.11.3. Other Applications

a) Co-firing and combustion

Industrial facilities like pulverized coal boilers could use fuel performed by torrefied biomass for firing or co-firing with coal (Li et al. 2012, Panahi et al. 2019). This could be a great help in cutting down the net CO_2 emissions and provide a greener solution to this industry (Agar et al. 2012). Chen et al. (2012) simulated the above procedure in a pulverized coal boiler. The considered torrefied biomass proportions were 0% (coal only), 25%, 50%, 75%, and 100% on a thermal basis. Firing 100% torrefied biomass in the boiler, didn't affect the efficiency and fluctuation in boiler load.

b) Gasification

Biomass, through gasification, is transformed into gas in an oxygen-lack environment. H_2 and CO are the main products (Chen et al. 2013, He et al. 2019). The use of torrefied biomass can improve the gasification efficiency since it has higher heating value and less volatile content than raw biomass. Nevertheless, tar byproduct can also be reduced. (Chen 2015)

c) Pyrolysis

Torrefaction could efficiently replace pyrolysis as a pretreatment method for bio-oil production (Chen et al. 2015, Chen et al. 2018). Bio-oils generated from torrefied biomass pyrolysis has lower humidity and superior carbon content compared to raw biomass pyrolysis (Meng et al. 2012). Bu et al. (2018) found that co-pyrolysis of low-density polyethylene (LDPE) and torrefied rice straw by microwave heating produced bio-oils with smaller humidity, and the major bio-oil components were phenols, ketones, hydrocarbons, esters, and alcohols.

d) Ironmaking

6.7% of the global CO_2 emissions are produced by iron and steel industry. Nevertheless, these industries require about 20% of the total industrial energy demand (Mousa et al.

2016). The above created the need of reducing emissions and energy demands of such industries. (Suopajärvi et al. 2014). Through torrefaction, biomass could become a coal substitute and reduce the extreme use of fossil fuels. This could make processes like iron ore agglomeration, metallurgical coke production, and pulverized coal injection less harmful (Ubando et al. 2019).

e) Adsorbent for pollutants

Nowadays, biochar is considered as a "green", sustainable inorganic and organic pollutant remover (Gwenzi et al. 2017, Wang et al. 2019). On top of that, using biochar to adsorb pollutants is much cheaper compared to typical adsorbents with greater price (Gan et al. 2018). Physicochemical specifications of biochar, like surface, pore size, and surface functional chemistry, play a major part in its adsorption performance (Gwenzi et al. 2017, Li et al. 2019).

2.12. Acid and enzymatic hydrolysis technology

2.12.1. Acid hydrolysis

Acid hydrolysis is a common technology widely used to achieve the transformation of biomass into monosaccharides. Some of the major acids used for hydrolysis are HCl, H_2SO_4, HNO_3, etc. This technology concludes in a greater sugar yield than other methods used for the same reason. It also provides good reproducibility (Chen 2015). Although acid hydrolysis creates a high sugar yield, it also creates a considerable volume of degradation products like furfural, hydroxymethylfurfural, formic acid and levulinic acid. To minimize the degradation products, parameters such as the type of acid, pH, temperature, and time must be chosen appropriately. The acid hydrolysis technology can be applied to MCW for fermentable to bioethanol sugars production. Enzymatic hydrolysis can be used as a second step during this process (Giakoumakis et al. 2021a).

One of the most trending applications nowadays is the use of acid hydrolysis as a pretreatment to produce nanocrystals from eucalyptus kraft pulp. Wang et al. (2020) produced functional and thermostable cellulose nanocrystals (CNCs). The acid hydrolysis system was created with H_2SO_4 (5-10%) and acetic acid (70-90%) which can be

easily recovered. Cellulose pulp was hydrolyzed at 80°C for some hours. CNCs were obtained. They were rod shaped and had length between 150 and 500 nm and diameter of 5-20 nm in high yield (Y_{max}=81%). The produced nanocrystals were highly, thermally, and dispersedly, stable in both phases, organic and aqueous.

Cheng et al. (2020), examined a simplistic and fast method to extract carboxylated cellulose nanocrystals (CCNCs). They used on-step hydrolysis procedure, using mixed acid system of sulfuric acid (SA) and nitric acid (H2SO4/HNO3). The surface hydroxyl groups on CNCs could be transformed into carboxyl sets effectively after 30 min treatment by launching HNO_3 as oxidizer. The reaction happened at 80 °C. The produced CCNCs were rod molded, had length of 186 ± 13nm and diameter of 9 ± 3 nm. More significantly, the CCNCs indicated brilliant dispersibility in water and some organic solvents due to the presence of negative carboxyl groups, which was advantage for their supporting applications and developing new applications by further surface functionalization.

Zhang et al. (2020), used the lemon (Citrus limon) seeds as waste to be utilized and extract CNCs by SA hydrolysis (S-LSCNC), ammonium persulfate oxidation (A-LSCNC) and TEMPO oxidation (T-LSCNC). The results were promising and showed that all CNCs retained cellulose Iβ structure and got a decent dispersion irrespective of extraction processes.

Wang et al. (2021) examined the production of CNCs. The experiments were carried out through acid hydrolysis using sulfuric and formic acid. SA (5–10 wt%) enhanced the hydrolysis effectiveness of formic acid (65–80 wt%), thus, very effective formulation of CNCs up to 70.65%. CNCs were rod shaped with high crystallinity.

Pandi et al. (2021) synthesized CNCs from cotton using ultrasound-assisted acid hydrolysis. Produced CNCs surface was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). X-ray diffraction (XRD) was used to study structural characteristics. The size of crystallites was 10–50 nm using XRD data, and the typical particle size was 221 nm, via PSD analysis.

Nevertheless, there are still many other applications found in modern use of acid hydrolysis as a pretreatment. Liu et al. (2022), established a kinetic model of biomass-

derived disaccharide hydrolysis over solid acid: A case study on hierarchically porous niobium phosphate.

Mendez-Montealvo et al. (2022), examined how long-term acid hydrolysis affect the progression of the crystalline and double-helical form shifts on achira starch. Crystallinity reduced from 36.6 to 21.1% within 3 days but improved to 27.0% after 15 days. Baruah et al. (2022), used banana agrowastes, to enhance their enzymatic digestibility of banana peduncle cellulose. He resulted in 81% cellulose recovery at optimal conditions.

Table 5 provides data of some experiments that used acid hydrolysis as a pretreatment method for certain reasons which are displayed as well.

Table 5. Acid Hydrolysis conditions and purposes

Biomass	Temperature (0C)	Time (min)	Catalyst	Results	Reference
bleached eucalyptus kraft pulp	80	300	H_2SO_4 (5-10%) and acetic acid (70-90%)	CNC production	Wang et al. 2020
microcrystalline cellulose	80	30	H_2SO_4/HNO3	CNC production	Cheng et al. 2020
citrus limon	45	90	H_2SO_4 64% w/w	CNC production	Zhang et al. 2020
bleached eucalyptus kraft pulp	80	180	H_2SO_4/HCOOH	CNC production	Wang et al. 2021
cotton	60	240	H_2SO_4 50%	CNC production	Pandi et al. 2021
disaccharides	100	360	solid acid	reaction efficiency of saccharide hydrolysis	Liu et al. 2022
achira starch	25	43200	HCl 7,5%	progression of the crystalline and double-helical form shifts	Mendez-Montealvo et al. 2022
lignocellulosic biomass	100-240	-	H_2SO_4 0-1,8%	development of a generalized severity parameter	Abatzoglou et al. 1992
populus tremuloides	125-145		0.2-1.7 w/w% SO2	combine severity parameter	Chum et al. 1990
barley straw	100	180-300	HCl 1%	saccharification	Sidiras and Koukios 1989

wheat straw	240	82	H_2O	saccharification	Sidiras et al. 2011
cellulose	170-190	40	H_2SO_4 0,4-1,6%	sugars decomposition	Saeman 1945

CNC= cellulose nanocrystals

2.12.2 Enzymatic hydrolysis and digestibility improvement pretreatments

Enzymatic hydrolysis, through cellulases, transforms cellulose into fermentable reducing sugars, which are converted by yeasts or bacteria to ethanol (Sun and Cheng 2002, Dimos et al. 2019). This process is a multistep reaction that occurs in a heterogeneous system. Insoluble cellulose initially separated into solid-liquid phase via endoglucanases and exoglucanases/cellobiohydrolases. As a next step, glucose is produced from β-glucosidase (Andric et al. 2010) through halfway product hydrolysis in the liquid phase. Such products are short cellulo-oligosaccharides and cellobiose. Enzymolysis, as a process, is cheaper than acid or alkaline hydrolysis since it occurs in moderate conditions and avoids corrosion (Duff and Murray 1996). Hydrolyzed cellulases may be produced by bacteria or fungi. Cellulosic Enzymatic hydrolysis is a three-step procedure: (i) adsorption of cellulases to the surface of the cellulose, (ii) hydrolysis of cellulose to glucose, and (iii) desorption of cellulases (Yang et al. 2011). Substrate concentration plays a critical part on the amount of yield and initial rate of enzymatic hydrolysis of cellulose. When substrate levels are low, there is need of increase of its concentration to expand yield and reaction rate of the hydrolysis (Cheung and Anderson 1997).

High concentration enzyme usage with the supplementation of β-glucosidases during hydrolysis, with simultaneous reduce of sugars during hydrolysis by ultrafiltration or simultaneous saccharification and fermentation, is among the major methods that reduce the inhibition of hydrolysis (Giakoumakis et al. 2021) Moreover, optimized high solids loading enzymatic hydrolysis/fermentation of cotton dust was achieved by Vignesh and Chandraraj (2021) using surfactant as additive.

Besides the above mentioned, the use of enzymatic hydrolysis for improving digestibility of cellulosic and lignocellulosic materials has been studied by numerous researchers extensively.

Ríos-González et al. (2021) compared 2 different two step enzymatic hydrolysis of agave. The first had as first step acid hydrolysis assisted by microwaves and the second assisted by ultrasound. The results showed that microwave assisted acid hydrolysis first step improved enzymatic hydrolysis comparing to ultrasound assisted acid hydrolysis since it removed more hemicelluloses and produced more glucose. Darus et al. (2022) managed to enhance enzymatic hydrolysis of oil palm empty fruit bunch using peracetic-SA pretreatment. The enhanced product had 77% enzymatic digestibility.

Wu et al. (2021) used intermittent ball milling to maximize lignocellulosic biomass conversion to glucose through enzymatic hydrolysis. Glucose production increased from 66.5% to 84.7% after ball milling lasted for 24 hours. Zhang et al. (2022), produced xylo-oligosaccharides and glucose via mechanical-hydrothermal pretreatment, as a greener approach. The glucose yield reached 92.6%. Dorleku et al. (2022), examined enzymatic hydrolysis of cassava peels without chemical or hydrothermal pretreatment using response surface optimization. The glucose recovery reached 94.8% at the optimal conditions.

Besides that, there are many more applications that can be found nowadays and show the benefits caused by enzymatic hydrolysis. Banvillet et al. (2021) produced cellulose nanofibrils from eucalyptus fibers using alkaline treatment combined with enzymatic hydrolysis NaOH assisted followed by pilot scale grinding. The enzymatic hydrolysis was improved. The crystallinity of the samples became higher. The nanofibrils produced had a rigid structure and their diameter ranged around 10-20 nm. Their length was between 150 to 350 nm.

Karnaouri et al. (2021) used isobutanol as organic solvent to efficiently delignify and fractionate beechwood using OxiOrganosolv method without using catalyst. Delignification reached 97%. Cellulose pulp recovery reached 92.6% w/w and it was used to synthesize optically pure D-lactic acid by L. delbrueckii sp. bulgaricus, as omega-3 fatty acids with high DHA via enzymatic hydrolysis.

Karnaouri et al. 2020 mild oxidative organosolv pretreatment occurred on beechwood pulps that resulted in 95% of lignin removal in a single stage and having a cellulose-rich solid fraction remaining. Enzymatic hydrolysis was used to test their ability to assist the growth and lipid accumulation of C. cohnii in batch and fed-batch cultures. Microalgae was successfully grown, and DHA went up to 43.5% of the cell's total lipids.

Araujo et al. (2021) used fish waste to simultaneously produce protein hydrolysates, collagen, and fish oil. The selected method or recovering these by products was enzymatic hydrolysis. 430 g of protein hydrolysate obtained in optimal conditions, followed by 10 g of collagen and 350 g of oil when processing 1 kg of fish waste. This method has an impact on fish waste volume as it reduces it around 75%.

Molina-Pĕnate (2022) contributed on providing green solutions and helping the improvement of circular economy by enzymatic hydrolyzing the organic fraction of municipal solid waste to examine the optimization of Bacillus thuringiensis biopesticide production through solid-state fermentation.

Giakoumakis et al. (2021a) optimized the production of fermentable sugar by acid pretreatment in combination with enzymatic saccharification of MCW and as a result prepare fermentable sugars for bioethanol production. The results showed a maximum conversion of cellulose to glucose of up to 95.6%.

Chapter 3. Energy, fuels, and materials produced by Medical Waste treatment

The MWTTs' energy recovery efficiencies (EREs) and impact on the environment can be estimated (Zhao et al. 2021). MWTTs such as incineration (rotary kiln or pyrolysis), plasma melting, and sterilization (steam or microwave), were studied using energy recovery analysis (ERA), LCA, and life cycle costing (LCC) methods. Moreover, incineration and sterilization MWTTs combined with co-incineration technologies gave improved energy recovery potential and improved environmental behavior. ERA estimated high ERE 83.4% for 'steam and microwave sterilization + incineration' and low ERE 19.2% for plasma melting. LCA results were encouraging for 'microwave sterilization + landfill' and discouraging for plasma melting. According to LCC pyrolysis incineration had the least economic cost, while plasma melting had the greatest. A low cost was found in the case of co-incineration of sterilized MW and municipal solid waste. These findings by Zhao et al. (2021) indicate that pyrolysis incineration is the most advantageous method regarding the economic aspect, while plasma melting has the highest operating cost. Now, heat from waste is not utilized efficiently enough because of the lack of appropriate methods of heat energy recovery. Northern China uses the MWTT-generated energy to provide heat. Southern China uses electrical power generation to utilize MWTT-produced heat, although limitations exist due to low power generation efficiency.

Dharmaraj et al. (2021) found that pyrolysis is a very effective technology for the degradation of COVID-19 MW. The plastic fraction of COVID-19 MW mainly contains polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), and polypropylene (PP). This fraction can be pyrolyzed to produce solid, liquid and gas fuels. Pyrolysis could potentially substitute incineration MWTT as regards the treatment of the MW plastic fraction produced due to the COVID-19 pandemic. It seems to be a less complicated and more environmentally friendly MWTT, resulting in valuable products such as solid and gas fuels. Efficient fuel productions need highly-organized MW collection and MW's plastic fraction separation.

Erdogan et al. (2021) used plasma gasification technology for H_2 and syngas production from MW. A 10-kW microwave air plasma generator was used, and the operating conditions were defined for maximum H_2 production. Although plasma gasification is a promising alternative low cost and sustainable technology for WMTT soon, further research is needed because of the lack of information about the harmful substances created during this procedure. The produced harmful substances levels must be below the official limits. Rasul et al. (2021) produced liquid fuel oil from the plastic fraction of MW by thermal cracking under oxidizing conditions at 500 ◦C for 40 min. The liquid fuel yield was 52% and HHV was 41.32 MJ/kg, i.e., comparable to commercial diesel. This pyrolytic MWTT produces clean fuels with a significant energy content, and, similarly to conventional pyrolysis, could substitute the incineration method. On the other hand, thermal cracking is not a mature MWTT, while it is not applied in large scale for MWT, and further pilot scale investigation is required. Similarly, Som et al. (2018) produced pyrolytic oil by thermal pyrolysis of plastic fraction MW at 200–300 ◦C. The pyrolytic oil's density was 840 kg/m^3, the HHV was 24.2 MJ/kg and the flash point is 39 ◦C. The maximum yield reached 53%, which is a promising result. Pyrolytic oil could substitute commercial diesel since they have similar HHV. They followed the trend of using pyrolysis as an alternative MWTT for the MW plastic fraction, which comes in complete agreement with Dharmaraj et al. (2021) research.

Shen et al. (2017) applied the co-hydrothermal carbonization technology to PVC containing MW mixed with lignocellulosic biomass (woodchips) and produced solid fuel in lab-scale and pilot-scale. In the pilot-scale application of the hydrothermal carbonization process, the presence of woodchips improved the dichlorination efficiency of MW. The low chlorine containing hydrochar product had better HHV (24.2 MJ/kg) and was appropriate to be used as a clean coal substitute, i.e., as an alternative fuel. It must be mentioned that with this lab scale autoclave reactor, lignocellulosic biomass has numerous uses for energy and fuel production. The combination of MW plastic fraction with lignocellulosic biomass is an ingenious idea, combining the MWM with lignocellulosic biomass evaluation and solid fuels production. Nevertheless, lignocellulosic biomass can be found in many MW categories, such as medical cotton (almost pure cellulose), cotton-based textiles (mostly cellulose) and paper (mainly cellulose with low amounts of lignin and hemicelluloses). Consequently, there are many

opportunities for further investigation on this method application in terms of energy recovery and large-scale economic feasibility.

Fang et al. (2020) pyrolyzed at 500oC mixed MW, produced liquid fuel (pyrolysis oil) and refined it by fractional condensation. The HHV of gas and solid products was 10995kcal/Nm3 and 5454 kcal/kg, respectively. This study contributes to the opinion that pyrolysis is a significantly suitable method for MWT. Nevertheless, in this case the pyrolysis feedstock included plastic, cotton, and glassware in considerable amounts. The results agree with the previous ones, giving pyrolysis strong fundamentals to become the most common MWTT soon.

Xin et al. (2019) applied the torrefaction technology to herbal medicine wastes, the results indicating that the torrefied herbal medicine wastes have great combustion properties and are appropriate to be used as solid fuels, e.g., for co-combustion with other fuels or for production of pellets. Torrefaction is not a common MWTT, and was used in lab scale, including limited MW categories, producing valuable products. However, it is a technology with great applicability in lignocellulosic biomass treatment and enhances the feedstock HHV. If MW separation were more structured, torrefaction might become a feasible MWTT probably in combination with lignocellulosic biomass treatment.

Giakoumakis et al. (2021a) optimized the production of fermentable sugar by acid pretreatment in combination with enzymatic saccharification of MCW. These sugars were useful for bioethanol production. This sequential procedure is a common method of treating lignocellulosic biomass. The novelty of that attempt was to engage in this procedure and examine its feasibility on MCW. There are strong limitations to this technology because MW separation methods need to be restructured to separate MCW. The results showed a maximum conversion of cellulose to glucose of up to 95.6%.

Li et al. (2019) and Gan and Peng (2020) concluded with similar results using cellulose as feedstock. Moreover, MCW could be separated from mixed MW and gathered with the rest of lignocellulosic MW (textiles, paper, etc.) to be treated appropriately in the future, to enforce the attempt to create recycled green fuels.

In addition, Giakoumakis and Sidiras (2020), used acid-pretreated recycled MCW as high HHV solid fuel. Moreover, they applied the torrefaction technology to

produce solid fuels with enhanced HHV from MCW (Giakoumakis and Sidiras 2017). The torrefied MCW can also be used as an adsorbent for industrial liquid waste cleaning. The results showed that the MCW substitute had similar properties to those of common commercial cotton, in both cases of torrefaction and acid hydrolysis treatment. Torrefaction, similarly, to acid hydrolysis, is a well-tested treatment method for biomass. There is space in the future for these technologies to become part of the MWTTs and contribute to a wide range of applications besides liquid/solid fuels and adsorbent production.

Dash et al. (2015) treated waste disposable syringes by thermolysis (pyrolysis at 400–550 ◦C) in a semi-batch reactor made up of stainless steel to produce liquid fuel. These syringes had bodies of polypropylene and pistons of high-density polyethylene. The produced pyrolysis oil had physical properties similar to a diesel or petrol mixture. So, pyrolysis is a highly efficient MWTT regarding MW plastic fraction treatment. This comes into total agreement with the literature that states that pyrolyzed MW plastic fraction produces value added fuels.

Baghdadi et al. (2017) produced a fibrous cellulose sulfate absorbent from MCW. This adsorbent was synthesized by sulfonation of MCW using CSA in DMF medium and was found appropriate for malachite green removal from aqueous solutions using batch and column apparatus.

Mohseni-Bandpei et al. (2019) produced char and oil by fast pyrolysis of HMW and found the formation of polycyclic aromatic hydrocarbons depending on the operating conditions. Fast pyrolysis technology can convert the MW to a useful hydrocarbon fuel. Fast pyrolysis is another pyrolytic application, for chemicals and fuel production based on MW mixtures containing plastic, paper, textiles, and glassware that demonstrates the pyrolysis advantages as a promising common MWTT.

Ismail and Talib (2016) produced biogas from industrial recycled MCW using thermophilic bio-digestion conditions to improve the biogas yield by 92%. Anaerobic digestion is a common technology for municipal waste organic fraction treatment, but not a conventional MWTT. The enhanced MW categorization/separation is expected to contribute to the path of energy and fuels production from cellulosic and lignocellulosic MW fractions such as MCW via several technologies such as anaerobic digestion, competitive to the traditional incinerating MWTTs.

Arcuri et al. (2014) constructed a bioanode, as the first step of an enzymatic fuel cell prototype fabrication appropriate, for energy production from blood and saliva in infectious MW. An enzymatic fuel cell could be an appropriate electrochemical device for the conversion of the stored chemical energy into electricity via oxidization of the substrate. This innovative laboratory scale MWT approach, must be considered far away from pilot scale application as a mature MWTT.

Alam et al. (2019) used a mixture of hydrothermally treated MW, pyrolytic plastic waste residue and biomass to produce low chlorine fuel pellets with 22 MJ/kg HHV which is like that of coal. Hydrothermally treated, disinfected MW, untreated and hydrothermally pretreated rice straw, fir sawdust, and pyrolyzed plastic waste were used for the preparation of thirteen types of fuel pellets. Most of the single feedstock made pellets failed to meet the specifications of the E.U. requirements, while most combined fuel pellets complied with the E.U. requirements. The pellets' chlorine and ash content caused a specification problem. On the other hand, the combined fuel pellets had a gross calorific value comparable to coal. In fact, the produced fuel pellets showed considerably higher O/C and H/C ratios compared to coal. Furthermore, mixed feedstock fuel pellets enhanced the fuel pellet quality. As a conclusion, low-chlorine clean lignocellulosic biomass fuel pellets of high gross calorific value can be successfully mixed with hydrothermally treated MW and pyrolytic plastic waste residue. This is a brilliant approach to combining three different kinds of pretreated waste, i.e., MW, plastic residue, and lignocellulosic biomass, in a common treatment process, i.e., pelletizing, for added value in solid fuel production.

Manegdeg et al. (2020) used a pyrolizer-Rankine cycle for MWT and electricity production from MW. They found that by employing a pyrolizer–Rankine cycle power plant to produce electricity from MW is feasible and profitable 400% in a 5-year cycle. Furthermore, Bujak (2015) used a rotary kiln for MW thermal treatment and found that from 180 kg/h of MW, the produced heat flux was 835.6 kW, the total thermal efficiency was 66.8%, the CO2 emissions were significantly reduced, and the project's

internal rate of return was 18.6%. This experiment lasted one month, providing sufficient information regarding economic, environmental, and energy production aspects. It was proven to be a cost-effective approach, with low daily greenhouse emissions and emissions well below average, while providing a significant amount of energy. It achieved significant on-site heat recovery during MW incineration. Moreover, he used an incinerator for MW (Bujak 2009), obtaining 6.6–8 kW/kg energy corresponding to 10–12 kg/kg of saturated steam, while 4.15 kW/kg heat flux was used as additional fuel. The incinerator's energy efficiency coefficient was 47–62%. Finally, he used systems for heat recovery from MW thermal treatment (Bujak 2015).

Swiechowski et al. (2021) used the torrefaction method to produce carbonized solid fuel from waste of medical peat. Torrefaction at 200–550 ◦C improved the peat waste HHV up to 21.3 MJ/kg compared to 19.0 MJ/kg of the untreated material. This was the first attempt to utilize torrefied medical peat, i.e., an innovative approach for lignocellulosic MW use on lab scale, showing the need for further investigation and upscaling of MW fractions torrefaction as an alternative MWTT. Chaiyat (2021) used an organic Rankine cycle in combination with an infectious MW incinerator for energy production and evaluated the system by energy, exergy, economic, and environmental analysis. The system produces 23.65 kWe while energy and exergy efficiency were only 0.91% and 0.89%, respectively. Further investigation is required, and many improvements must be made in concern of energy production and system efficiency improvement, since the hot fluid and hot water loops could be connected in one cycle.

In Table 6 are presented various MW treatment technologies and the produced energy, fuels, and materials potential. Moreover, Figure 3, is presenting a simplified schematic diagram of energy (heat and power), fuels (gas, liquid, solid) and materials (adsorbents) production from MW and MW fractions (plastic, cotton, blood, saliva) using various treatment technologies (acid hydrolysis, combined acid and enzymatic

hydrolysis, anaerobic digestion, enzymatic oxidation, hydrothermal treatment, incineration, pyrolysis, microwave or steam sterilization, plasma gasification/melting, sulfonation, and torrefaction).

Table 6. MW treatment technologies and energy/fuels/materials production.

Country	Material	Technology	Fuels/materials	Energy content	Energy /Recovery Efficiency	Reference
Bangladesh	plastic MW	Thermal cracking (Batch reactor)	Liquid 52%	41.3MJ/kg		Rasul et al. 2021
Bangladesh	plastic MW	Pyrolysis	Liquid	41.3 MJ/kg		Som et al. 2018
China	MW	Rotary kiln incineration			64%	Zhao et al. 2021
China	MW	Pyrolysis incineration			55%	Zhao et al. 2021
China	MW	Plasma melting			19%	Zhao et al. 2021
China	MW	Steam sterilization			83%	Zhao et al. 2021
China	MW	Microwave sterilization			84%	Zhao et al. 2021
China	MW	Incineration			30%	Zhao et al. 2008
China	MW	Autoclave			10%	Zhao et al. 2008
China	PVC MW	Hydrothermal carbonization	Hydrochar particles	24.2 MJ/kg		Shen et al. 2017
China	MW	Pyrolysis	Gas/liquid/solid	46 MJ/ Nm3, 37.6 MJ/kg, 22.8 MJ/kg		Fang et al. 2020
China	medicine herbal waste	Torrefaction	Solid	20.3 MJ/kg		Xin et al. 2019
Greece	cotton MW	Acid/enzymatic hydrolysis	Bioethanol/sugars			Giakoumakis et al. 2021
Greece	cotton MW	Torrefaction	Solid	20.1 MJ/kg		Giakoumakis and Sidiras 2017
Greece	cotton MW	Acid hydrolysis	Adsorbent			Giakoumkais and Sidiras 2020
Greece	cotton MW	Torrefaction	Adsorbent			Giakoumakis et al. 2018

India	Medical syringes	Pyrolysis	Gas 17%	42.5 MJ/kg		Dash et al. 2015
India	plastic MW (PET)	Pyrolysis	Liquid/gas			Dharmaraj et al. 2021
India	plastic MW (HDPE)	Pyrolysis	Liquid/gas			Dharmaraj et al. 2021
India	plastic MW (LDPE)	Pyrolysis	Gas/liquid/solid			Dharmaraj et al. 2021
India	plastic MW (PVC)	Pyrolysis	Liquid/gas			Dharmaraj et al. 2021
India	plastic MW (PP)	Pyrolysis	Gas/liquid/solid			Dharmaraj et al. 2021
India	plastic MW (PS)	Pyrolysis	Liquid/gas			Dharmaraj et al. 2021
Iran	cotton MW	Sulfonation	Adsorbent			Baghdadi et al. 2017
Iran	plastic MW	Pyrolysis	Solid 24% / gas 2.5%			Mohseni-Bandpei et al/ 2019
Iraq	cotton MW	Anaerobic digestion	Biogas 51.6 ml/g			Ismail and Talib 2016
Italy	Blood/saliva MW	Enzymatic oxidation	Electric energy			Arcuri et al. 2014
Korea	solid MW	Hydrothermal treatment	Pellets	28.3MJ/kg		Alam et al. 2019
Philippines	noninfectious MW	Pyrolysis, Rankine cycle		30 MJ/kg		Manegdeg 2020
Poland	MW	Rotary kiln incineration		25 MJ/kg		Bujak 2015
Poland	MW	Incineration			62%	Bujak 2009
Poland	MW	Incineration/Steam heat recovery system			80%	Bujak 2015
Poland	peat MW	Torrefaction	Solid	21.3 MJ/kg		Swiechowski et al. 2021
Russia	MW	Pyrolysis	Gas/solid			Chaiyat 2021
Spain	Plastic MW	Incineration		30.7 MJ/kg		Álvarez 2018

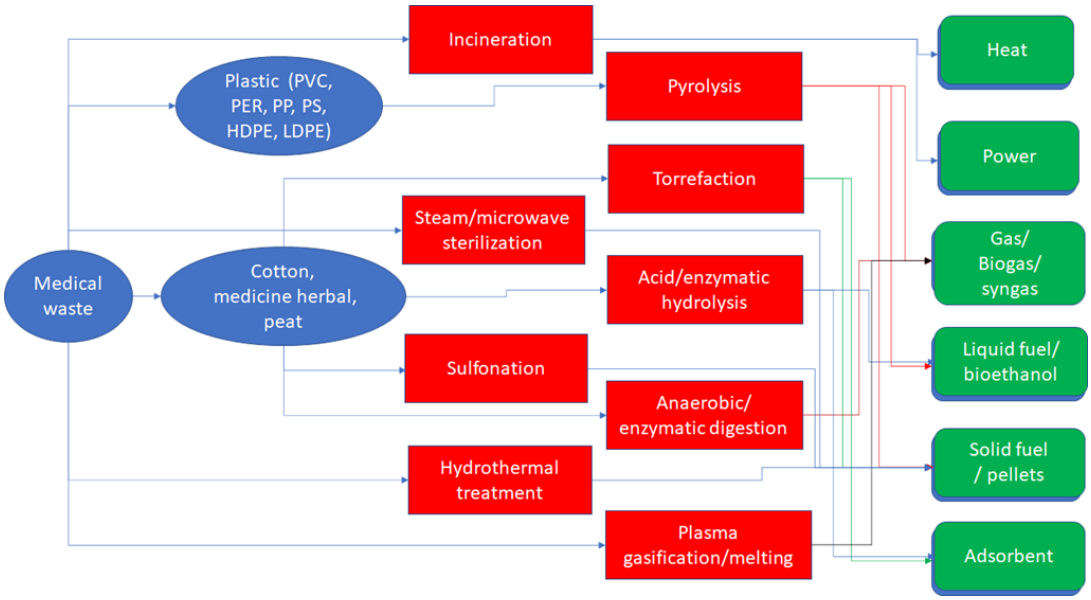


Figure 3. A schematic diagram on energy/fuels/materials production from MW and MW fractions via various treatment technologies

Chapter 4. Optimization treatment process limitations and economic feasibility

The limitations in terms of MWTTs processes optimization and economic feasibility must be considered as regards MWTTs development. Ökten et al. (2015) suggested the use of the best available techniques for MWT, mentioning that incineration seems to be the optimal option in terms of public health and environmental protection, but pollutes the air with dioxin, furan, and PCBs, due to incomplete plastics burning. On the other hand, comparing the economic feasibility of the converting, autoclaving, and ozonation MWTTs resulted that ozonation MWTT was the optimal from the economical point of view. Soares et al. (2013) used LCA and cost analysis as decision-making tools to define the MWTT with the best environmental performance, among (i) microwave, (ii) autoclave and (iii) lime disinfection technology, followed by transportation/landfilling.

Kargar et al. (2020) designed an efficient and reliable infectious MW reverse logistics network to control the spread of COVID-19. They achieved the minimization of costs and risks related to the network's operation, dealing with various infectious MWG healthcare facilities. They developed a linear programming model to minimize the total costs, the transportation risks, the infectious MWT risks and the maximum uncollected MW in healthcare facilities. Similarly, Govindan et al. (2021) developed a bi-objective mixed-integer linear programming model for MWM during the COVID-19 pandemic, by simultaneously minimizing the total costs and of the population's exposure to pollution risks. Additionally, He et al. (2021) used the operational flow of MW to optimize the automated MW sorting system problem, using a mixed-integer programming model for the MW assignment, presorting stations, and automated guided vehicles optimization.

Liu et al. (2021) proposed coordinating governments, hospitals, communities, and other departments in the MWD process, as well as developing guidelines for MWD

nationwide to deal with potential risks and optimize MWM systems using the green governance principle. Torkayesh et al. (2021) developed a novel multi-objective optimization model to assist the optimized decision-making by the MWG companies, considering the economic/environmental/social aspects of the sustainability concept. They aimed to minimize the transportation/processing/establishment costs, as well as the MW transportation environmental risks/emissions in combination with the maximization of job creation opportunities. They investigated the applicability and feasibility of an Improved Multi-Choice Goal Programing approach as regards multi-objective optimization model solving. Ghannadpour et al. (2021) used a self-adaptive evolutionary algorithm for triple bottom-line objective optimization of sustainable MW collection and routing.

Rolewicz-Kalinska (2016) focused on the logistic factors in an MWM system, considering current legal constraints, organizational factors, and economic aspects. An MWM system's structure must include the goals and constraints as regards their implementation in full scale. The sustainable function of an MWM system needs effective MW logistics and sense of balance among MWG locations and MWT services. Van Straten et al. (2021) investigated the applicability of the circular economy concept for recycling stainless-steel MW and reusing old medical instruments. They found that circularity gives a sustainable model for surgical MWM, with cost reduction and environmental advantages.

According to Yao et al. (2020), the solution to the complex relationships among stakeholders is to find the optimal locations of the MWD centers. They reduced risks and mitigated costs by optimizing the MWD centers location–allocation problem using a soft-path solution, i.e., a risk mitigation-oriented bilevel equilibrium optimization model employing the Stackelberg game behavior as regards local government and healthcare facilities.

Arun and Wang (2021) investigated the implementation of industry 4.0 to decrease procedural MW, considering the system/service/procedural/product hierarchical innovation levels. They found that industry 4.0 concept application contributes to a more efficient use of resources in the healthcare sector, but more research is required as regards its im-pact on the production of procedure-caused MW. Ranjbari et al. (2022) worked on the (i) mapping of the research and development on MW, (ii) identification of the research themes/trends, and (iii) development of a MWM research agenda within the circular economy transition and sustainable environmental concepts. They highlighted (a) MW minimization, sustainable management, and policymaking, (b) MW incineration and its environmental effects, (c) HMW management practices, and (d) MW handling and occupational safety and training. Chaerul et al. (2008) presented a planning model based on a trans-shipment goal programming approach optimizing the MW flow as regards multiple objectives under different priority structures/relative importance. They found that, when the MWM is biased toward a higher level of safety protection/infection control, they must compromise on cost/environmental pollution control. Nursetyowati et al. (2019) achieved the goal of choosing the most optimal alternative for hazardous MWM (reducing, sorting, storing, transporting, treatment, until burial), by conducting pair comparisons, with Expert Choice 11 software for the data processing. Finally, Mei et al. (2021) constructed a multi-period MW emergency reverse logistics network siting model to minimize the cost, the safety risk, and the time for the safe/quick MWD, considering bottlenecks of the existing facilities' disposal capacity due to the COVID-19 pandemic.

Recommendations for future research to possibly overcome the above limitations follow:

- More work can be done as regards the optimization of the MW collection and transportation processes, in combination with the location/allocation of MWT facilities installation problem.

- The categorization and separation of MW can be significantly improved, while the segregation of MW at the location where it is generated (hospitals, healthcare facili-ties, etc.) can substantially enhance the economic feasibility of the following steps as regards the MWTTs applied for energy, fuels, and materials production.
- The thermal energy produced during MWT via incineration and similar technologies can be utilized more efficiently by innovative recycling and recovering techniques while the environmental impact via thermal pollution will be eliminated.
- The determination of the HHV values and the physic/chemical properties of the specific MW fractions will facilitate the processes optimization and the costs minimization.
- MWTTs data from pilot and full scale MWT facilities can be collected to improve the accuracy and universality of the processes optimization results and the economic feasibility of the proposed applications.
- Further research is needed on the application of the MW plastic or lignocellulosic fraction (cotton, paper/cardboard, textiles) conversion technologies, focusing on the fuels/materials production.
- Finally, more work can be done on the co-processing of the MW plastic or lignocellulosic fraction (cotton/paper/cardboard/textiles) with similar fractions coming from municipal/ industrial solid waste (plastics or cotton /paper/ cardboard/ textiles/ wood) or agricultural (straw/ wood/ husks/ chaff/ cobs /bagasse can) and forest (wood/ bark/ leaves/ stems/ roots) lignocellulosic biomass, aiming at value added fuels/materials production technologies with low-cost (see Figure 4).

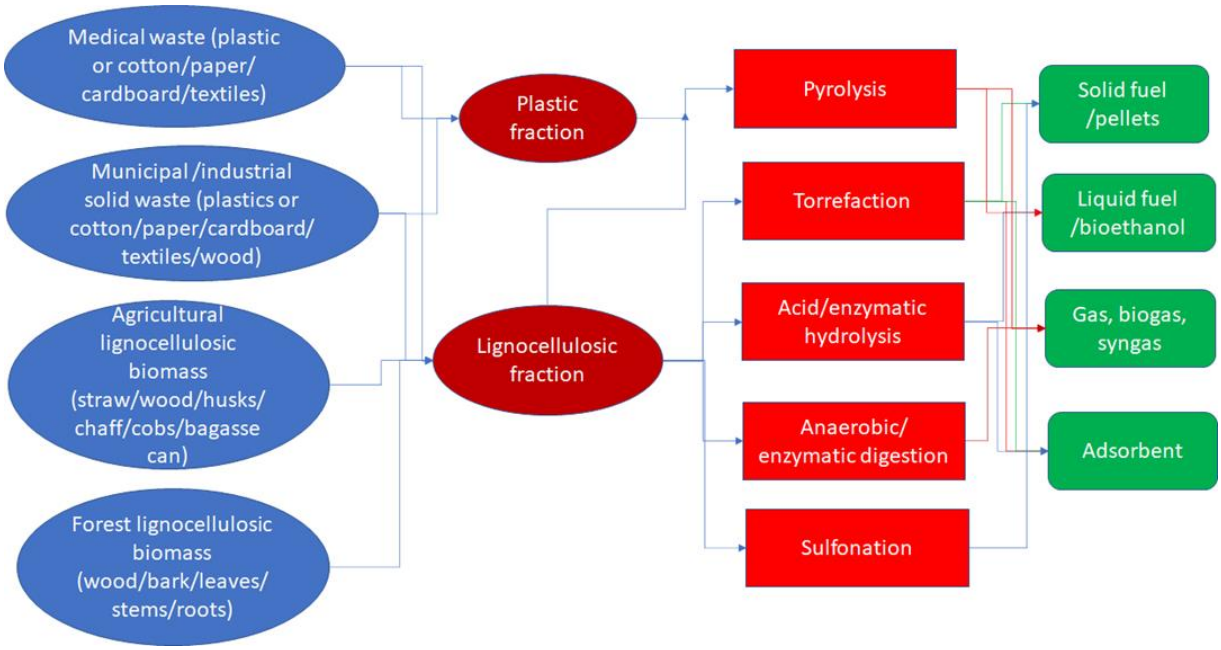


Figure 4. A schematic diagram on co-processing of the plastic/lignocellulosic fraction of MW with munici-pal/industrial solid waste fractions and/or agricultural/forest lignocellulosic biomass for fuels/materials

Chapter 5. Materials and methods

5.1. Medical cotton waste properties

Medical cotton used for the experiments of this study, was supplied from a medical equipment supplier (Xgermanos S.A., Greece), manufactured according to the standards of European Pharmacopoeia for quality, absorbency, trash content and average fiber length (not less than 10mm). The cotton batch was cut into small pieces by hand and placed into the batch reactor It was cut to achieve better homogeneity on the final product. Compositional analysis of the material was performed according to the protocols from National Renewable Energy Laboratory (NREL; Golden, CO, USA) (Sluiter et al. 2019) and showed that cotton consists of 95% wt. cellulose. The non-cellulosic compounds (5% wt.) consist of proteins, waxes, pectin, and inorganics (Hsieh 2007). To simulate the real MW infected with human blood, 20 ml of tested blood from healthy donor, provided by the Blood Bank of Attikon, University Hospital of Athens, Greece, was mixed with 50g of medical cotton to create medical cotton waste substitute (MCW-S).

5.2. Medical paper waste properties

The medical paper waste used was obtained from a medical facility, as a suitable source for full-scale/industrial applications. The moisture content of the material when received was 9% w/w; after manual cutting, the fraction with particle sizes between 5 and 10 mm was isolated. Compositional analysis of the raw material was performed according to the protocols from National Renewable Energy Laboratory (NREL; Golden, CO, USA) (Sluiter et al. 2019) and showed the following results, expressed in % w/w on a dry weight basis: 49.8% cellulose measured as glucan; 18.4 hemicelluloses (53% measured as manan, 47% measured as xylan); 8.3% Klason acid-insoluble lignin, 11.0% ash, and 12.5% extractives and other acid soluble components (e.g., acid soluble lignin etc.). Wastepaper composition is comparable to those reported at the literature [14,15].

5.3. Pretreatment Processes

5.3.1. Torrefaction

The torrefaction method applied to treat cotton occurred in a blast furnace. Cotton was put in a weighted porcelain capsule and inserted in the blast furnace. The blast furnace had starting temperature equal to 23ºC. The heat increase curve was from 23ºC up to 340ºC. Each experiment had different reaction time. Time was rising with 5 minutes step from 20 minutes to 50 minutes (20, 22,5, 25, 27,5, 30, 32,5, 35, 37,5 40, 42,5, 45, 47,5 50 minutes). There was not preheating time. When torrefaction process ended, the porcelain capsule was removed instantly from the blast furnace. It was put in a dryer for 15 minutes. The porcelain capsule was weighted to measure its tare. Cotton has been taken by hand and put in a weighted zip-lock bag for 24 hours. After 24 hours torrefied cottons' moisture was measured in the oven and the result was 3%. The heating conditions that applied in cottons' moisture measurement were 110ºC for 24 h in the oven.

5.3.2. Acid hydrolysis

Dilute acid pretreatment of medical cotton (MC) occurred in a 3.75 L Parr 4553 batch reactor (Parr Instrument Company, IL, US). Different sets of experiments were conducted to evaluate the effect of three different parameters: acid concentration, temperature, reaction time. 50 g of untreated cotton were mixed with the appropriate amount of water and H2SO4 to reach a final acid concentration between 11 – 35 mM and fed to the reactor. The total volume of the liquid phase was 2 L (liquid to solid ration, LSR equal to 40:1). Each experiment began at room temperature as a starting point and after heating up, the temperature reached the desired value that ranged between 180-220ºC. Experiments with temperature limit at 180ºC needed approximately 55 min to reach the desired temperature, with temperature 200ºC needed around 60 min and with temperature 220ºC needed around 70 min. Reaction time was set up at 0, 20 and 40 minutes; after that point, the reactor was cooled down until it reached room temperature. Cooling time, regardless the momentary temperature, was

around 50 minutes to achieve temperature equivalent to 30 ºC. Then, the solid fraction was separated from the liquid fraction through vacuum filtration. The solid fraction was washed until its pH become around 5.5 and then placed in the oven at 110 ºC for 24 h. The solid fraction recovery was determined gravimetrically. Compositional analysis of the pretreated fractions was performed according to the protocols from National Renewable Energy Laboratory (Sluiter et al. 2019).

5.3.3. Enzymatic hydrolysis

Enzymatic hydrolysis of untreated and pretreated solid fractions was performed in 2 mL Eppendorf tubes to assess different pretreatment conditions and correlate them with the saccharification efficiency. Cellic® CTec2 enzyme mixture from Novozymes A/S (Bagsværd, Denmark) was used for the hydrolysis experiments, at an enzyme loading of 20 mg/g biomass. All reactions took place in duplicates, at 50 ºC under agitation (1100 rpm), at an initial substrate concentration of 30 g/L, in 0.1 M citrate-phosphate buffer (pH 5.0) in presence of 0.02 % (w/v) NaN_3. At different time intervals (24 and 48 h), samples were taken, and enzyme was inactivated after boiling for 5 min. Then, the samples were centrifuged to remove all solids from residual cotton biomass, and the supernatant was filtered (0.45 μm pore size) and analyzed for the presence of glucose. The production of glucose was estimated by the determination of the % cellulose conversion = [glucose (g/L)] / [substrate (g/L) * cellulose content * 1.11] * 100, where 1.11 is the conversion factor of cellulose to glucose.

5.4. Severity factor

Since modeling of complex reaction systems is viable only when the sequence of all the elementary steps is known and just a few complex reactions have such conditions, there was a need of an alternative solution. Severity factor (SF) was introduced to cover this need and attempt to combine the effect of many operational variables. Severity factor was introduced as H factor from Vroom (1957) in his effort to simulate the complicated chemical reactions of the kraft pulping process. The H-factor was:

$$H\_\text{factor} = \int_0^t k\, dt = \int_0^t A \exp(-E_A/RT)dt \quad (1)$$

while k was provided by following equation of Arrhenius

$$k = A \exp(-E_A/RT)$$

(2)

where A stands for the frequency factor, E_A for activation energy, T for temperature in K, t for time and R for universal gas constant (UGC).

Based on H-factor, Brasch and Free (1965) created P-factor or 'reaction ordinate' for the prehydrolysis-kraft pulping of Pinus radiata. It was further evolved for steam-aqueous fractionation of lignocellulosics by Overend and Chornet (1987) and became:

$$P\_\text{factor} = [\exp((T - 100)/14.75]\cdot t \quad (3)$$

where T stands for temperature and t for time. P-factor combines the effect of time and temperature into a single ordinate. It can also be written as it can be seen below (Villegas and Gnansounou, 2008):

$$R_0 = [\exp((T - T_b)/\omega]\cdot t \quad (4)$$

where Tb is the base temperature (usually 100 ^oC) and

$$\omega = T_f^2 R/E_a \quad (5)$$

where T_f is the floor temperature, E_a is the activation energy and R is the UGC.

Abatzoglou et al. (1992) examined the phenomenological kinetics of multifaceted systems and established a 'general severity parameter for the lignocellulosic fractions. Chum et al. (1990) improved the P-factor in order to characterize the effect \ of acid or alkali catalyst in the batch reactors liquid phase, including the pH value in the equation as follows:

$$R'_0 = 10^{-pH}.t.\exp[(T - 100)/14.75] \quad (6)$$

or,

$$R_0^* = 10^{-pH} \cdot \int_0^t e^{\frac{T_\theta - 100}{14.75}} dt \qquad (6a)$$

This severity factor is commonly named as combined severity factor (CSF) and combines the outcome of three reaction conditions (temperature, time, and pH) into one ordinate, and has been used as it can be seen above or in logarithmic form (Villegas and Gnansounou, 2008, Weinwurm et al., 2017, Sidiras et al. 2011)

5.5. Design of Experiments – Response Surface Methodology

Response Surface Methodology (RSM) was chosen as a statistical method of analyzing the effect of different parameters on the pretreatment outcome, as it offers a large amount of data using limited number of experiments. Moreover, RSM enables the identification the interactions between the studied variables, thus it clearly depicts the effects of the parameters on the selected response. In this study, an experimental design was set up to evaluate the effect of three different parameters, namely temperature (A), residence time (B) and SA concentration (C) on the pretreatment efficiency. The Design Expert® 7.0 (Stat-Ease inc.) software was used to generate the different experimental conditions, by employing the Box-Behnken design option (Ferreira et al. 2007). Temperature was set at 180, 200 and 220 ^{o}C, residence time at 0, 20 and 40 min, while acid concentration was tested at 11, 22.5 and 35 mM. These parameter values were chosen based on preliminary experiments showing sufficient product yields. The Box-Behnken experimental design includes 15 experimental runs with different conditions and 3 experiments with identical parameters, identified as the central points of the design (200 ^{o}C, 20 min, and 22.5 mM). The effect of three variables A, B and C (time, temperature, and acid concentration, respectively) on the pretreatment efficiency was evaluated on the total cellulose recovery (% wt.) and the saccharification yield (expressed in % cellulose conversion to glucose).

The second-order polynomial model below shows how RSM fits the experimental responses using this equation:

$$y = a + a_1A + a_2B + a_3C + a_{11}A_2 + a_{22}B_2 + a_{33}C_2 + a_{12}AB + a_{13}AC + a_{23}BC \quad (7)$$

where y refers to the predicted response, namely % solid residue yield (% SRY), % glucose recovery in the solid fraction (% CRS) and enzymatic digestibility of cellulose to glucose (ED). The values for x_1, x_2 and x_3 represent the independent variables; a stand for the model constant and a_1, a_2 and a_3 are linear coefficients; a_{12}, a_{13} and a_{23} are cross product coefficients and a_{11}, a_{22} and a_{33} quadratic coefficients. The chosen model that was used to express the equation of all responses versus A, B and C was the quadratic model.

Optimization of the pretreatment parameters was also performed by the same software, with the aim to maximize all three response variables. The efficiency of the model was evaluated by estimation of the p-value, R^2 and standard error estimate (SEE). The optimal pretreatment condition leading to the maximal sugar yields (both in acid pretreatment and enzymatic digestion) was then applied to the MCW substitute (MCW-S) as substrate.

5.6. Analytical techniques

5.6.1. Quantitative saccharification

Quantitative saccharification (QS) is a commonly used method for controlling carbohydrate structure in lignocellulosic materials. QS requires a primary hydrolysis, which transforms polysaccharides (Pi) to oligosaccharides (Oi) applying great SA at modest temperatures, and a consequent hydrolysis, which transforms oligosaccharides (Oi) to monomeric sugars (Mi) using dilute acid at high temperatures. During the above processes, some carbohydrates degrade. Consequently, it is necessary to guarantee full conversion of polysaccharides to monosaccharides and prevent any significant degradation of monomeric carbohydrates.

The scientists at the NREL issued the first HPLC-based QS (M1) in 1996 based on Saeman's method. They used 3.00 mL of 72% w/w SA for 1h at 30 °C as the primary hydrolysis and diluted the hydrolysate to 4% w/w SA for 1h at 121 °C as the secondary

hydrolysis. The monomeric sugars after deactivation were calculated by HPLC with a carbohydrate assay column. Given that some polysaccharides were degraded throughout the whole process, the degradation degrees of five monomeric sugars (glucose, xylose, arabinose, galactose, and mannose) were expected for adjusting the degradation degrees of the polysaccharides.

In 2006, the researchers at NREL released a revised protocol (M2) with some modifications. They suggested (i) to abbreviate the primary hydrolysis time from 2 to 1h in order to cut sugar degradation and save measurement time and (ii) to calculate the correction coefficients of the controls—monomeric sugars only in the secondary hydrolysis because only a minor fraction of polysaccharides was transformed to monomeric sugars and an insignificant quantity of monomeric sugars was degraded in the main hydrolysis.

It is remarkable that the degradation degrees of polysaccharides are constantly lesser than those of monomeric sugars. When the degradation changes between polysaccharides and monomeric sugars are considerably big, polymeric carbohydrate composition defined by QS would be miscalculated.

Currently, there is an urgent need to develop rapid, high output analytic instrumental methods for the quick measurement of carbohydrate structure in lignocellulose, where QS is applied as a calibration method.

5.6.2. HPLC for sugar analysis

The compositional analysis, to determine the sugars of the solid fraction, was made in HPLC, by employing a liquid chromatography system (1260 Infinity II LC System, Agilent) equipped with an Aminex HPX-87H column (Biorad, U.S.) column, and the analysis was performed at 50 ^{o}C, with 0.3 g/L H_2SO_4 as the mobile phase and a flow rate of 0.6 ml/min. The liquid fraction was analyzed with to determine the presence of degradation products from the biomass-derived sugars, such as 5-(hydroxymethyl) furfural (5-HMF), as well as to estimate the total amount of sugars

(glucose, xylose, mannose) at the same HPLC, column and conditions. The glucose released after enzymatic saccharification was analyzed by employing the glucose oxidase/peroxidase (GOD/POD) assay (Raabo and Terkildsen 1960).

5.6.3. Higher Heating Value

A Parr 1341 Plain Jacket Calorimeter was used to take the necessary measurements. 0.5 g of cotton was put in the combustion vessel. The combustion vessel was charged with oxygen to 25 atmospheres. The calorimeter bucket was filled with 2000 mL of distilled water. The bucket was attached in the calorimeter and then the combustion vessel was put in the bucket. The two ignition lead wires were pushed into the terminal sockets on the bombs' head. The cover was set on the jacket and the stirrer was turned manually to ensure that runs freely. If it turns normally then the drive belt is slipped onto the pulleys and the motor is started. The Temperature indications were taken via the 6775 Parr Digital Thermometer each minute for 5 minutes to achieve equilibrium into the calorimeter. At the start of the sixth minute the ignition button was pushed, and temp measurements were taken each minute until the temperature was stable again. The rise of the temperature will be rapid during the first minutes and slow when we get close to the equilibrium. The diagram below shows how the temperature is affected from the stages explained above.

5.6.4. Spectrophotometric determination of methylene blue.

Spectrophotometry is a kind of electromagnetic spectroscopy related to the quantitative measuring of the reflection or transmission attributes of a substance as an act of wavelength. Spectrophotometers are used for such purposes, that calculate the depth of a light beam at several wavelengths. Radiation used in spectrophotometry is commonly ultraviolet, visible, and infrared. Current spectrophotometers can examine wide swaths of the electromagnetic spectrum such as x-ray, ultraviolet, visible, infrared, and/or microwave wavelengths.

A HACH DR6000 UV-VIS spectrophotometer at λ=664 nm was used for the experiments. The dye used to simulate the liquid waste was Methylene Blue (MB) with a chemical formula of C16H18ClN3S.xH2O and 373.9 10-3 kg mol-1 molecular weight. A stock solution was prepared by dissolving 5 g of MB in 25 L distilled water. The solution analyzed was created by 184ml of water and 16ml of MB stock solution. A magnetic stirrer was used sustain homogeneity. 1g of MCWS was included in the 100ml solution and 2 samples were taken every 5 minutes. The total reaction time was 90 minutes.

Chapter 6. Results & discussion

6.1. Torrefied medical cotton waste as methylene blue adsorbent

MCW was examined as a low-cost substitute of activated carbon for wastewater cleaning. The growing demand for efficient and low-cost treatment methods as well as the importance of adsorption has brought attention to low-cost adsorbents. The purpose of this study was to discover whether torrefied cotton is an efficient material regarding basic dyes removal like Methylene Blue (MB) from substitute wastewater. The conditions applied were a non-isothermal heating up to 340^{o}C for 20-50 minutes. The effect of torrefaction pretreatment conditions, i.e., reaction time and temperature on MB adsorption, was investigated using UV-visible spectrophotometry. The applicability of various adsorption kinetic models was studied herein.

Kinetic models' equations: The kinetics of adsorption of MB on untreated and torrefied medical cotton has been extensively studied using four kinetic equations. The widely used Lagergren equation (Lagergren 1898) is shown below:

$$q - q_t = q \cdot e^{-k \cdot t} \tag{8}$$

where q and q_t are the amounts of MB adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium time ($t \rightarrow \infty$) and adsorption time t, respectively, while k is the pseudo-first order rate constant for the adsorption process (in min^{-1}). Furthermore,

$$q = (C_0 - C_e)V / m \text{ and } q_t = (C_0 - C)V / m \tag{9}$$

where C, C_0, C_e are the concentrations of MB in the solution at time t, 0, and ∞, while m is the mass of the adsorbent used (in g), and V is the solution volume (in mL). Further modification of eq. (2) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - k \cdot t \tag{10}$$

The commonly used second-order kinetic model (Freundlich 1906) is the following:

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \tag{11}$$

or

$$q_t = q - \frac{1}{\frac{1}{q} + k_2 t} \tag{12}$$

The possibility of intra-particle diffusion was investigated by using the intra-particle diffusion model (Langmuir 1916):

$$q_t = c + k_p \cdot \sqrt{t} \tag{13}$$

where q_t is the total MB adsorbed at time t, c is a constant (mg g^{-1}) and k_p is the intra-particle diffusion rate constant in mg g^{-1} $min^{-0.5}$. Severity factor was used to as a combined parameter analytical tool to examine the kinetics of the above models.

Table 6.1. Severity factor values for the modification of torrefied medical cotton waste

R_0	$logR_0$	t(min)	SRY%
2.12E+07	7.33	20	75.87
6.87E+07	7.84	25	62.36
1.16E+08	8.07	30	49.49
1.61E+08	8.21	35	41.75
1.87E+08	8.27	40	40.20
1.93E+08	8.29	45	39.80
2.02E+08	8.31	50	39.41

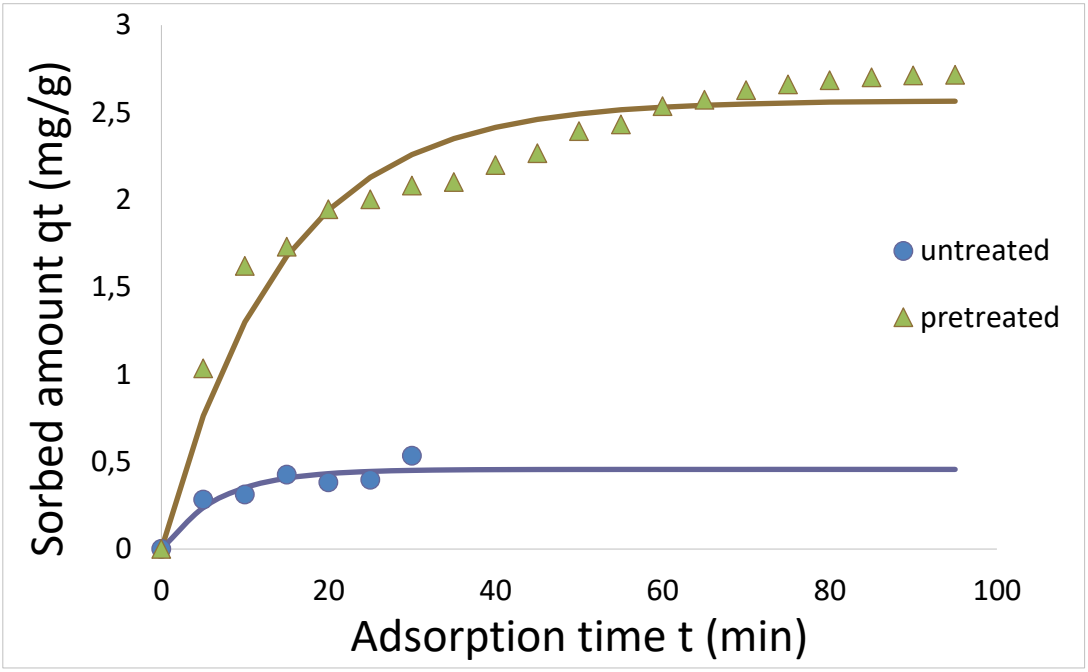


Figure 6.1. Lagergren kinetics for MB adsorption on untreated and pretreated torrefied cotton 50min.

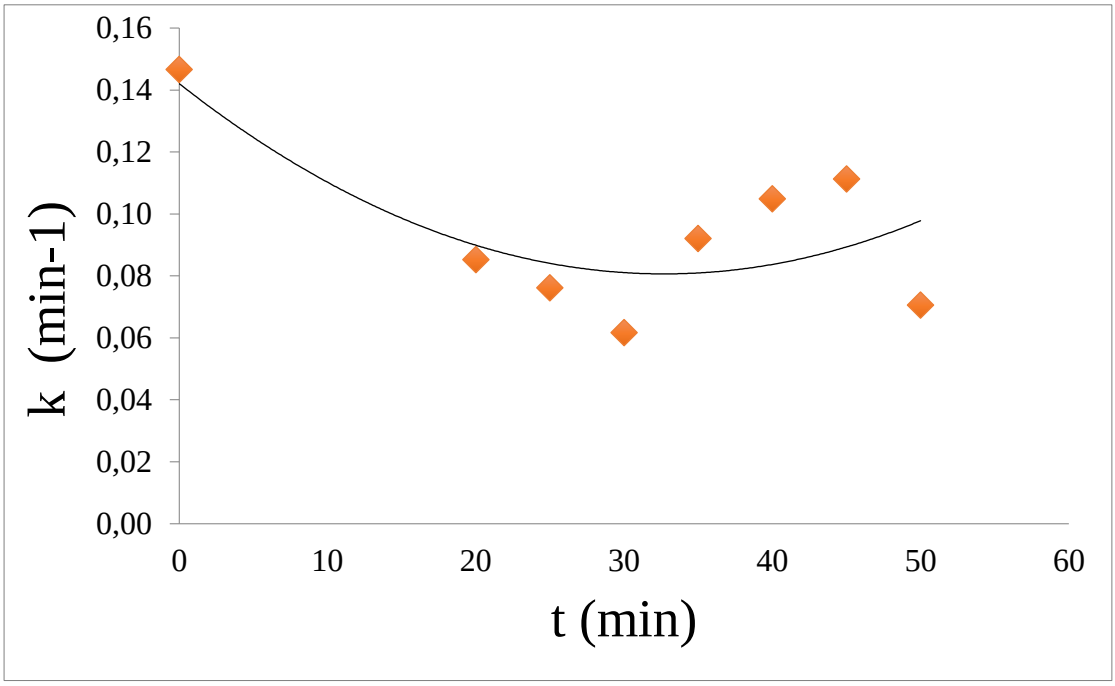


Figure 6.2. Pseudo-first order rate constant relevance to torrefaction time.

Table 6.1 provides information about the severity factor values and the solid residue yield of each experiment. The dependence of the Lagergren pseudo-first order kinetic model parameter k and q on untreated and modified, regarding the severity factor mentioned above is presented in Table 6.2.

In Fig. 6.1 the MB maximum amount adsorbed vs. untreated and torrefaction pretreated cotton (50 min) is presented. The torrefaction cotton adsorption capacity has improved in comparison to the untreated (see Fig.6.1).

Fig. 6.2 Depicts how k is affected to the time of each experiment. The designed curve is described from the following equation.:

$$y = 6E\text{-}05x2 - 0{,}0038x + 0{,}142 \quad (14)$$

and has coefficient of determination $R^2 = 0{,}5603$

In Table 6.2 all the parameters of the Lagergren pseudo-first are presented.

In Fig.6.3 according to the pseudo-second order kinetic is shown the MB maximum amount adsorbed vs. the untreated and torrefaction, at high pretreatment conditions, cotton. It is also given the MB maximum amount adsorbed vs. the untreated and the torrefaction pretreated cotton (50 min regarding the intra-particle kinetic model in Fig.6.5. In Table 6.3 all the parameters of the second-order kinetic model and in Table 6.4 the parameters of intra-particle diffusion model are presented.

Table 6.2. Parameters of Lagergren kinetic models of Methylene blue adsorption on untreated and pretreated cotton

Torrefaction Time t (min)	*k* (min^{-1})	*q* ($mg\ g^{-1}$)	*SEE*
0	0.147	0.456	0.056
20	0.085	2.29	0.058
25	0.076	2.30	0.092
30	0.062	2.36	0.044
35	0.092	2.22	0.132
40	0.105	2.16	0.177
45	0.111	2.50	0.167
50	0.071	2.57	0.165

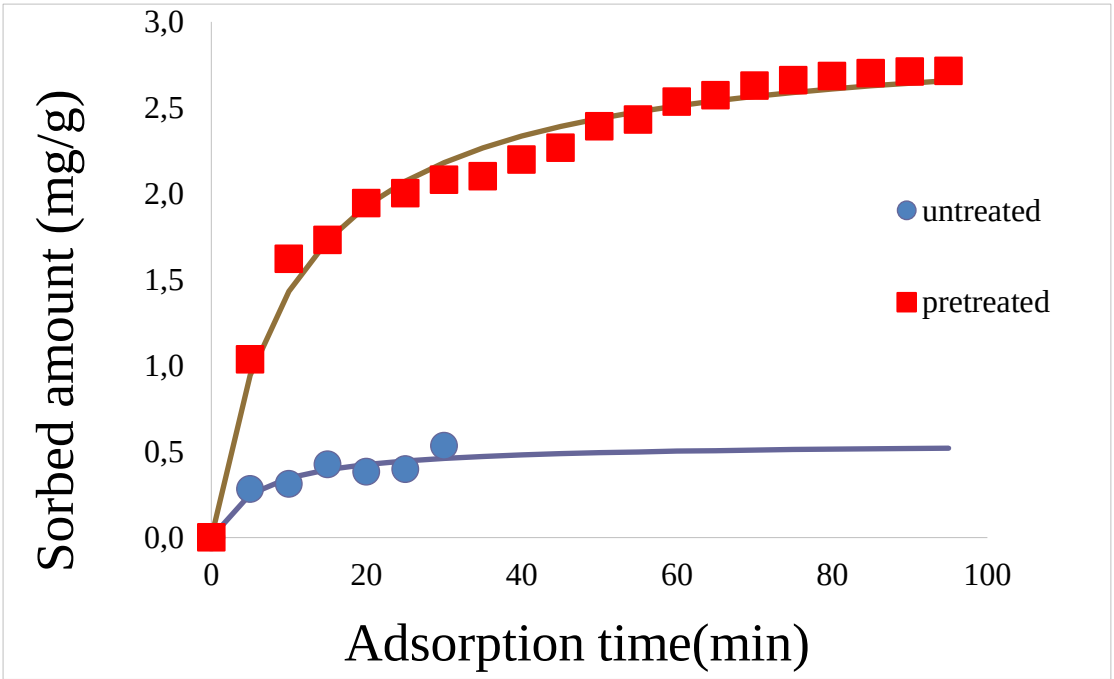


Figure 6.3. The pseudo-second-order adsorbent amount qt of MB on untreated and pretreated torrefied cotton 50min.

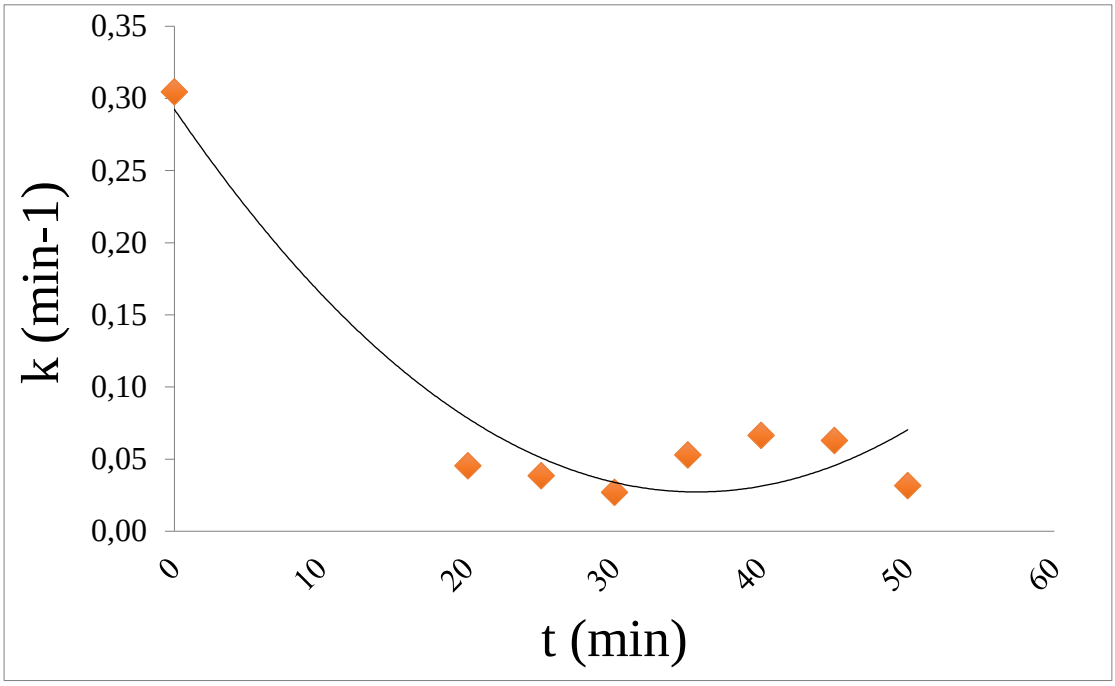


Figure 6.4. Pseudo-second order rate constant relevance to torrefaction time.

Fig. 6.4 Depicts how k is affected to the time of each experiment. The designed curve is described from the following equation.:

$$y = 0{,}0002x2 - 0{,}0149x + 0{,}2925 \quad (15)$$

and has coefficient of determination $R^2 = 0{,}9141$

Table 6.3. Parameters of pseudo-second-order kinetic model of Methylene blue adsorption on untreated and torrefied cotton.

Torrefaction Time t (min)	k_2 (g mg^{-1} min^{-1})	q (mg g^{-1})	*SEE*
Untreated	0.305	0.55	0.026
20	0.045	2.59	0.046
25	0.039	2.64	0.024
30	0.027	2.78	0.065
35	0.053	2.50	0.063
40	0.067	2.39	0.105
45	0.063	2.75	0.084
50	0.032	2.96	0.092

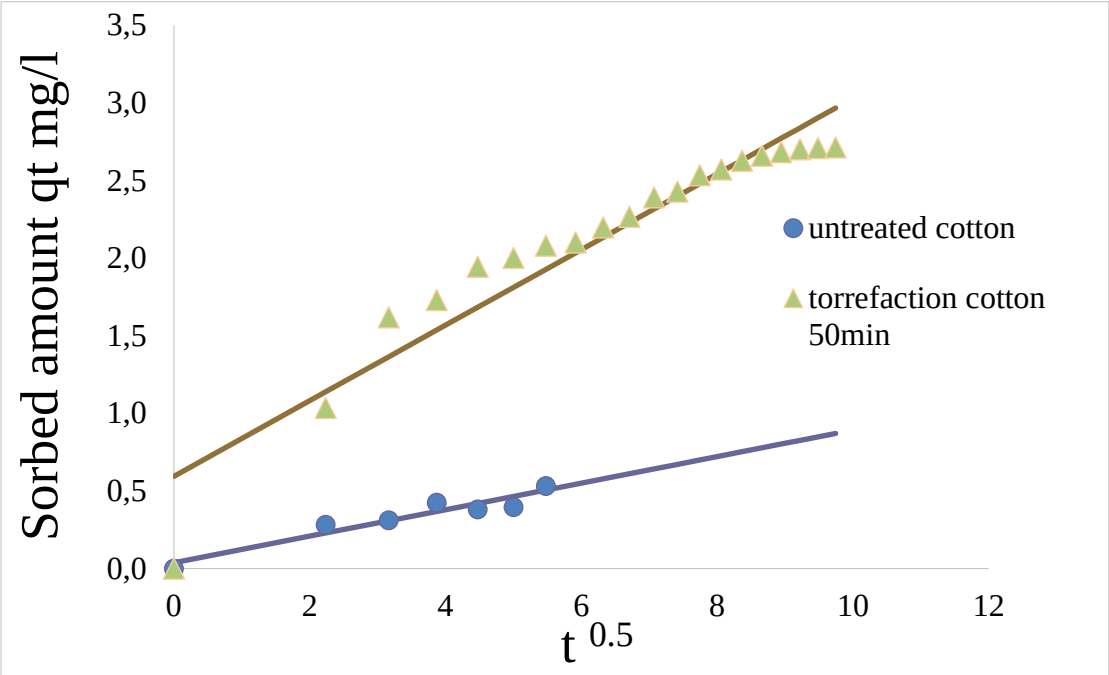


Figure 6.5. The intraparticle sorbed amount qt of MB on untreated and torrefied medical cotton waste.

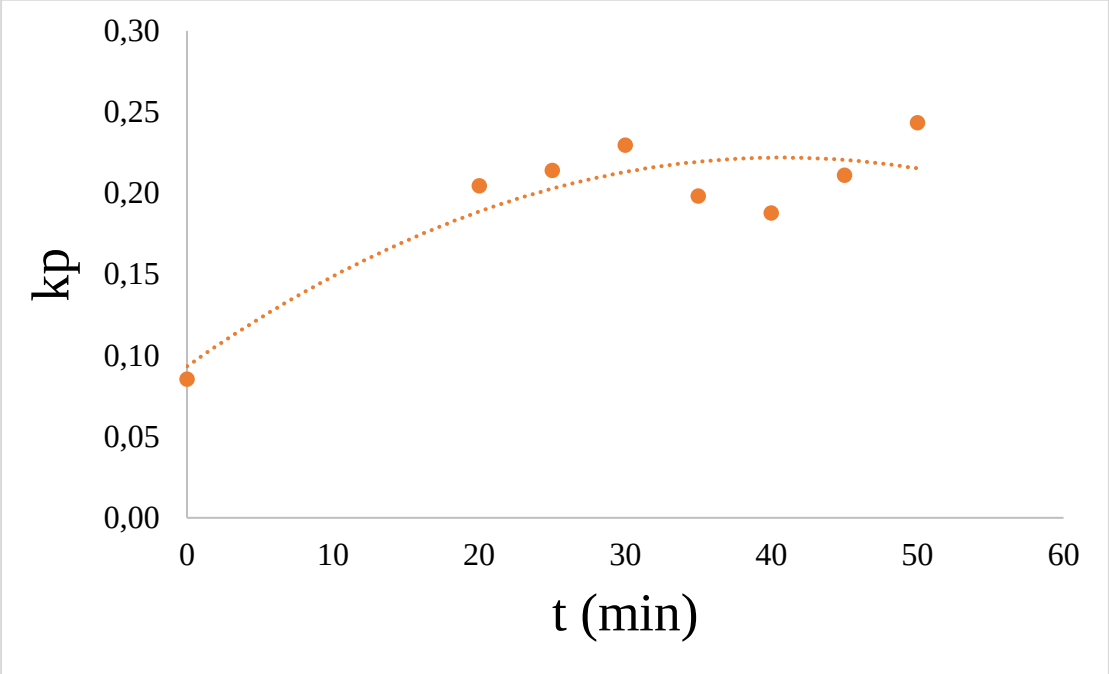


Figure 6.6. Intraparticle order rate constant relevance to torrefaction time.

Fig. 6.6 gives information about how k is affected to the time of each experiment. The designed curve is described from the following equation.:

$$y = -8E\text{-}05x2 + 0{,}0063x + 0{,}0934 \quad (16)$$

and has coefficient of determination $R^2 = 0{,}8033$

Table 6.4 Parameters of intra-particle kinetic models of Methylene blue adsorption on untreated and torrefied medical cotton waste

Torrefaction Time t (min)	c	kp	SEE
Untreated	0,038	0,085	0,028
20,0	0,654	0,205	0,256
25,0	0,577	0,214	0,212
30,0	0,452	0,230	0,233
35,0	0,665	0,198	0,213
40,0	0,701	0,188	0,209
45,0	0,867	0,211	0,266
50,0	0,594	0,243	0,204

The first order kinetics was estimated for MB for untreated and torrefied cotton. All *SEE*-values were found a little lower than the *SEE*-values of the second-order kinetic model and of the intra-particle kinetic model, indicating the marginally higher applicability of the first-order kinetic equation to the adsorption of MB on cotton.

Torrefaction pretreatment conditions were investigated for enhancing medical cotton waste adsorbency. The most intense conditions were found to maximize adsorbency of torrefied medical cotton waste for the removal of MB from wastewater. Nevertheless, moderate conditions of torrefaction have similar results to intense conditions and less yield%. The adsorption kinetic data were found to follow the pseudo-second-order kinetic model. In conclusion, torrefied medical cotton waste could replace activated carbon, as a low-cost substitute for the removal of basic dyes and other types of pollutants from wastewater.

Adsorption of MB in cotton have been studied extensively. Adsorption of MB via carbonization method resulted in 102.23mg/g of pretreated carbon fiber aerogel material created by abandoned cotton (Li et al. 2017). In another study, the performance of cotton stalk, cotton waste, and cotton dust were tested regarding their MB adsorbance.

The results were among 26.0% and 48.36% for cotton stalk between 50.0% and 85.41% for cotton waste and between 62.0% and 97.50% regarding cotton dust (Ertas¸ 2010). Cellulosic materials are used for such purposes like wastewater cleaning. Such an application is the effective recovery of terbium ions from aqueous solutions with the use of cellulose based bioabsorbent from cellulosic material extracted from rose stems with efficiency of 97% (Alkaraz et al. 2020). Torrefaction with similar pretreatment conditions has been applied for the removal of lead and terbium from wastewater. For lead removal the conditions were 250 ^{o}C and 75 min and for terbium were 280 ^{o}C and 60 min. The results were 30mg/g and 9.4mg/g for lead and terbium respectively (Demey et al. 2019).

6.2. Acid hydrolyzed medical cotton waste as methylene blue adsorbent.

The purpose of this study is to discover whether acid hydrolysis pretreatment makes medical cotton waste an efficient material regarding basic dyes removal from substitute wastewater. A 3.75 L batch reactor was used to achieve acid hydrolysis. The conditions applied were a result of a design of experiments (DoE) using time, temperature, and acid concentration as parameters. The effect of the pretreatment conditions on MB adsorption, was investigated. The applicability of pseudo-first order adsorption kinetic model was studied.

Kinetic models' equations: The kinetics of adsorption of MB on untreated and torrefied medical cotton has been extensively studied using the pseudo first kinetic order and examined via severity factor.

Table 6.5. Severity factor, pH, and parameter values for dilute acid hydrolysis of MCW

Run	T (^{0}C)	t (min)	SA (mol/m^3)	pH before	pH after	logRo*
1	180	0	22.50	1.7	1.8	1.63
2	180	40	22.50	1.7	1.6	2.83
3	220	0	22.50	1.61	1.55	2.52
4	220	40	22.50	1.55	1.53	3.74
5	180	20	10.00	2.11	1.97	1.83
6	180	20	35.00	1.29	1.38	2.65
7	220	20	10.00	2.06	2.12	2.56
8	220	20	35.00	1.32	1.33	3.39
9	200	0	10.00	2.1	1.92	1.81
10	200	0	35.00	1.4	1.42	2.51
11	200	40	10.00	2.04	1.96	3.09
12	200	40	35.00	1.46	1.52	3.63
13	200	20	22.50	1.61	1.82	2.89
14	200	20	22.50	1.61	1.55	2.93
15	200	20	22.50	1.61	1.56	2.89

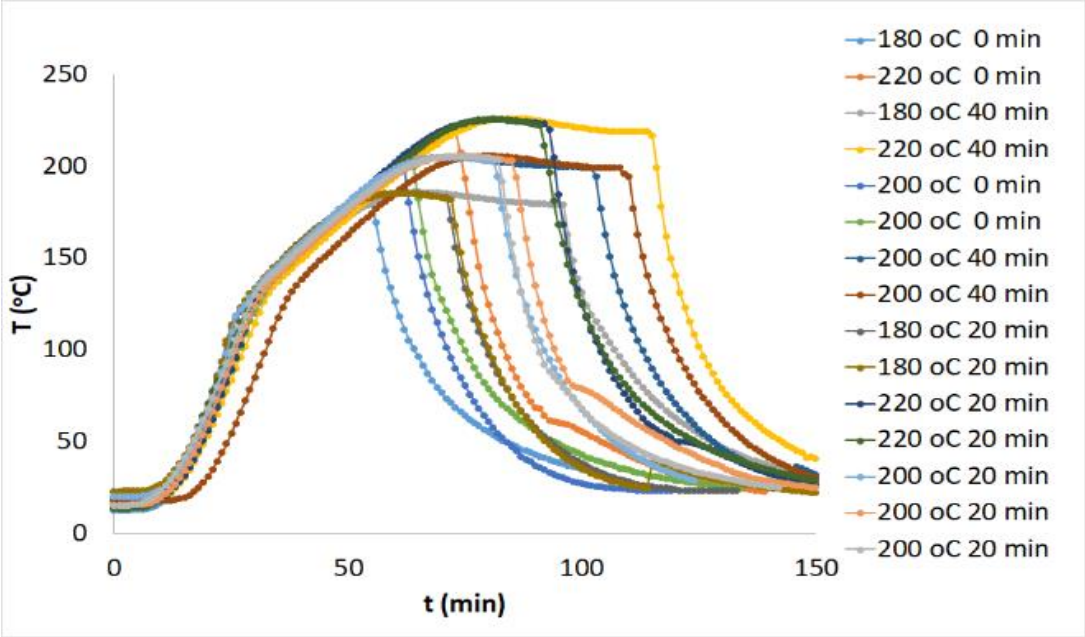


Figure 6.7. Acid hydrolysis pretreatment's temperature vs. time.

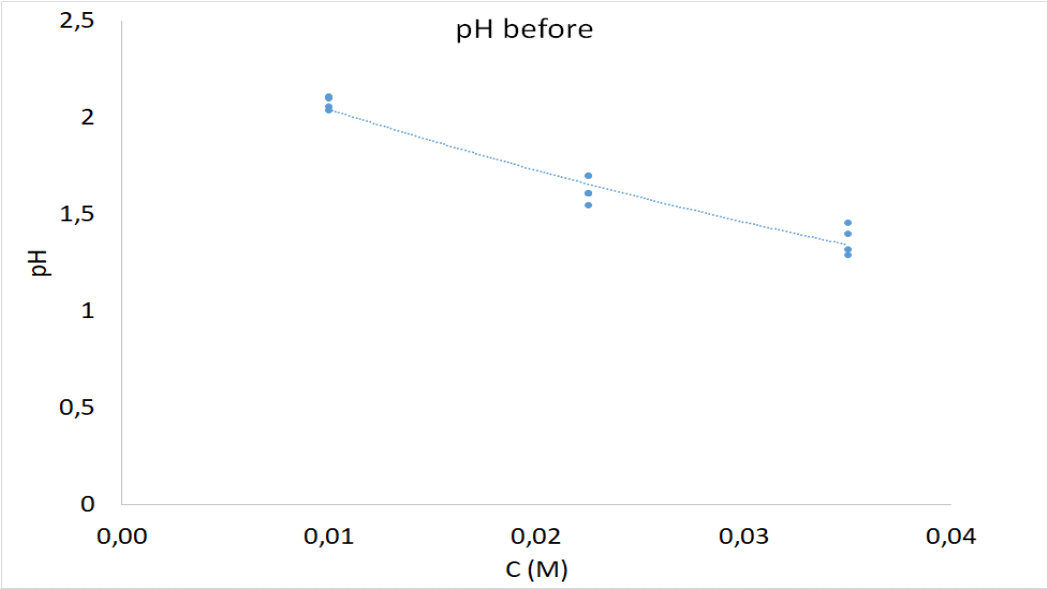


Figure 6.8. pH before pretreatment as affected by sulfuric acid concentration.

Table 6.5 gives thorough information about the DOE and the parameters in each run. It also shows the severity factor and the logarithm of severity factor in each experiment. Finally it includes the pH before and after the treatment time. Figure 6.7 represents the relation between time and temperature during the acid hydrolysis procedure of medical cotton waste. pH was measured before and after the experiment occurred.

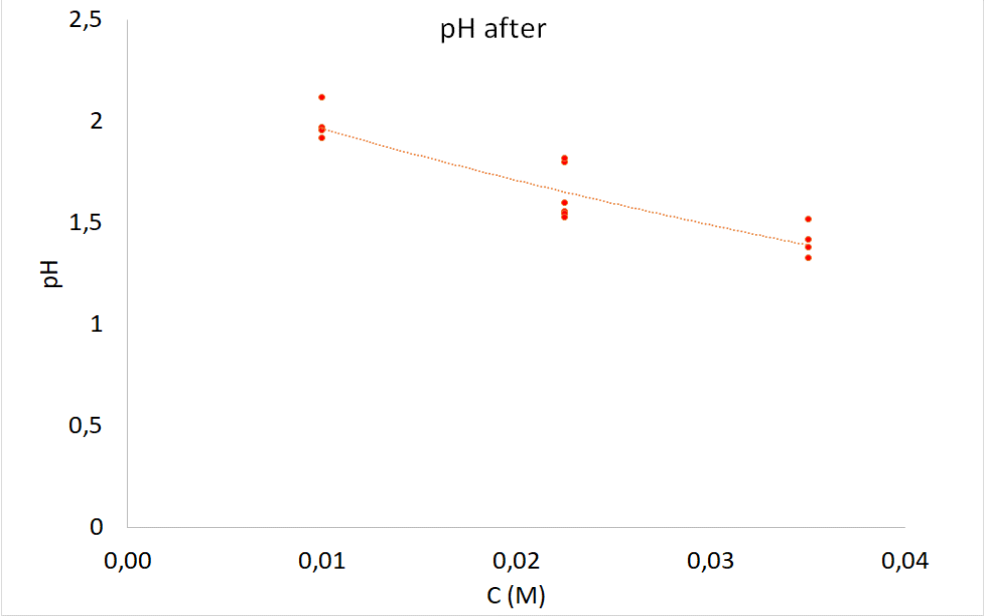


Figure 6.9. pH before pretreatment as affected by sulfuric acid concentration.

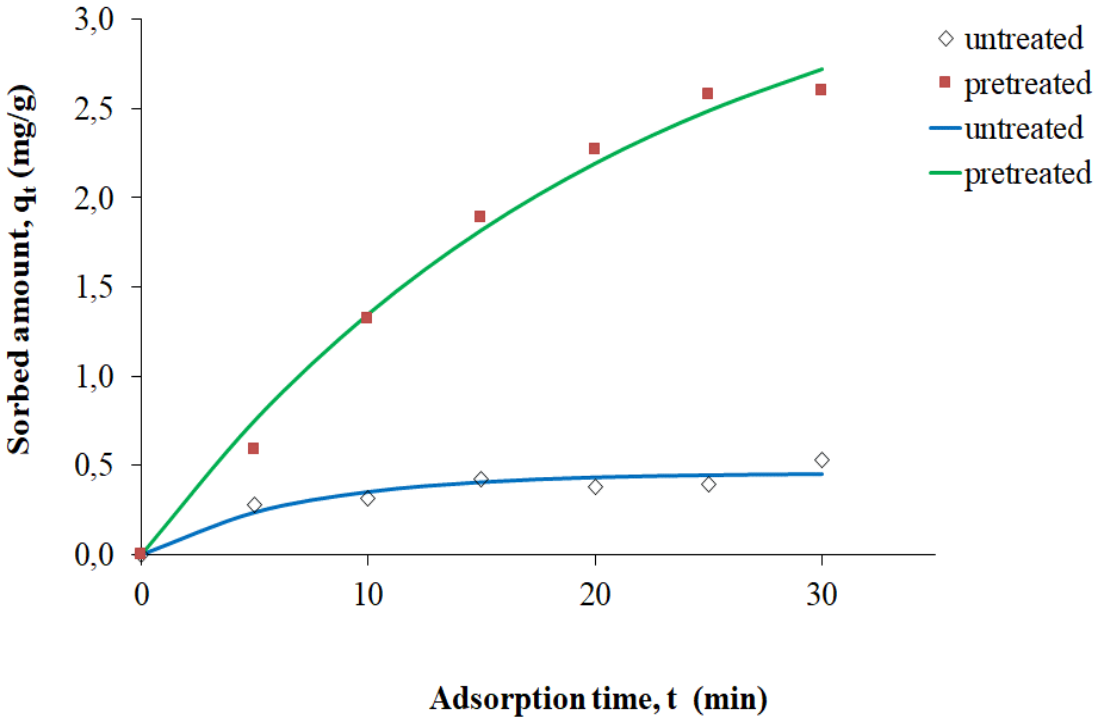


Figure 6.10. Lagergren kinetics for MB adsorption on untreated and pretreated medical cotton waste on run 11.

The pH levels had a normal variation, and the prices were like the expected (see Table 6.5). Figure 6.8 depicts these pH values before the pre-treatment. Figure 6.9 shows the pH values after the treatment process.

In Fig. 6.10 the MB maximum amount adsorbed is compared between untreated and pretreated medical cotton (Run 11). The result is quite promising since cotton adsorption capacity has greatly improved in comparison to the untreated (see Fig.6.10). The relevant equation is:

$$q_t=-0.0021t^2+0.1508t+0.025 \quad (17)$$

while the coefficient of determination is $R^2 = 0,9994$.

Table 6.6 provides information about the parameters and standard error of estimate of the pseudo-first kinetic order equation compared to severity factor.

MB adsorption via acid hydrolysis have been studied extensively in many forms of cellulose. Adsorption of MB dye by partially hydrolyzed polyacrylamide/cellulose nanocrystal nanocomposite hydrogels had an efficiency greater than 90% following the pseudo-second order and Elovich models (Zhou et al 2014). Cellulose nanocrystals have been used in another for the same reason. Their fabrication came from Carex meyeriana Kunth via acid hydrolysis and they were tested on their adsorbency. MB adsorbance reached 217 mg/g on the optimal conditions (Yang et al. 2017). Another study tested cellulose nanowhiskers created from acid hydrolyzed cellulose on its MB adsorbance efficiency. The results showed that the optimal condition achieved almost entire MB removal (Kumari et al. 2016).

Table 6.6. The pseudo-first-order kinetic parameters k (min-1), q (mg g-1) and standard error of estimate vs. the severity factor of medical cotton waste.

Run	$logR_0^*$	k	q	SEE
untreated		0.1467	0.456	0.0155
1	1.63	0.0470	0.918	0.0011
2	2.75	0.0815	2.710	0.1052
3	2.52	0.0384	2.159	0.0128
4	3.74	0.0679	3.109	0.0061
5	1.83	0.0446	0.681	0.0063
6	2.65	0.0729	2.910	0.0166
7	2.56	0.0895	2.025	0.0209
8	3.39	0.0749	2.983	0.0136
9	1.81	0.0275	1.197	0.0092
10	2.51	0.0617	1.259	0.0233
11	3.09	0.0469	3.609	0.0631
12	3.63	0.0859	2.868	0.0059
13	2.83	0.0698	2.673	0.0437
14	2.93	0.0569	3.011	0.0475
15	2.89	0.0606	2.806	0.0667

In Fig.6.11 according to the pseudo-first order kinetic is shown how k is affected from the logarithm of severity factor. There is not such a good response and there are many fluctuations. The first order equation that describes this dependence is:

$$k=0.0258 logR_0^{*0,8476} \quad (18)$$

and the $R^2 = 0.4019$.

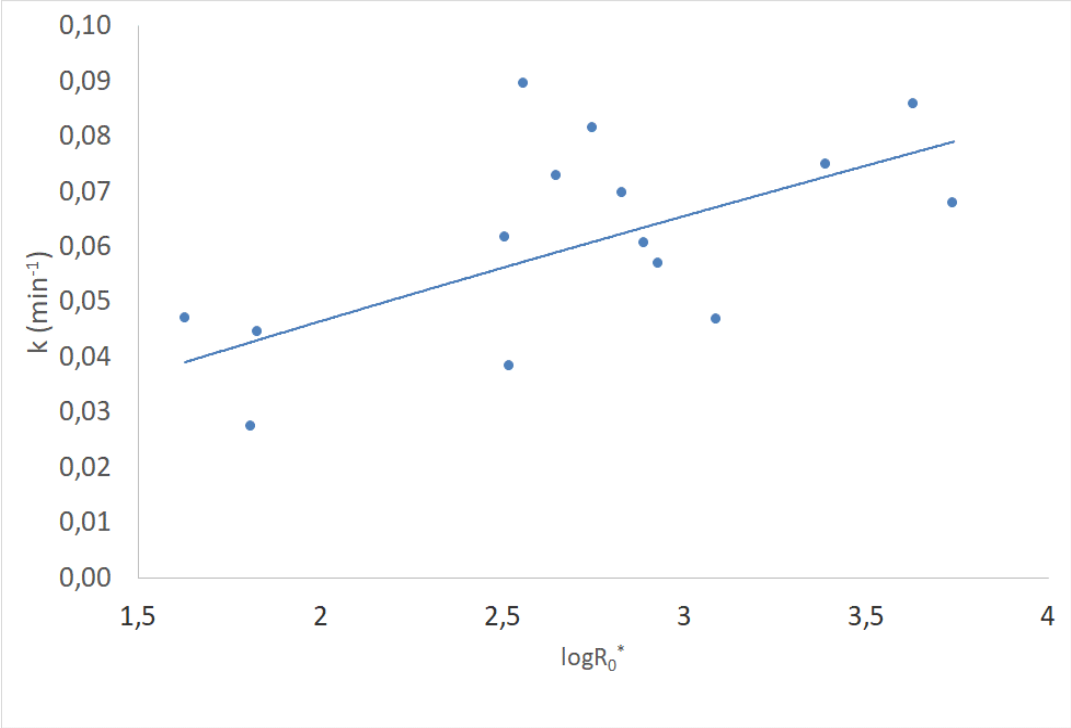


Figure 6.11. The pseudo-first order rate constant for the adsorption process compared to logarithm of severity factor.

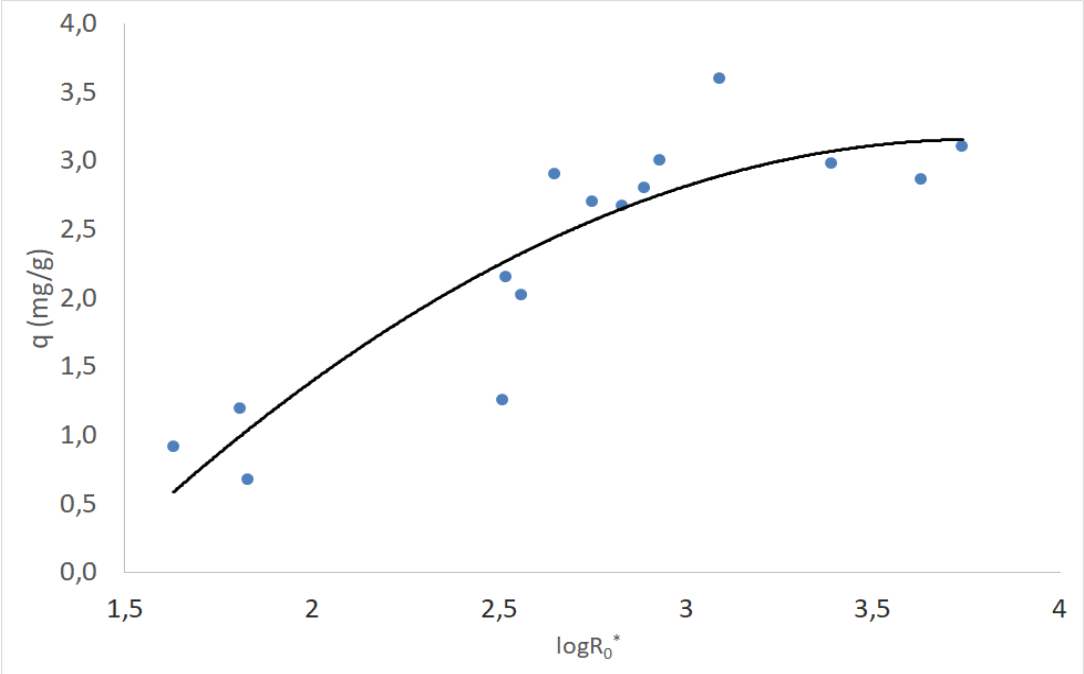


Figure 6.12. The sorbed amount q of MB compared to logarithm of severity factor.

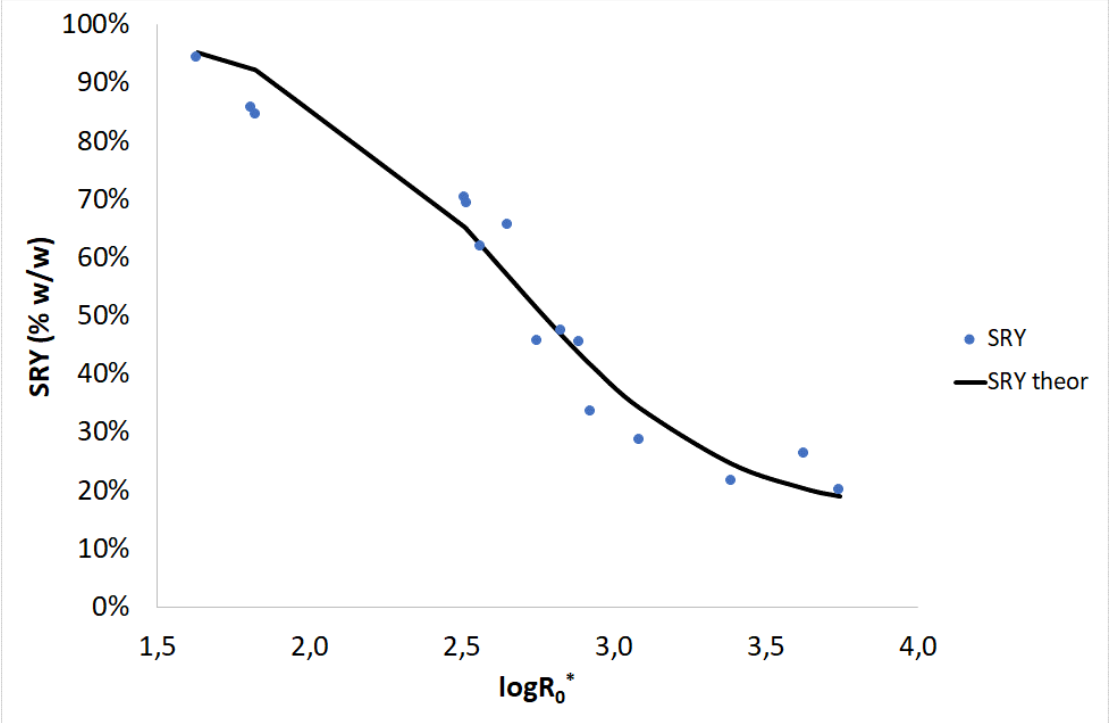


Figure 6.13. The solid residue yield of medical cotton vs. logarithm of severity factor.

Figure 6.12 depicts the increase of the sorbed amount of MB with the increase of logarithm of severity factor. The second order equation that describes the dependence of q to $logR_0^*$ is:

$$q=-0,5543logR_0^{*2}+4,1965logR_0^{*}-4,7801 \quad (19)$$

and has $R^2 = 0,8005$.

Figure 6.13 shows how severity factor affect the solid residue yield of the pretreated medical cotton. In Table 6.12, the values for the parameters that apply to the Box-Behnken eq. (7) regarding % SRY are presented. The equation has p-value = 0.0061, R2 = 0.9580 and SEE = 0.0487.

Moreover, solid residue yield (SRY) of medical cotton waste is shown in Table 6.7. The mass loss is getting higher as logarithm of severity factor grows and its variation is from 13% up to 85%.

Table 6.7. Solid residue yield of acid hydrolyzed cotton.

Run	T (^{0}C)	t (min)	SA (mol/m^3)	logRo*	SRY % w/w
1	180	0	22.50	1.63	94.5%
2	180	40	22.50	2.83	45.7%
3	220	0	22.50	2.52	69.5%
4	220	40	22.50	3.74	20.1%
5	180	20	10.00	1.83	84.6%
6	180	20	35.00	2.65	65.7%
7	220	20	10.00	2.56	61.9%
8	220	20	35.00	3.39	21.7%
9	200	0	10.00	1.81	85.9%
10	200	0	35.00	2.51	70.3%
11	200	40	10.00	3.09	28.8%
12	200	40	35.00	3.63	26.3%
13	200	20	22.50	2.89	47.6%
14	200	20	22.50	2.93	33.7%
15	200	20	22.50	2.89	45.5%

In this study, dilute acid pretreatment conditions were investigated for enhancing medical cotton waste adsorbency. Intense conditions were found to maximize adsorbency of pretreated medical cotton waste for the removal of MB from wastewater. The most intense condition showed decrease of the sorbed amount of MB which concludes that the chosen parameters were correct since we found the peak of the sorbed substance. In conclusion, acid hydrolyzed medical cotton waste could replace activated

carbon, as a low-cost substitute for the removal of basic dyes and other types of pollutants from wastewater.

6.3. Torrefied medical cotton waste as enhanced solid fuel – HHV

The purpose of this study is to discover whether cotton is an efficient material for energy purposes and then to see in what conditions its higher heating value (HHV) or gross heat of combustion can be maximized. More specifically we used a blast furnace to achieve torrefaction. The conditions applied were a non-isothermal heating up to 340^{o}C for 20-50 minutes with 2.5 min step. The investigations of how pretreatment conditions, affected cottons HHV happened in a calorimeter. The diagrams show analytically the dependence between time and temperature with HHV.

The kinetics of HHV of raw and torrefied cotton has been comprehensively examined using ISO 1716:2010 (2010). The commonly used HHV equation is shown beneath,

$$HHV = \frac{tW - e_1 - e_2 - e_3}{m} \quad (20)$$

, where m exists for mass of sample measured in grams. e_1 describes the calories correction for heat of formation of nitric acid, e_2 to calories correction for heat of formation of SA and e_3 to calories correction of heat of combustion caused by the fuse wire. W is the calorimeter energy equivalent, defined during standardization. t stands for the net corrected temperature increase. The below equations provide additional information regarding these variables,

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad (21)$$

$$e_3 = l_f x 2{,}3 \quad (22)$$

$$W = 2426\, {}^{cal}/_{{}^{o}C} \quad (23)$$

Where a represents firing time, b time when temperature reaches 60% of its total rise, and c the time when rate of temperature change becomes constant. t_a signifies temperature at firing time and t_c temperature at time c. r_1 is the rate where the temperature was

rising until the fifth minute and r_2 the rate at which the temperature rising during the 5-min period after the time c. l_f stands for the length of fuse wire consumed during firing. Severity factor was used to integrate the effects of reactions time and temperature into one variable during torrefaction. The SF and logarithm of SF rates for each experiment were projected in Table 6.8.

Table 6.8. Severity factor values for each experiment.

t(min)	Ro	$\log R_0$
20	2.12E+07	7.33
22.5	2.76E+07	7.44
25	5.13E+07	7.71
27.5	7.51E+07	7.88
30	1.04E+08	8.02
32.5	1.21E+08	8.08
35	1.45E+08	8.16
37.5	1.57E+08	8.20
40	1.73E+08	8.24
42.5	1.79E+08	8.25
45	1.88E+08	8.27
47.5	1.92E+08	8.28
50	2.01E+08	8.30

Table 6.9. The table shows the mass decrease during the torrefaction process.

R_0	$LogR_0$	t(min)	yield%
2.12E+07	7.33	20	75.87
2.76E+07	7.44	22.5	69.04
5.13E+07	7.71	25	62.36
7.51E+07	7.88	27.5	56.06
1.04E+08	8.02	30	49.49
1.21E+08	8.08	32.5	45.89
1.45E+08	8.16	35	41.75
1.57E+08	8.20	37.5	41.15
1.73E+08	8.24	40	40.20
1.79E+08	8.25	42.5	39.90
1.88E+08	8.27	45	39.80
1.92E+08	8.28	47.5	39.70
2.01E+08	8.30	50	39.41

In Table 6.9, is shown, for each experiment carried out, how mass at starting time (m_0) lowers to mass at the end of each experiment (m_t). Yield% shows the shrinkage percentage of the mass through time.

Figure 6.14, as it can be seen below, displays how yields' percentage decreases rapidly for small severity factor values and as severity factor increases this decrease shortens

and it becomes more stable. The equation that shows how yield is affected by severity factor is the following.

$$yield\% = -4 \cdot 10^{-7} R_0 + 82.59 \quad (24)$$

The coefficient of variation was $R^2 = 0.994$.

In Figure 6.15 the percentage of loss of mass during the torrefaction procedure compared to logarithm of severity factor is presented. As it can be seen as time rises yield is less affected. The kinetic equation that shows mass decreasing as logarithm of severity factor increases is given below:

$$yield\% = -37.97\, log\, R_0 + 353.5 \quad (25)$$

The coefficient of variation was $R^2 = 0.991$.

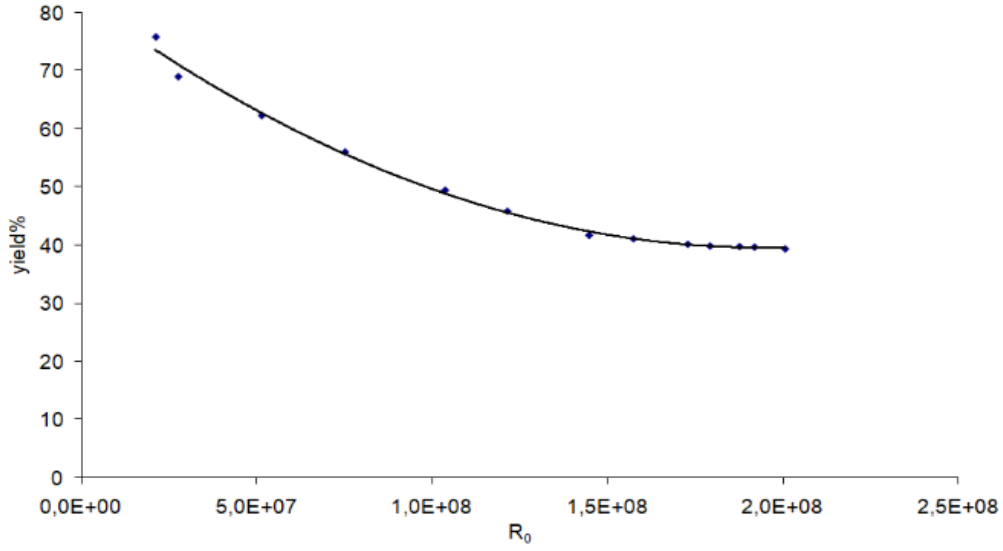


Figure 6.14. Torrefied cotton mass yield as affected by severity factor

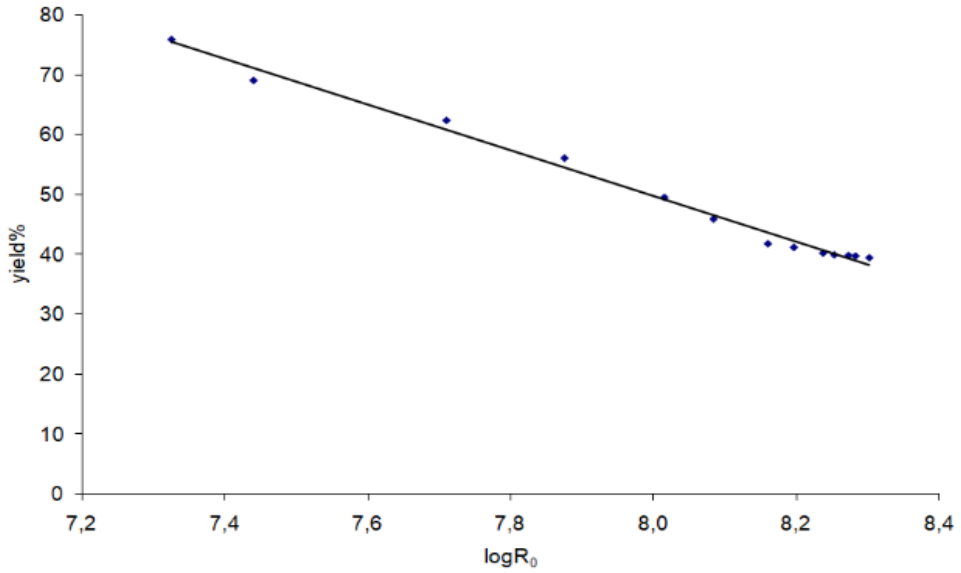


Figure 6.15. Torrefied cotton mass yield as affected by severity factor in logarithmic form.

Table 6.10. HHV changes through time.

R_0	$\log R_0$	HHV (MJ/kg)	ΔHHV%
2.12E+07	7.33	17.2	5.3%
2.76E+07	7.44	17.6	7.8%
5.13E+07	7.71	17.7	8.4%
7.51E+07	7.88	18.6	13.9%
1.04E+08	8.02	20.1	23.1%
1.21E+08	8.08	20.6	26.1%
1.45E+08	8.16	20	22.4%
1.57E+08	8.20	19.8	21.2%
1.73E+08	8.24	19.9	21.8%
1.79E+08	8.25	19.8	21.2%
1.88E+08	8.27	19.6	20.0%
1.92E+08	8.28	19.4	18.8%
2.01E+08	8.30	19.5	19.4%

Table 6.10, shows, how HHV increases for different torrefying reaction time. The ideal time that gives the biggest output (ΔHHV %) is 30 minutes were HHV increased 26.1%. The HHV for the untreated medical cotton was measured 3 times. Its average found 16.3 MJ/kg and its standard deviation 0.3 (1.9%).

Figure 6.16 shows the dependence of HHV from the severity factor. As it seems a moderate torrefaction optimizes the procedure since maximum HHV is found at 32.5 minutes reaction time. This dependence is given from the following equation.

$$HHV = -6 \cdot 10^{-8} R_0 + 15.84 \quad (26)$$

The coefficient of correlation was $R^2 = 0.9$.

Figure 6.17 shows how HHV grows as logarithm of severity factor increases. The kinetic equation that describes this figure is shown below.

$$HHV = 21.22(log\, R_0)^3 + 496.7(log\, R_0)^2 - 3868\, log\, R_0 + 10042 \quad (27)$$

The coefficient of correlation was $R^2 = 0.918$.

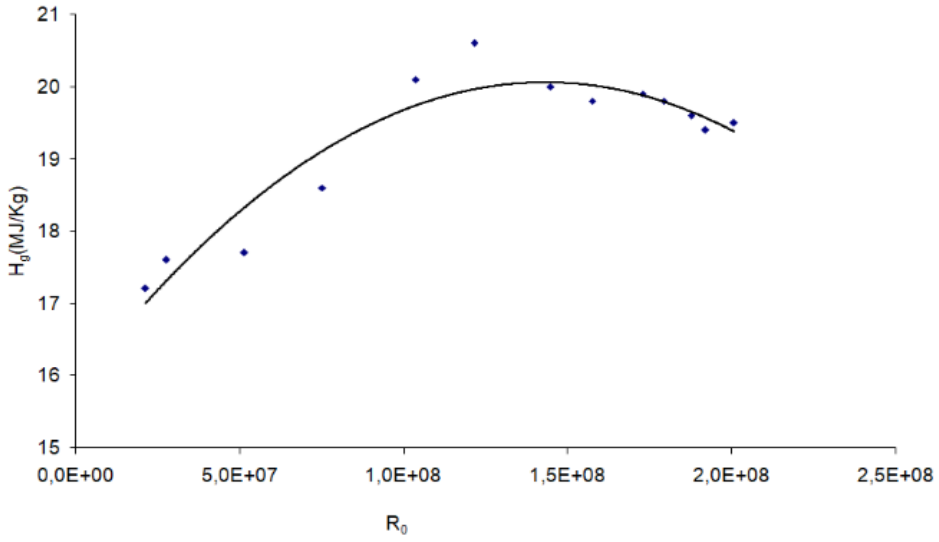


Figure 6.16. HHV vs severity factor.

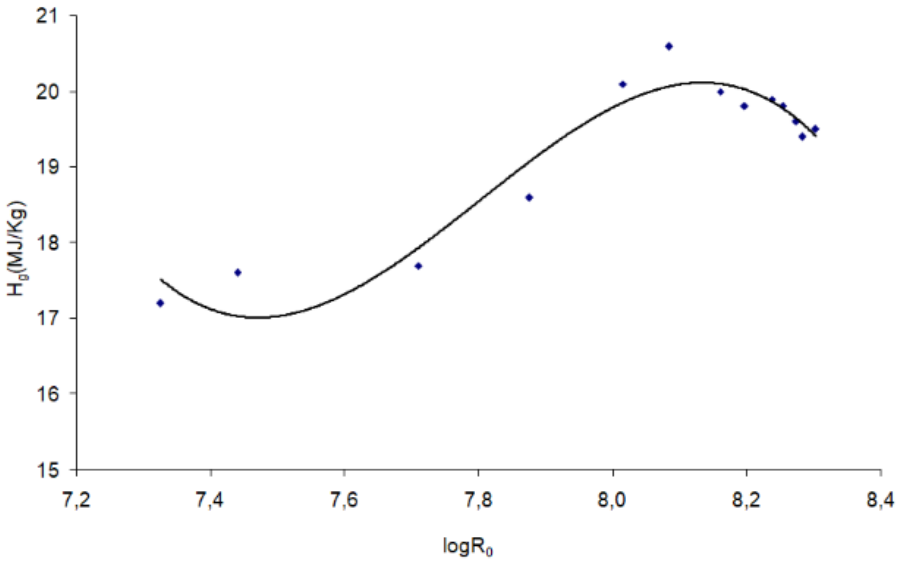


Figure 6.17. HHV compared to logarithm of severity factor

Torrefaction is a common method for exploiting biomass as a heating material. Budde et al. (2018) examined cotton stalk as a heating material by using torrefaction (300 ^{0}C and 60 min) as a pretreatment method. He resulted at a 36% increase of HHV at 24,6MJ/kg. Accordingly, Tian et al (2020) reached 50% raise at 300 ^{0}C for 30 min at 28,1 MJ/kg using corncob as the examined biomass.

Zhang et al. (2019) used corn stalk digest and achieved 41% higher HHV than the untreated material at 21.6 MJ/kg when torrefied for 30 min at 300 ^{0}C, while Cardona et al. (2019) torrefied Eucalyptus tree residues at 300 ^{0}C for 60 min and reached 23.5 MJ/kg providing 30% increase to the initial HHV.

In this study, torrefaction conditions were investigated for increasing medical cottons' HHV. Modest treatment conditions were found to maximize its value. Torrefied medical cotton became sterilized with 26% higher HHV compared to untreated medical cotton when modest conditions were applied to it.

6.4. Acid hydrolyzed medical cotton waste as enhanced solid fuel – HHV

This study was conducted to investigate medical cotton wastes' HHV in a set of experiments. MCW was pretreated in a batch reactor. The reaction happened was acid hydrolysis of MCW with time, temperature, and concentration of dilute acid solution as pre-treatment parameters. The chosen acid was diluted SA for the treatment aquatic solution. Temperature (180; 200 and 220^0C), acid concentration (0.01; 0.023 and 0.035M), and reaction time (0; 20; 40min) was chosen as the experiment parameters. The number and the sequence of experiments were based in an experimental design. The produced solid material of the pre-treatment was dried and weighted (around 0,5g ±0,1g) before it was put in the calorimeter. The HHV was calculated. CSF was selected as the defining method of the optimal conditions that permit to MCW to produce heat.

6.4.1. The pH, solid residue, and higher heating value.

As it was foresaid, pH was measured before and after the experiment occurred. The pH levels had a normal variation, and the prices were like the expected (see Table 6.5). Moreover, solid residue yield (SRY) of medical cotton waste is shown in Table 6.7. The mass loss is getting higher as logarithm of severity factor grows and its variation is from 13% up to 85%. As it can be seen in Figure 6.13, the kinetic equation that describes this diagram has good convocation. Box-Behnken equation (7), with parameters values as seen in Table 12, is the above equation mentioned. The equation has p-value = 0.0061, R2 = 0.9580 and SEE = 0.0487.

The major interest of our research is focused on Table 6.11. There it can be seen how HHV is affected by the logarithm of the severity factor. As $\log R_0$ increases H_g rises as well. The optimal price is given at experiment 4 where $\log R_0$* is 3.74 and H_g 24.90 MJ/Kg. Compare to untreated cotton which has HHV 16.2 MJ/Kg with standard deviation 0.3, the optimal conditions increase the heating value of our pretreated material by 53%. Figure 6.18 shows diagrammatically how HHV is affected by the logarithm combined severity factor. The 2nd class kinetic equation that follows these

results is shown below.

$$HHV = 3.7443x^2 - 15.794 \log R_0^* + 32.325 \quad (28)$$

The coefficient of variation was. $R^2 = 0.9495$

Table 6.11. Determination of HHV

Run	T (^{o}C)	t (min)	SA (mol/m^{3})	HHV (Mj/Kg)
1	180	0	22.5	16.30
2	180	40	22.5	16.94
3	220	0	22.5	16.43
4	220	40	22.5	24.90
5	180	20	10.0	16.22
6	180	20	35.0	16.50
7	220	20	10.0	16.60
8	220	20	35.0	22.40
9	200	0	10.0	16.10
10	200	0	35.0	16.75
11	200	40	10.0	21.10
12	200	40	35.0	24.70
13	200	20	22.5	17.55
14	200	20	22.5	17.36
15	200	20	22.5	17.12

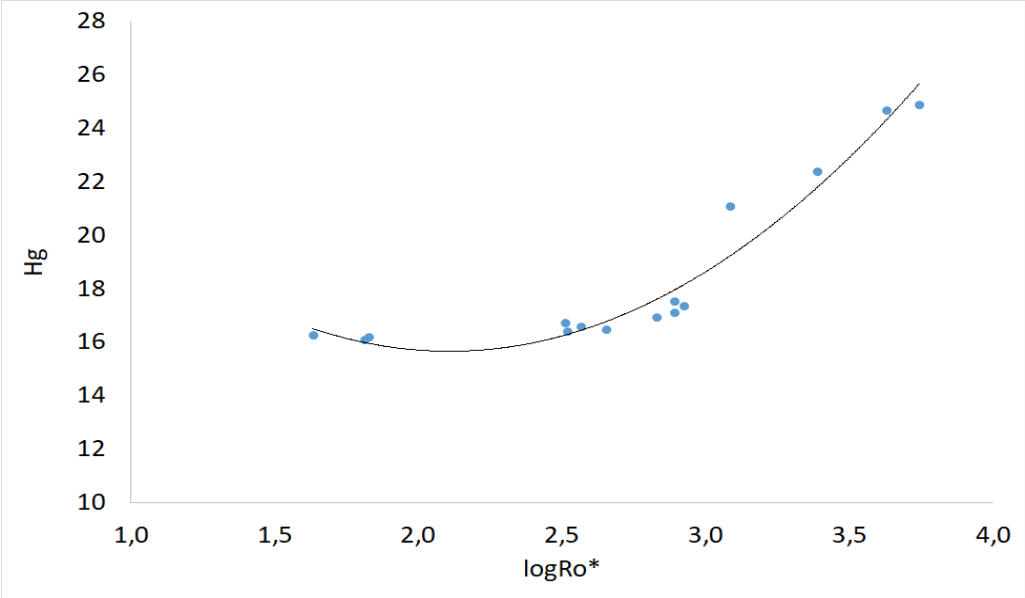


Figure 6.18. HHV vs Combined Severity Factor (logR0)*

The purpose of this study was to enhance the HHV of medical cotton waste and make it a recycled material. The pre-treatment with acid hydrolysis in a batch reactor help the material to improve and become a considerable source of energy. The higher the severity of the coefficients the bigger the SRY and the HHV become. Its thermal energy is increased 53% in the optimal conditions compared to untreated cotton. Theoretically the HHV increases as we use more severe conditions, but this will have a negative effect on the SRY.

6.5. Acid hydrolyzed medical cotton waste for ethanol production – fermentable sugars – glucose via enzymatic hydrolysis.

The purpose of the present study was to develop an efficient, cost-effective process towards the valorization of MCW. Application of dilute acid pretreatment as an initial step partially degrades the cotton cellulosic fibers rendering the material more amenable to enzymatic hydrolysis towards the production of glucose. MCW was treated with SA, in a batch autoclave, at various temperature conditions. An experimental design was set up and applied to study cotton's behavior to acid hydrolysis. The pretreatment process variables included temperature, time and SA concentration targeting maximal cellulose recovery and enzymatic saccharification yields. The results showed a maximum cellulose conversion to glucose of 95.6% wt. after pretreatment at 220 °C with 22.5 mM acid concentration. To the best of our knowledge, this is the first report in the literature suggesting a treatment process for the utilization of MCW as a source of fermentable sugars.

6.5.1 Evaluation of biomass solubilization after pretreatment

Experimental conditions used for the pretreatment tests generated with Box-Behnken design, as well as the combined severity factor values, CSF logarithm ($logR_0$*), and pH values that correspond to each run, are described in Table 6.5. % SRY, defined as the dry mass of the solid fraction recovered after the dilute acid pretreatment, is greatly affected by the conditions, more specifically it is inversely related to $logR_0$*, as shown in Figure 6.13. The tenser the conditions (increased severity factor) become, the higher is the mass loss due to solubilization. The highest % SRY value corresponded to 94.5% wt. of the initial mass, while the lower % SRY value, recorded in the experiment with the most severe conditions (Run No.4), is 20% wt. of the initial mass. The pretreatment conditions of Run No.6 were applied on MCW-S. In case of pure cotton, % SRY value was Figure 6.19a shows the dependence of % SRY from time (A) and temperature (B) when acid concentration (C) was set at the central point (22.5 mM). These data come to complete agreement with the severity factor-based analysis. It was

shown that for A=0 min and B=180 ^{o}C (lower values of these parameters), the highest amount of solid biomass is recovered after pretreatment (97% wt.), while when these two parameters are increased, the % SRY value shrinks to low percentages. Figure 6.19b explains how A and C affect % SRY for B=200 ^{o}C. It can be observed that at this temperature, % SRY does not reach its maximum percentage and it is strongly affected by the acid concentration (C). Figure 6.19c depicts the change at the percentage of % SRY when B and C diversify and A=20 min. % SRY shows decent results (91% wt.) for the mild condition (180 ^{o}C and 10 mM). % SRY decreases sharply as B and C increase, which is an indication of how strong the effect of the pretreatment conditions is to cotton solubilization. In Table 6.12, the values for the parameters that apply to the Box- Behnken eq. (7) regarding % SRY are presented. The equation has p-value = 0.0061, R^2 = 0.9580 and SEE = 0.0487.

Table 6.12. Actual factors of the second-order polynomial model Box-Behnken design equation for each response

	SRY	CRs	GRL	ED-24h	ED-48h
a	+878.17	+801.66	-908.38	-1289.75	-1212.09
a1	-1.22	-0.96	+5.70	+8.41	+11.038
a2	-6.31	-5.24	+7.85	+11.48	+10.40
a3	-4.63	-4.38	+7.50	+10.98	+12.12
a11	-3.421E-004	-2.98E-003	-0.024	-0.037	-0.046
a22	-0.021	-0.036	-0.025	-0.013	-0.035
a33	+0.013	+8.43E-003	-0.03	-0.043	-0.042
a12	+0.026	+0.037	-7.96E-003	-0.010	-0.021
a13	+0.011	+8.55E-003	-0.01	-0.024	-0.021
a23	+0.037	+0.054	-0.01	-0.039	-0.058

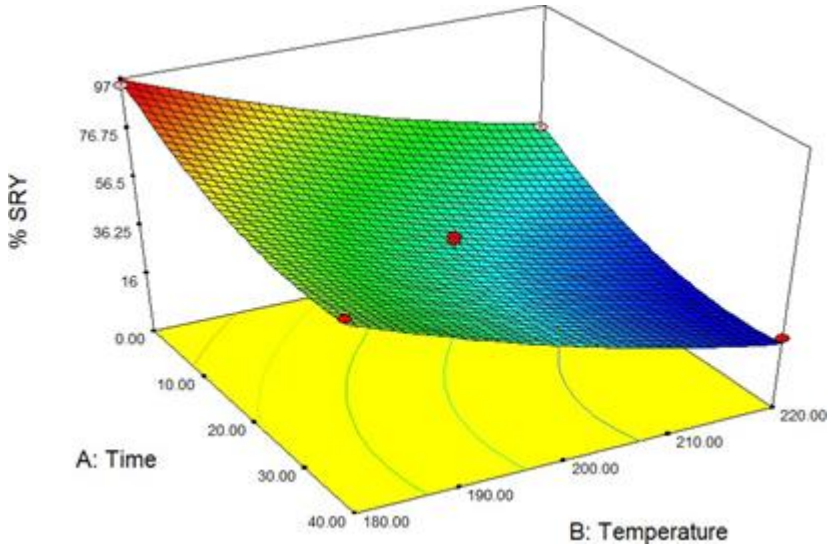


Figure 6.19a. Ternary graph showing the predicted % SRY values as a function of pre-treatment time and temperature.

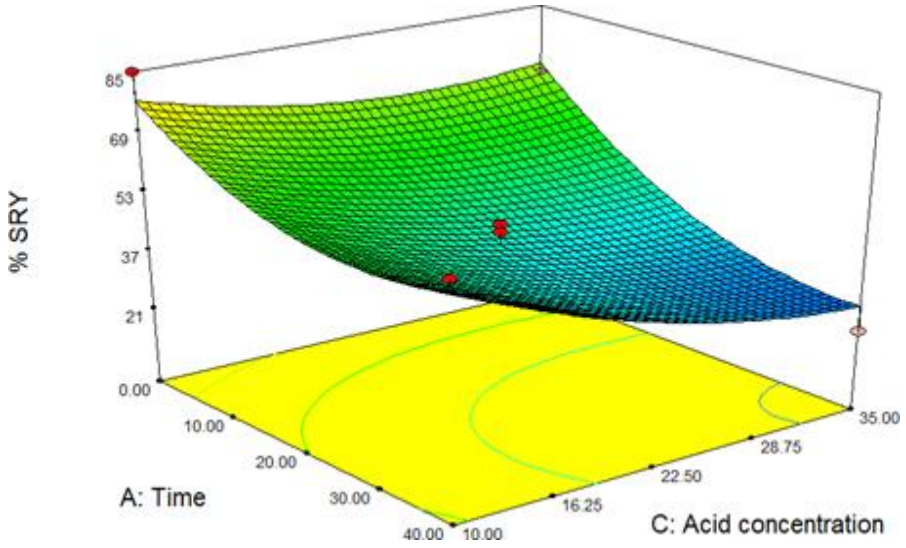


Figure 6.19b Ternary graph showing the predicted % SRY values as a function of pre-treatment time and acid concentration

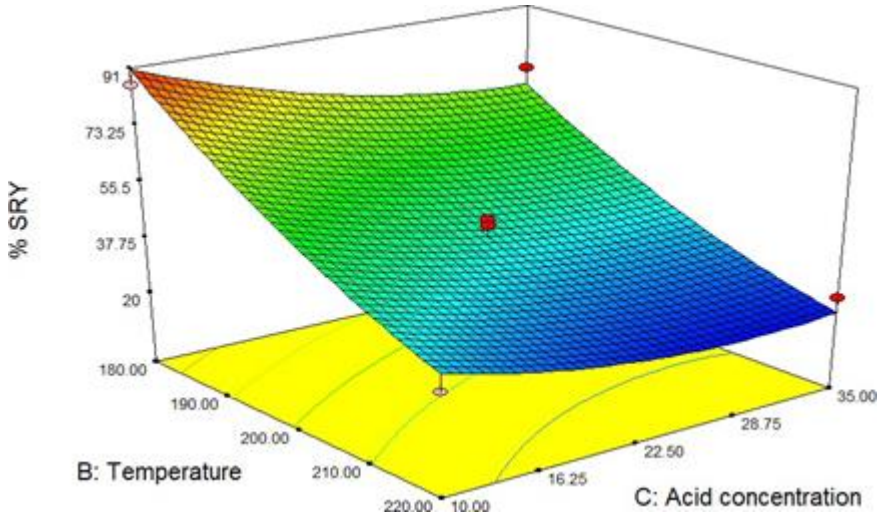


Figure 6.19c Ternary graph showing the predicted % SRY values as a function of pre-treatment temperature and acid concentration.

6.5.2. Cellulose recovery in the solid fraction

Figure 6.20a provides information about the % cellulose recovery in the pretreated solid phase, showing the effect of the $logR_0$* on cellulose recovery after the acid hydrolysis pretreatment. It can be observed that higher cellulose removal occurs as the experiment conditions become more severe. Cellulose is degraded into glucose and further transformed into other degradation products like 5-HMF, carboxylic acids

(levulinic and formic acid) and humins (Rasmussen et al. 2014). The severity of the conditions of each experiment allows this transformation to progress. Cellulose recovery reaches its higher value at 94 % wt. under mild conditions and 1.5% wt. when the most intense conditions are applied. MCW-S cellulose recovery (Run 6. conditions) had an imperceptible difference from pure cotton sample.

The correlation between % CRS and $\log R_0^*$ is described by the empirical equation:

$$CRS = 1 - (K/(1+m.\exp(-b.\log R_0^*))) \quad (29)$$

The equation parameters and SEE are estimated using non-linear regression analysis (NLRA): K=1.01, m=48144, b=4.02 and SEE=0.0758.

Figure 6.20b provides information about correlation of CRS with A and B when C is set at the central point (22.5 mM). Cellulose recovery reaches the highest value when these two parameters are set on their lower value, while as they increase, the remaining cellulose yield has severe losses. Figure 6.20c provides information about the level of dependence between A and C with CRS for B=200 ^oC. It can be observed that the CRS values are highly affected from C. In Figure 6.20d, CRS is related with B and C when A=20 min. These data indicate that acid concentration is the main factor that affects cellulose recovery in the solid pulp. In Table 6.12, the factors that relate to the Box-Behnken equation regarding % CRS are observed. The equation is fitted in the quadratic model and has p-value=0.0035, R^2=0.9667 and SEE = 0.0568.

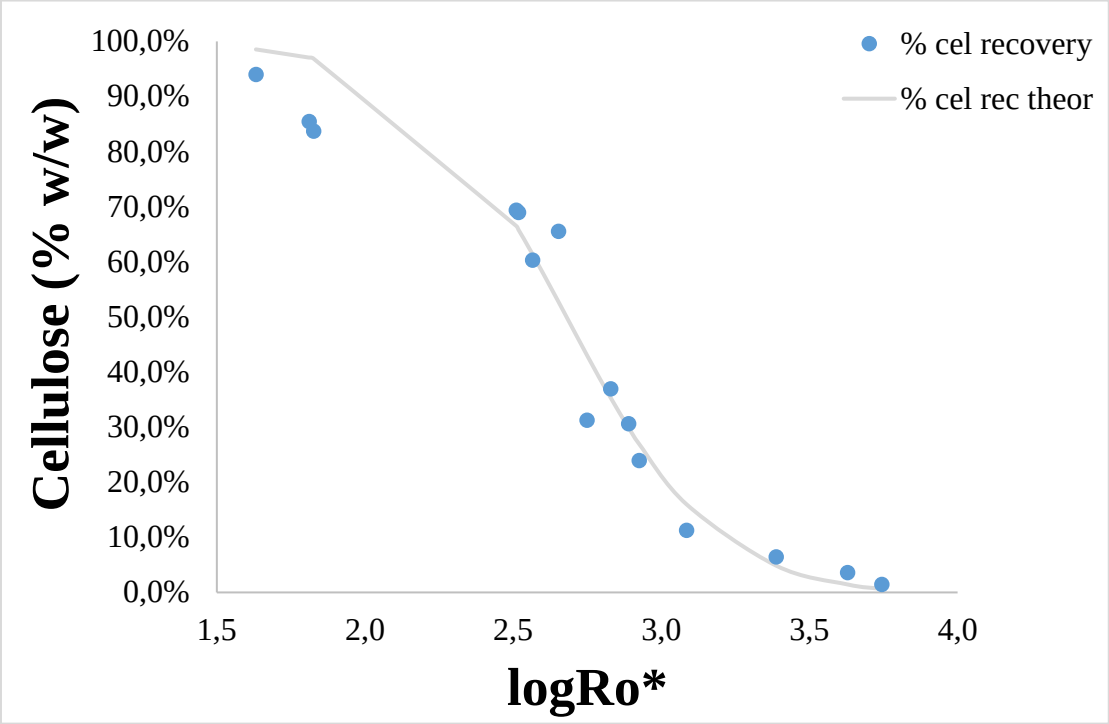


Figure 6.20a. Effect of pretreatment severity (logR0) on cellulose recovery on solid fraction (% CRS)*

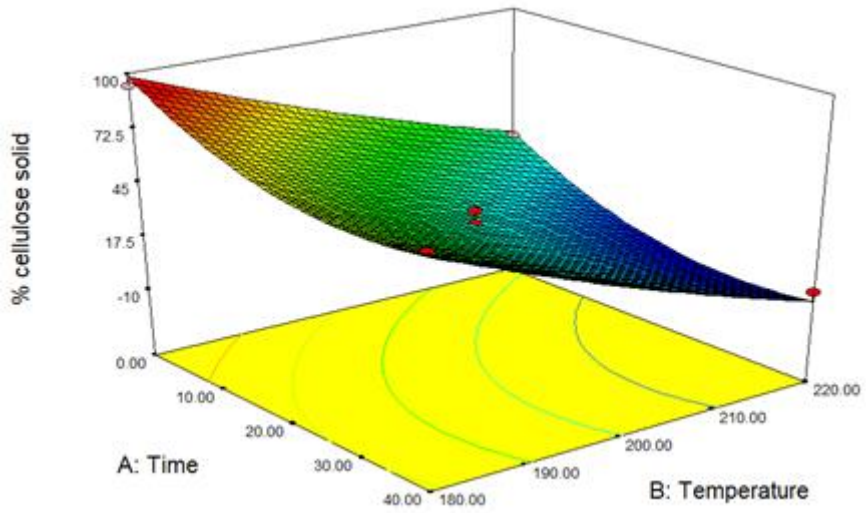


Figure 6.20b Ternary graph showing the predicted % CRS values as a function of pre-treatment time and temperature.

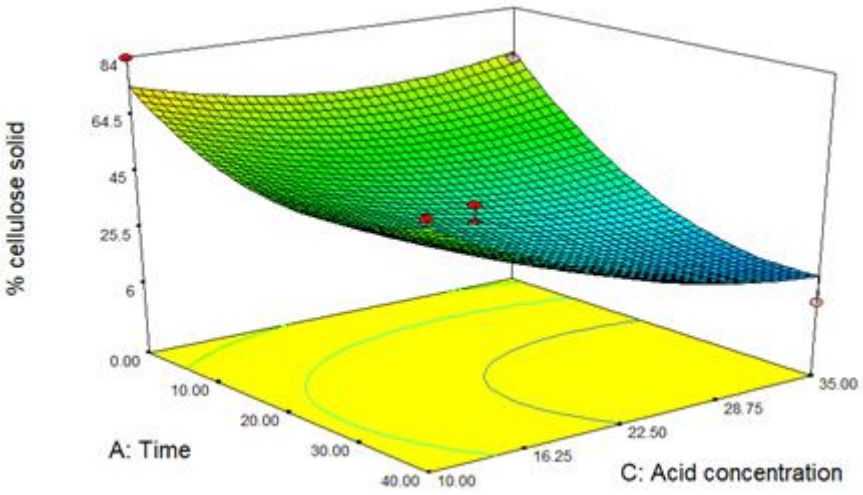


Figure 6.20c. Ternary graph showing the predicted % CRS values as a function of pre-treatment time and acid concentration.

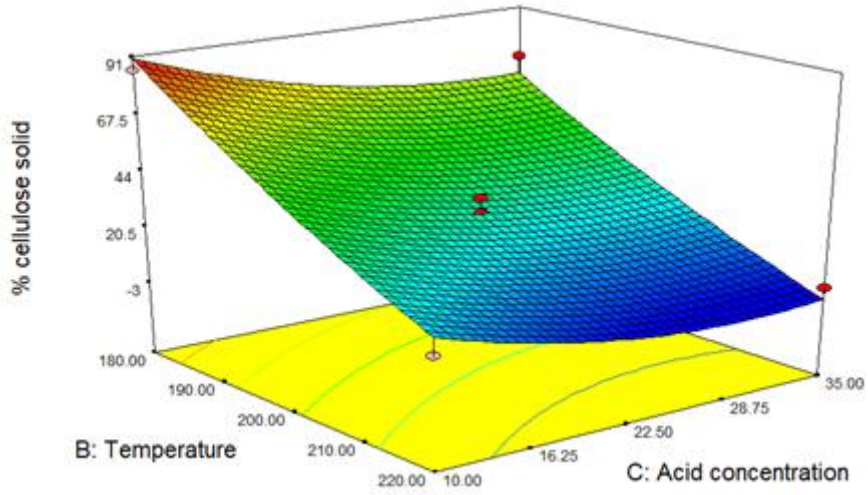


Figure 6.20d Ternary graph showing the predicted % CRS values as a function pre-treatment temperature and acid concentration.

6.5.3. Properties of the liquid fraction

Figure 6.21a provides information about the amount of glucose and 5-HMF that were detected in the liquid phase of the pretreatment. The maximum amount of glucose released in the liquid fraction was observed for the run No.6 (200 ^{o}C, 0 min and 35 mM acid concentration) and corresponded to 6.96 g/L or 27.5% wt. glucose recovery of the

total initial cellulose. The percentage of glucose recovery in cellulose treated with diluted acid solution in similar conditions had a maximum at 30 % wt. (Sidiras 1997, Millett et al. 1979) and in pretreated yellow poplar at 35% wt. (Kim et al. 2001). Since cotton consists almost entirely of cellulose, it was expected to come up with similar results with literature. In our study, the maximum glucose recovery in the liquid fraction was 27.5 % wt. of the total initial cellulose. In case of MCW-S, glucose in the liquid fraction reached 26.8 % wt., indicating that the presence of blood practically did not affect the results of the pretreatment, as shown above for that CRS values, corroborating the idea that MCW-S is behaving in a similar way as pure cotton. The slight difference that is observed can be probably attributed to the presence of ions, proteins, nutrients, wastes, and dissolved gases, which are contained in blood (10 % wt.) (Matthew et al. 2019) and have an obstructive effect on this conversion.

In the acid hydrolysates, glucose is converted into 5-HMF, among other degradation products, during acid pretreatment. Furthermore, 5-HMF is transformed into levulinic, formic acid and humins at the late stages of the reaction (Kim et al. 2018). Severity factor increase has a simultaneous increasing effect on 5-HMF concentration. Regarding the upper and lower values of the experimental conditions employed in this study and the statistical analysis that was applied, the function was not able to calculate the 5-HMF maximum value within these intervals. The most severe acid hydrolysis conditions gave a local maximum value equal to 20.1 % wt. Although glucose recovered in the liquid fraction is not excessive, fermentation of the hydrolysates' glucose to ethanol is a possible application to reclaim the liquid fraction of the acid pretreatment (Dussán et al. 2014). Detoxification of the hydrolysate to remove the degradation products, such as 5-HMF that have an inhibitory effect on the fermentation process, might provide promising results. Various methods for the detoxification of the hydrolysate have been reported in the literature (Martinez et al. 2001, Kim 2018).

The equation that fits the correlation of glucose recovery from liquid fraction (GRL) (% wt.) with $logR_0$* can be described from the following empirical equation:

$$GRL=B.\ (p1/\ (p2-p1)).(exp.\ (-p1.R_0^*)-exp.\ (-p2.R_0^*)) \quad (30)$$

The equation parameters and SEE were estimated using NLRA: B=8.98, p1=3.81.10-4, p2=4.57.10-3 and SEE=0.0234.

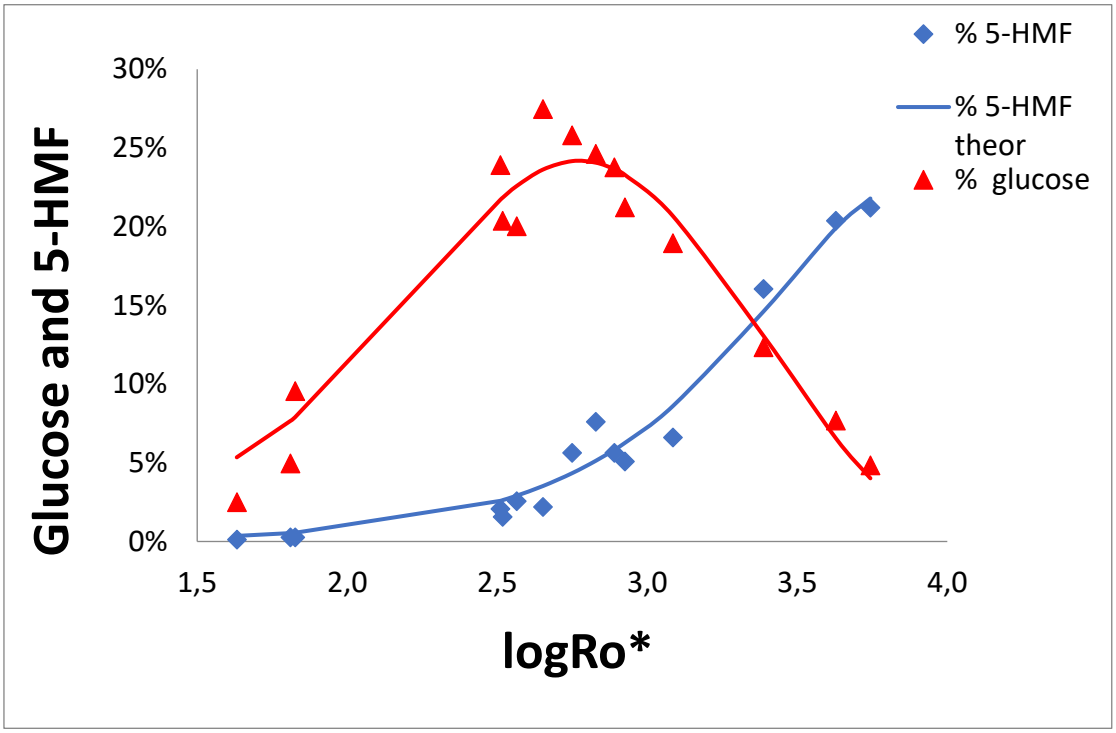


*Figure 6.21a. amount of glucose and 5-HMF detected in the liquid phase compared to $logR_0$**

Figures 6.21b, c and d summarize the correlation of A and B, A and C, B and C factors when C=22.5 mM, B=200 ºC and A=20 min, respectively. In Figure 6.19c, the conditions resulting in a maximum value of GRL are depicted. Run No.6 (200 ºC, 0 min and 35 mM acid concentration) is pointed at the top right corner. The optimization analysis with Design Expert® software suggests the following parameter values: A=0 min, B= 204.28 ºC, C=35 mM with desirability 100 %, that reach the maximum of 27.26% glucose recovery. There is great correlation between the two approaches (CSF and RSM) regarding parameter values and maximum glucose recovery percentage.

LogR_0* that applies to the RSM conditions is 2.72 while logR_0* of Run No.6 is 2.65. The CSF and RSM methods gave the approximately same logR_0* value for optimal conditions. Table 6.12 describes the factors that are related to the Box-Behnken equation regarding GRL %. The equation has p-value = 0.0009, R2 = 0.9810 and SEE = 0.0115.

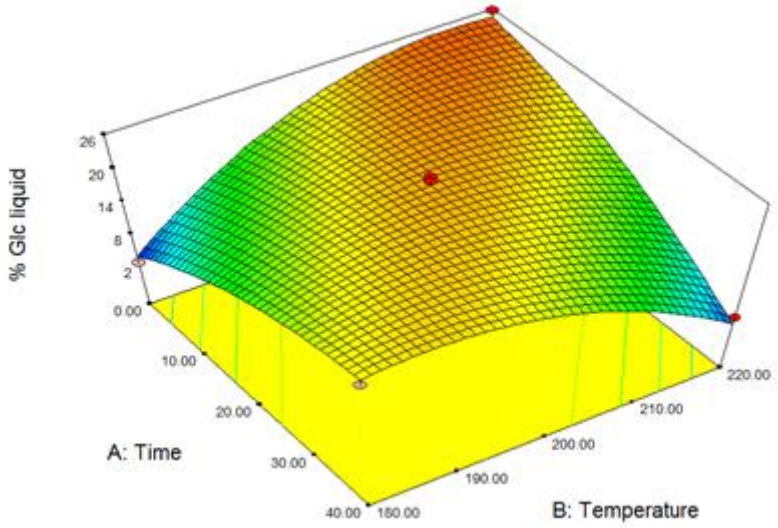


Figure 6.21b. Ternary graph showing the predicted % GRL values as a function of pretreatment time and temperature.

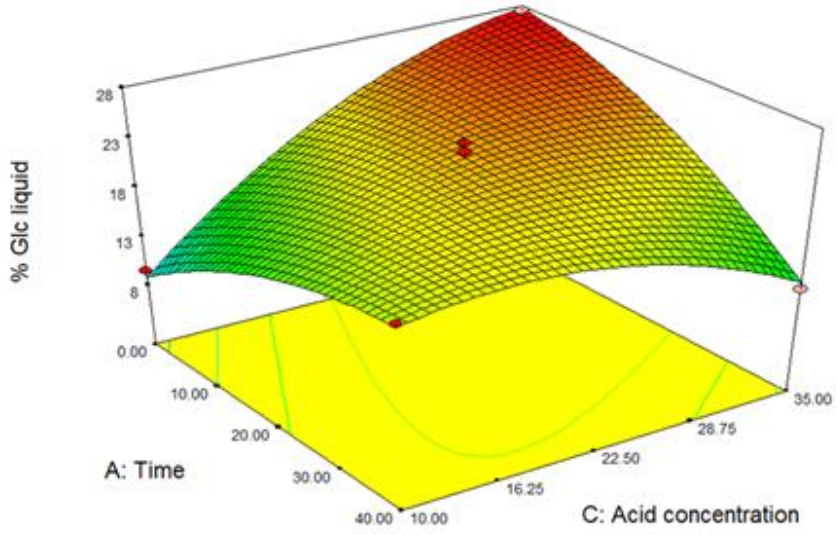


Figure 6.21c. Ternary graph showing the predicted % GRL values as a function of pretreatment time and acid concentration.

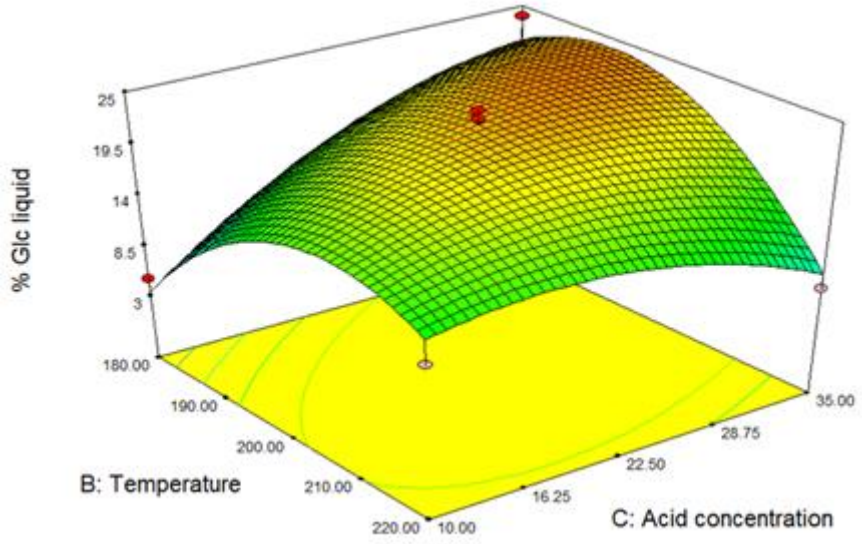


Figure 6.21d. Ternary graph showing the predicted % GRL values as a function of pretreatment temperature and acid concentration.

6.5.4. Total mass balance and distribution of cellulose in different fractions

Table 6.13 shows the losses that occur after each experiment, and it is arranged by increasing logarithm of severity factor to show the effect of $logR_0$* to the mass losses. The columns presented contain the remaining cellulose after the acid treatment, the acid insoluble fraction which is the solid degradation products on solid residue expressed as % wt. of initial cotton waste, glucose and 5-HMF recovered from the liquid phase their sum and the total losses. All of them are expressed as % wt. of initial cotton waste. Losses consist mostly of other water-soluble degradation products from glucose (except 5-HMF). Severe conditions facilitate glucose degradation. Mild conditions lead to a 6.8 % mass loss, while the highest severity factor rises that percentage to 55.3 %.

Table 6.13 The effect of $logR_0$ on mass losses (mass equilibrium).*

Run	$logR_0$*	Cellulose (%)	Acid-Insoluble fraction (%)	Glu-cose (%)	5-HMF (%)	Total (%)	Losses (%)
1	1.63	89.3	1.4	2.4	0.1	93.2	6.8
9	1.81	81.2	1.8	4.7	0.3	88.0	12.0
5	1.83	79.6	0.9	9.1	0.3	89.8	10.2
10	2.51	65.9	3.0	22.7	2.0	93.5	6.5
3	2.52	65.6	0.9	19.4	1.5	87.3	12.7
7	2.56	57.3	2.7	19.0	2.4	81.5	18.5
6	2.65	62.3	1.3	26.1	2.1	91.8	8.2
2	2.75	29.7	13.7	24.5	5.4	73.3	26.7
13	2.83	35.1	9.5	23.4	7.2	75.3	24.7
15	2.89	29.1	13.6	22.6	5.3	70.7	29.3
14	2.93	22.8	10.1	20.2	4.8	57.9	42.1
11	3.09	10.7	17.9	18.0	6.3	53.0	47.0
8	3.39	6.1	15.0	11.7	15.2	48.1	51.9
12	3.63	3.4	20.3	7.3	19.4	50.3	49.7
4	3.74	1.4	18.5	4.6	20.1	44.7	55.3

6.5.5 Evaluation of saccharification efficiency of pretreated solid fractions

Figure 6.22a shows how glucose recovery from the enzymatic hydrolysis is correlated to severity factor. Maximum % glucose recovery was 95.6 % wt., which corresponds to 654 mg glucose per g biomass and takes place at moderate conditions (220 oC, 0 min, 22.5 mM), i.e., modest severity factor value. The highest mg glucose

per g of biomass was found at run 3 and was 901 mg/g while % glucose recovery was 90.7 % wt. The bell-shaped curve that corresponds to the theoretical % wt. cellulose conversion to glucose shows that the experimental design parameter values were chosen correctly. Comparison of the ED of pure and MCW-S cotton sample pretreated under the same conditions (Run No.6), showed that total cellulose to glucose conversion was 41.8 % after 24 h and 52.4 % after 48 h of reaction, in case of pure cotton and 57.2 % at 24 h and 76.3 % after 48 h for MCW-S.

The equation that describes the dependence of ED, expressed as glucose recovery % wt. of sample cellulose, on logR0* can be found at the below empirical equation:

$$ED=B.\ (p1/\ (p2-p1)).(\exp.\ (-p1.R0^*)-\exp.\ (-p2.R0^*)) \quad (31)$$

The equation parameters and SEE were estimated using NLRA: B=0.74, p1=1.72.10-2, p2=9.06.10-5 and SEE=0.0579.

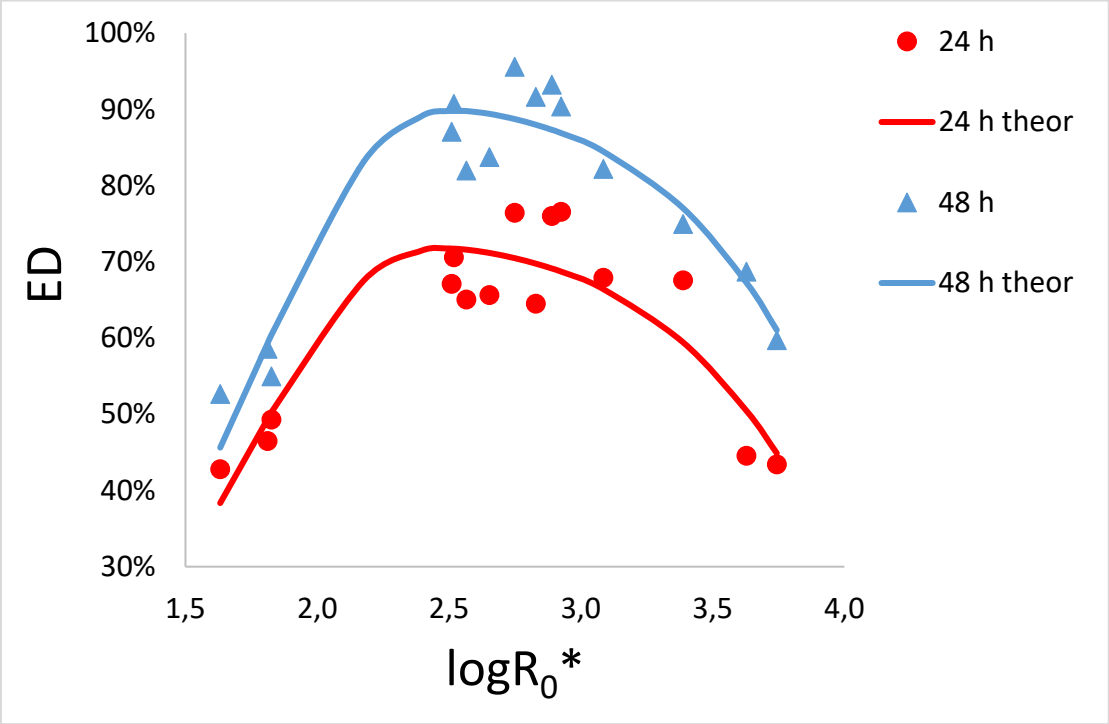


Figure 6.22a. Effect of pretreatment severity ($logR_0$) on enzymatic digestibility of cellulose to glucose after 24 and 48 h of hydrolysis (% ED-24h and %ED-48h respectively).*

Figures 6.22 b, c and d focus on the saccharification of cotton at 48 h with the use of design expert. The figures show the combined effect of A and B, A and C, B and C with enzymatic digestibility when C= 22.5 mM, B= 200 ^{o}C A= 20 min, respectively. Fig. 5.20b has better approach to the maximum ED values. It can be observed that for C= 22.5 mM and A, B reversed accordingly we achieve a wide area of high ED values. RSM differentiates from CSF method on the maximum ED (% wt.) and the experimental parameter that conclude to it. RSM suggests that A= 39.98 min, B= 180 oC and C=25.96 mM and reach a 94.56 % wt. of cellulose to glucose conversion with desirability 100 %, while CSF method shows that maximum (95.6 % wt.) occurs when A=0 min, B=220 ^{o}C, and C=22.5 mM. Table 6.12 provides the factors that are in connection with the Box-Behnken equation regarding ED %. The equation and has p-value = 0.0005, R2 = 0.9850 and SEE = 0.0178.

Acid and enzymatic hydrolysis have been applied sequentially into lignocellulosic materials for efficient glucose production (Cornejoa et al. 2019) and reduced sugar recovery (Gundupalli and Bhattacharyya 2019). According to literature, enzymatic hydrolysis from pretreated cellulose provides similar or lower results. Dissolution pretreatment via ionic liquid (Li et al. 2019) resulted in a maximum of 89% wt. conversion. Unlocking recalcitrance of cellulose through reversible covalent chemistry of carbon dioxide pretreatment (Gan and Peng 2020) achieved 97.5% wt. glucose conversion. Such amounts of glucose can be fermented to many valuable products, like lactic acid (Wischral 2019), ethanol (Ghods et al. 2018) and biosurfactants (Vanavil and Rao 2018).

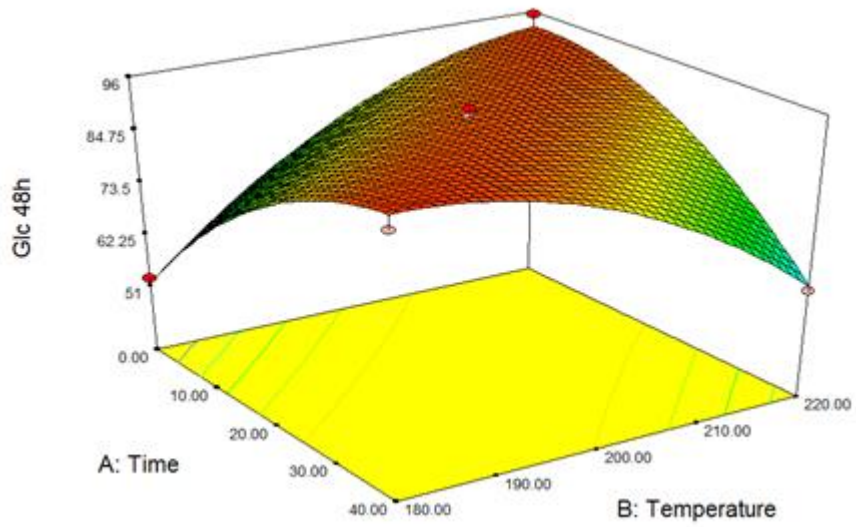


Figure 6.22b. Ternary graph showing the predicted % ED-48h values as a function of pretreatment time and temperature.

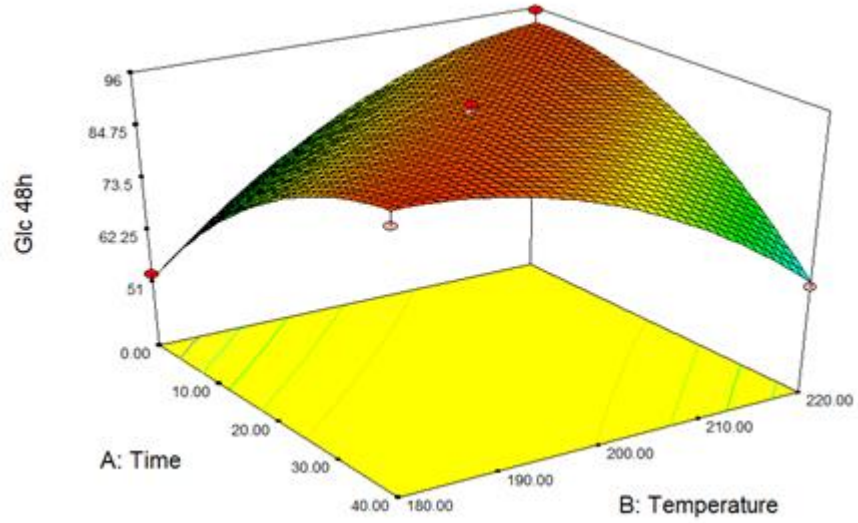


Figure 6.22c. Ternary graph showing the predicted % ED-48h values as a function of pretreatment time and acid concentration.

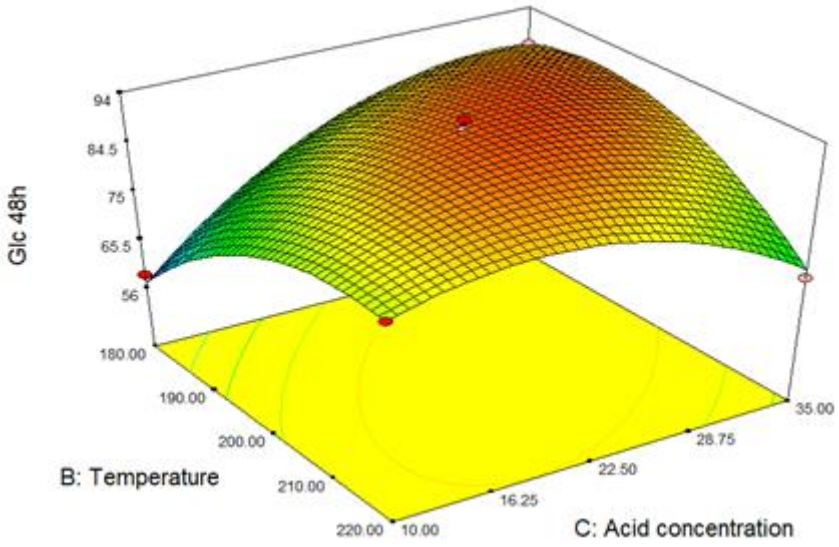


Figure 6.22d. Ternary graph showing the predicted % ED-48h values as a function of pretreatment temperature and acid concentration.

6.5.6 Optimization of pretreatment conditions with Box-Behnken design

Design Expert® software was used to optimize the conditions that provide the optimal results in a combined selection of responses. As it can be seen in Table 6.14,

three responses (% SRY, % GRL and ED-48h) were combined. The goal was to maximize the combinatorial percentage of these responses to find the conditions for high % SRY and considerable percentage of fermentable glucose in both acid and enzymatic liquid fractions. These conditions predicted SRY 69 % wt., with 26.9 % wt. glucose recovery and ED-48h equal to 84.8 % wt. This combination provided significant amount of pretreated solid mass that has substantial enzymatic digestibility. In Table 6.14 the value range of the three variables and the importance of both variables and responses are presented. Optimal conditions that maximize the efficiency of both % SRY %, GRL and % ED-48h values (200 ^{o}C, 0 min and 35 mM acid concentration) where chosen to compare MCW-S behavior to pure cotton.

Table 6.14. Upper and lower limits for the different variables studied in the experimental design and optimal conditions that maximize the % SRY, GRL and enzymatic hydrolysis after 48 h in a combined way.

Variable	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
t (min)	is in range	0	40	1	1	3
T(°C)	is in range	180	220	1	1	3
C H2SO4 (mM)	is in range	10	35	1	1	3
% SRY	maximize	20.1	94.5	1	1	3
% GR_L	maximize	2.5	27.5	1	1	3
% ED 48h	maximize	52.7	95.6	1	1	3

Solutions

t (min)	T(°C)	$C\ H_2SO_4$ (mM)	SRY %	GR_L %	% ED-48h	Desirability
0	200.0	35.0	69.0	26.9	84.8	0.784

In this study, dilute acid pretreatment was investigated as a possible process to enhance MCW glucose conversion in the liquid phase and its cellulose conversion to glucose in the solid phase via enzymatic hydrolysis. Glucose maximum conversion in the liquid phase was found to occur in intermediate conditions (200 °C, 0 min, 35 mM). Enzymatic hydrolysis of the solid fraction reached the maximum yield of cellulose conversion to glucose (95.6 %) after pretreatment at 220 °C, for 0 min and with addition of 22.5 mM SA. Enzymatic digestibility of pure cotton compared to MCW-S pretreated under the same conditions showed similar results, which underlines the potential of the proposed process to simultaneously provide sterilization and recycle MCW together with converting it into fermentable glucose with great output.

6.6. Acid hydrolyzed medical paper waste for ethanol production – fermentable sugars – glucose via enzymatic hydrolysis.

The aim of this study was to examine the possibility of using pretreated cellulosic MW as a remarkable source of glucose production and maximize enzymatic digestibility efficiency of cellulose. The pretreatment approach that was used to enhance medical paper waste enzymatic digestibility was sequential acid and enzymatic hydrolysis. The independent variables of the acid hydrolysis pretreatment conditions were time, temperature, and concentration of dilute acid solution. Diluted SA was chosen as the treatment solution. The acid hydrolysis temperature was 180, 200 and 220 ^{o}C, the acid concentration was 0.01, 0.0225 and 0.035 M and the isothermal reaction time was 0, 20 and 40 min. The combinations of the experimental conditions were depicted by using Stat-Ease 360, the latest-release of Design-Expert® software. These condition sets operated simultaneously for cellulose enzymatic digestibility optimization, as well as a sterilization procedure for the medical paper waste which contains many harmful and toxic substances for humans. The product of acid hydrolysis process was separated in solid cellulosic phase and liquid glucose containing phase. The solid product of acid hydrolysis was studied as a recycled sterilized material for fermentable to ethanol glucose production via enzymatic hydrolysis.

In the present study, dilute acid pretreatment followed by enzymatic hydrolysis was investigated as a possible process to promote MPW conversion to glucose. The main goal is to combine direct solubilization of the substrate and glucose removal in the liquid phase together with cellulose recovery in the solid fraction and subsequent conversion to glucose via enzymatic hydrolysis. Enzymatic digestibility of pretreated MPW showed that it can become a recycled, sterilized product with considerable output of fermentable glucose compared to untreated MPW.

Table 6.15 shows the experimental conditions used in this set of experiments, given by the software using RSM and box Behnken methodology. The experimental design is like the experimental design used to treat MCW, to make their results comparable.

Table 6.15. Design of Experiments according to Box Behnken methodology.

Experimental Run No.	Temperature T (^oC)	Time t (min)	Acid Concentration C_{H2SO4} (mM)
1	180	0	22.5
2	220	0	22.5
3	180	40	22.5
4	220	40	22.5
5	200	0	10
6	200	0	35
7	200	40	10
8	200	40	35
9	180	20	10
10	180	20	35
11	220	20	10
12	220	20	35
13	200	20	22.5
14	200	20	22.5
15	200	20	22.5

The autoclave experiments temperature profiles are given in Fig. 6.23(a), (b) and (c), as a function of the acid hydrolysis time of the pretreatment using the 2-L batch reactor. The preheating time, the isothermal period and the cooling time are shown in this figure. The pH values of the liquid phase resulting after the autoclave acid hydrolysis vs. (a) the initial concentration of SA solution used in each experiment, and (b) the combined severity factor in logarithmic form. The combined severity factor Ro* and its logarithmic form $logR_0$* are presented in Table 6.16 according to the Experimental Run No of the Box Behnken DoE.

Table 6.16. The values of Combined Severity Factor R_0 and Combined Severity Factor in logarithmic form logR_0*.*

Experimental Run No.	R_0^*	logR_0^*
1	38.2	1.58
2	756.0	2.88
3	353.0	2.55
4	5671.6	3.75
5	78.7	1.90
6	405.0	2.61
7	342.8	2.53
8	2411.9	3.38
9	79.6	1.90
10	316.2	2.50
11	1335.1	3.13
12	3964.0	3.60
13	608.8	2.78
14	902.3	2.96
15	821.4	2.91

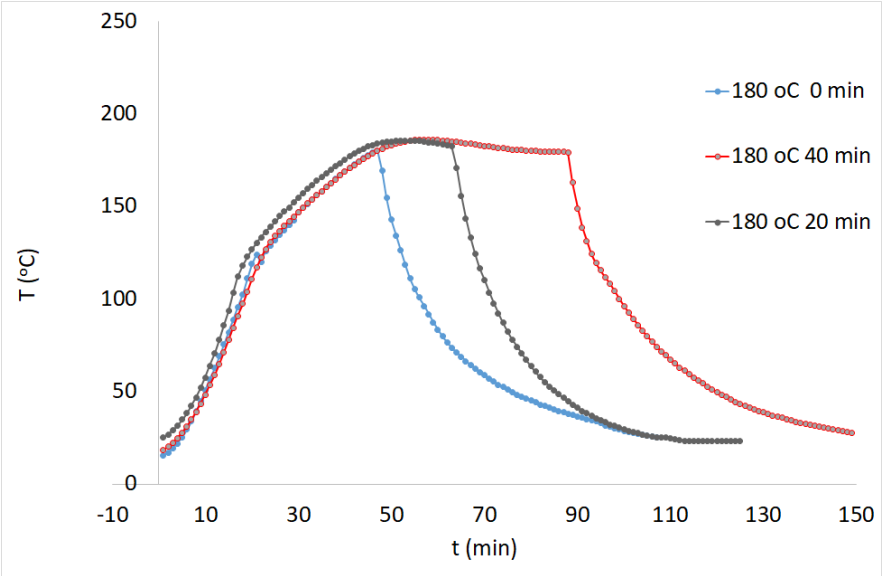


Figure 6.23a. Autoclave temperature profile vs. time of the acid hydrolysis batch experiments using the 2-L batch reactor (autoclave) at 180°C

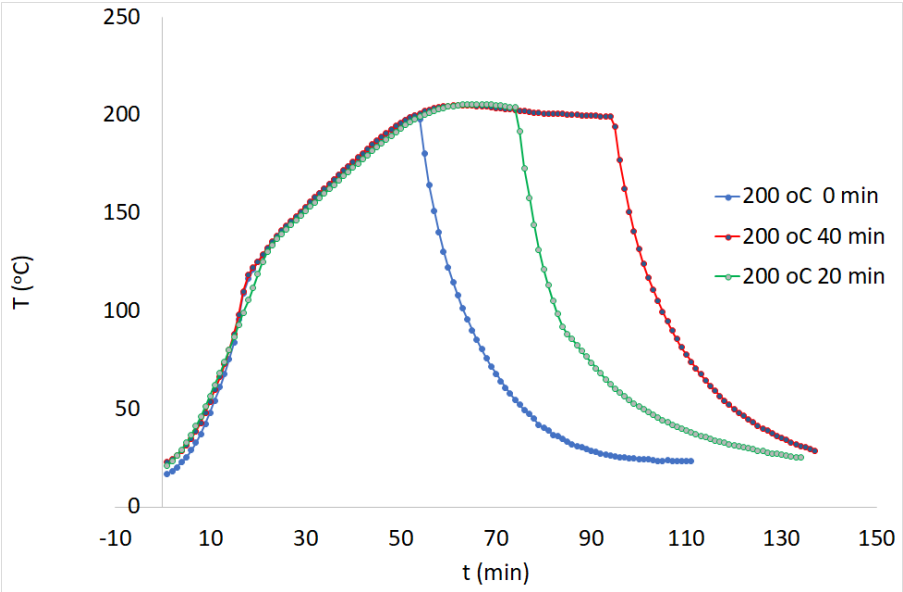


Figure 6.23b. Autoclave temperature profile vs. time of the acid hydrolysis batch experiments using the 2-L batch reactor (autoclave) at 200°C

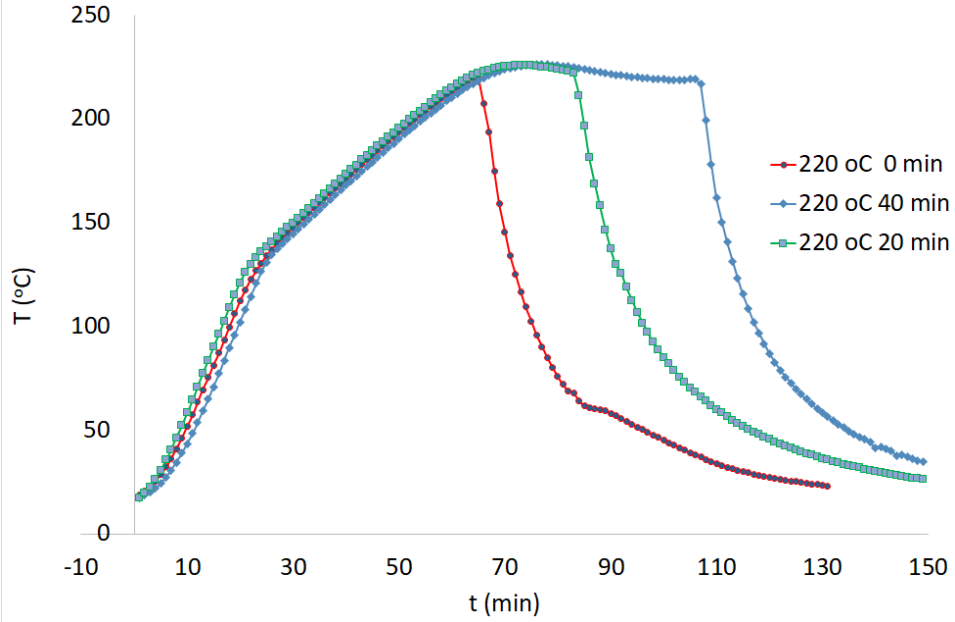


Figure 6.23c. Autoclave temperature profile vs. time of the acid hydrolysis batch experiments using the 2-L batch reactor (autoclave) at 220°C

The acid hydrolysis solid residue yield (SRY) is presented in Fig.6.24. Moreover, the acid hydrolysis solid residue cellulose recovery is shown in Fig.6.25 while the hemicelluloses recovery values of the solid phase, resulting after the autoclave acid treatment are given in Fig.6.26 as a function of the combined severity factor in logarithmic form $\log R_0$*.

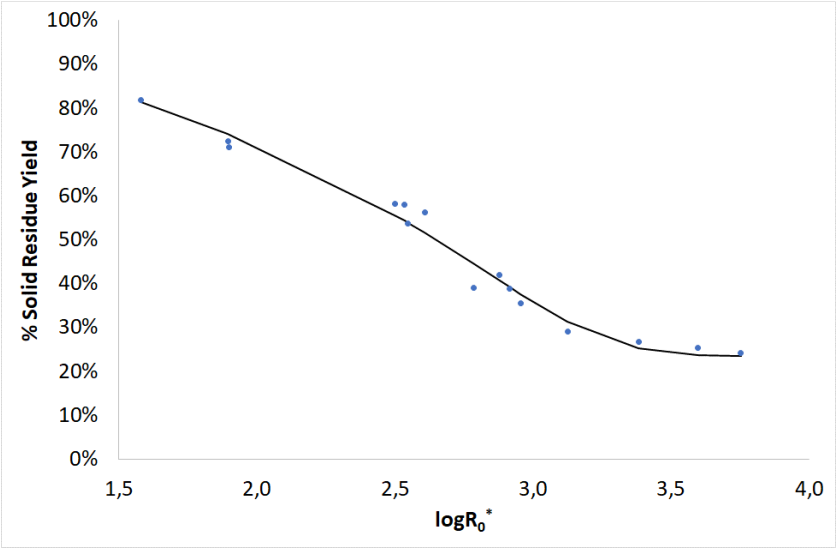


Figure 6.24. Solid residue yield (SRY) affected by logarithm of severity factor

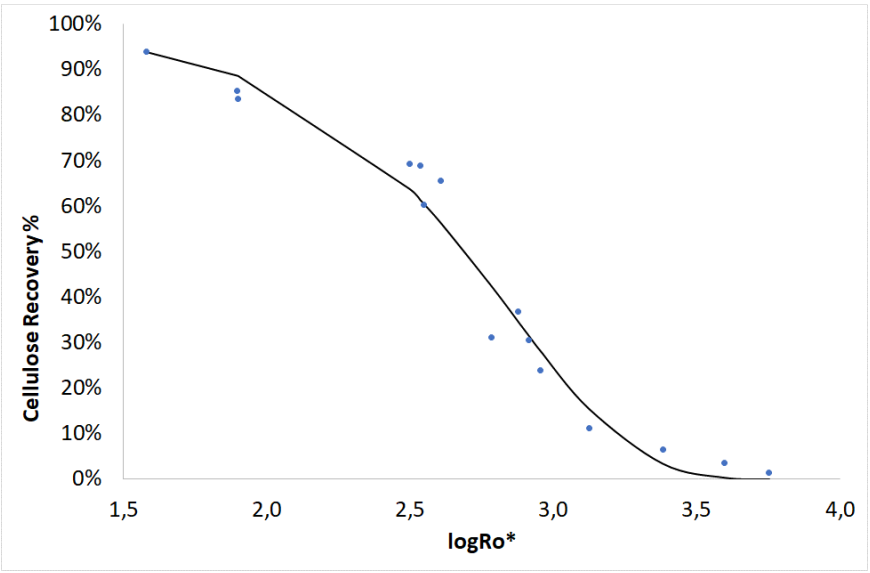


Figure 6.25 Cellulose recovery affected by logarithm of severity factor

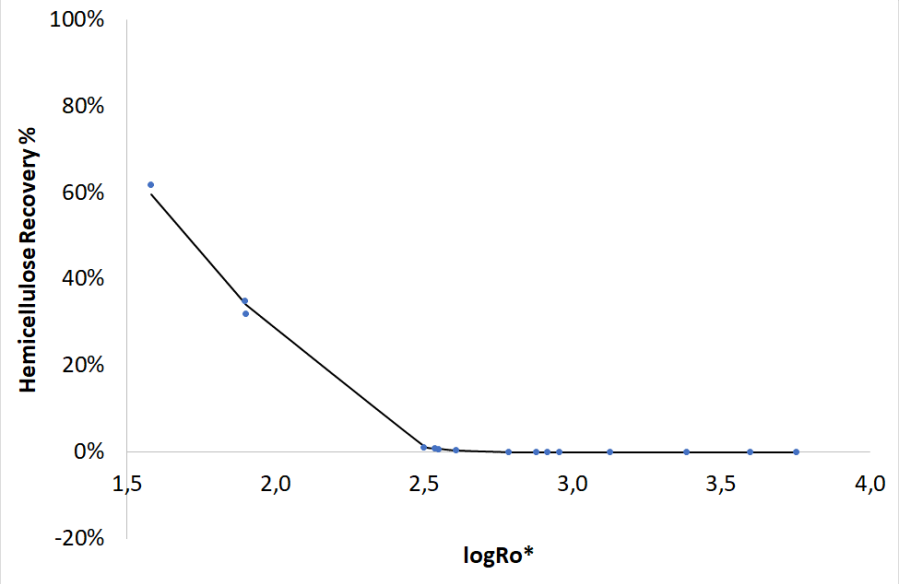


Figure 6.26. Hemicelluloses recovery affected by logarithm of severity factor

In addition, acid hydrolysis Glucose is given in Fig.6.27. Xylose is shown in Fig.6.28 and the Total Sugars values of the liquid phase, resulting after the autoclave acid treatment, are presented in Fig.6.29 via the combined severity factor in logarithmic form $logR_0$*.

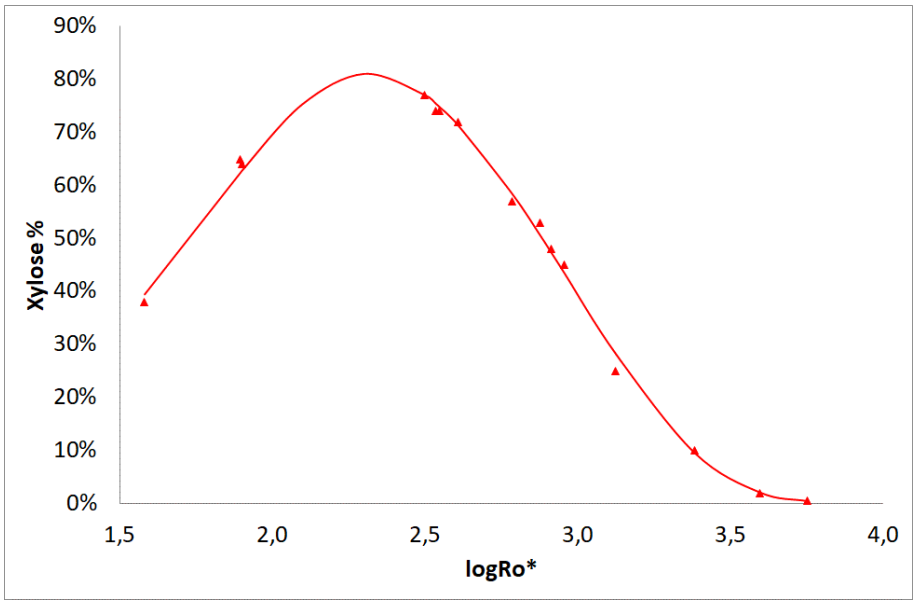


Figure 6.27. Xylose recovery affected by logarithm of severity factor

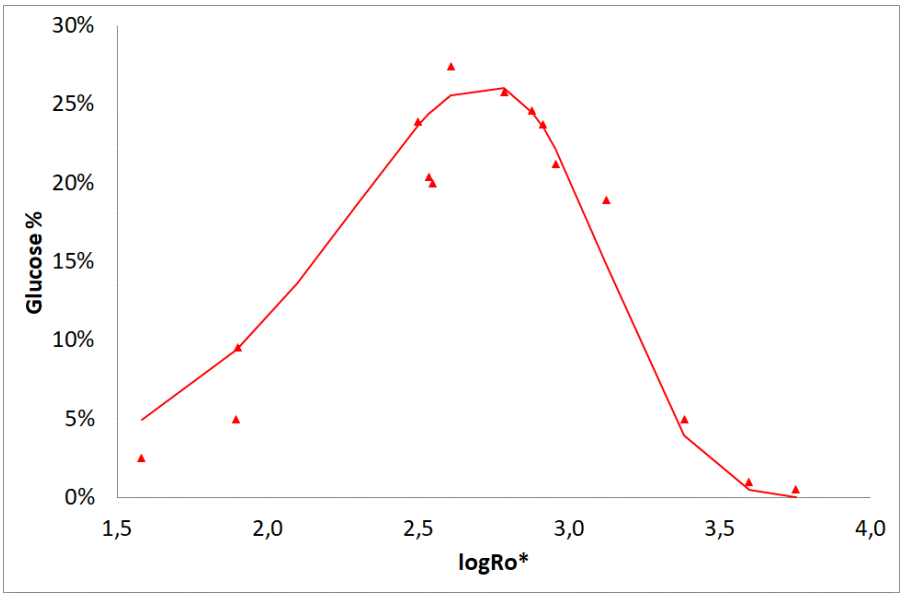


Figure 6.28. Glucose recovery affected by logarithm of severity factor

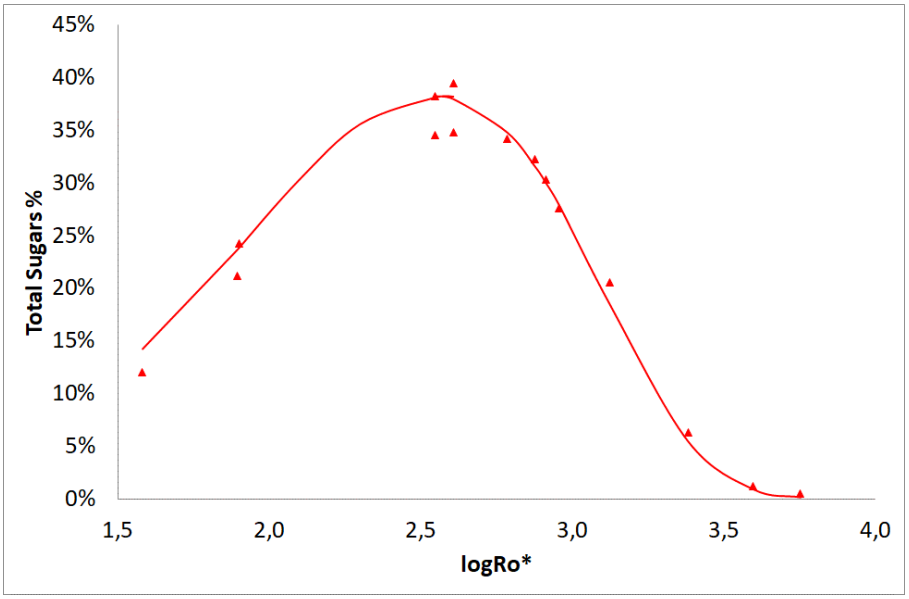


Figure 6.29 Total sugars recovery affected by logarithm of severity factor

In Fig.6.30 is presented the Cellulose Enzymatic Digestibility (CED) expressed as the enzymatic hydrolysis Glucose values, resulting after (a) 24 h and (b) 48 h enzymatic treatment of the acid hydrolysis cellulosic solid residue, as a function of the combined severity factor (in logarithmic form, $logR_0*$), of acid hydrolysis pretreatment.

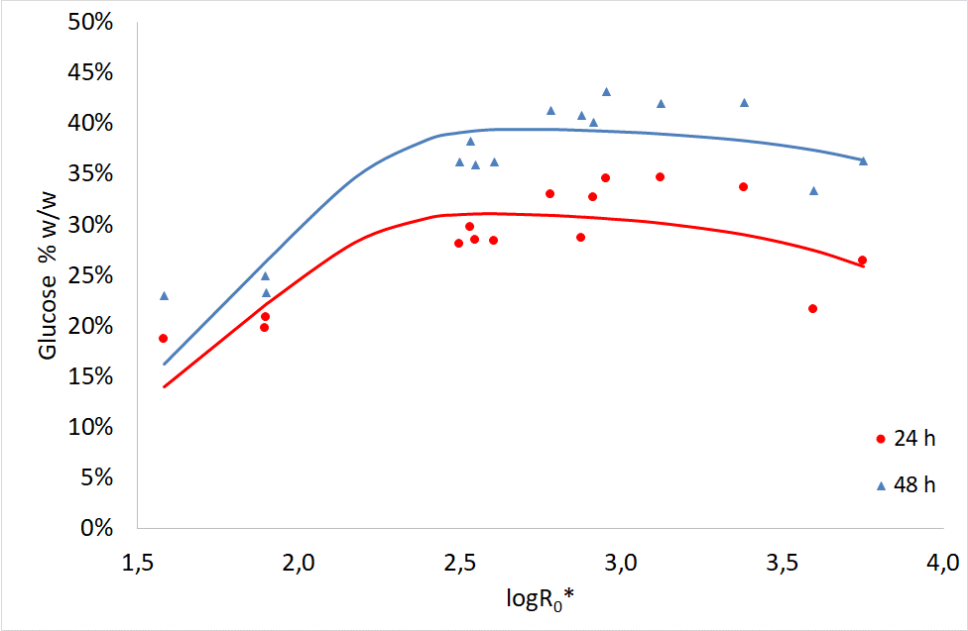
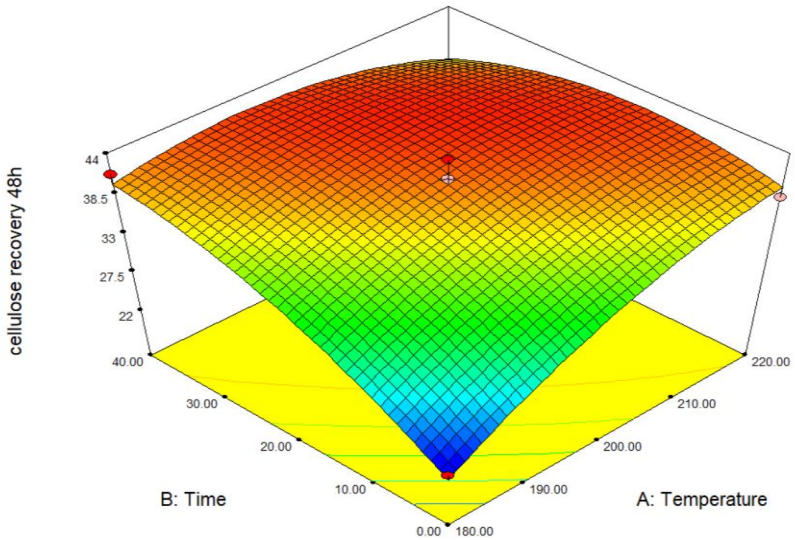


Figure 6.30. Cellulose Enzymatic Digestibility expressed as enzymatic hydrolysis Glucose values, resulting after (a) 24 h and (b) 48 h enzymatic treatment of the acid hydrolysis cellulosic solid residue, vs. the combined severity factor (in logarithmic form, $logR_0$)*

Moreover, in Fig.6.31 is shows the Cellulose Enzymatic Digestibility expressed as enzymatic hydrolysis Glucose values, resulting after 48 h enzymatic treatment of the acid hydrolysis cellulosic solid residue, as a function of (a) Temperature and Time of acid hydrolysis pretreatment, (b) Temperature and SA Concentration and (c) Time and SA Concentration of the acid hydrolysis pretreatment.



(a)

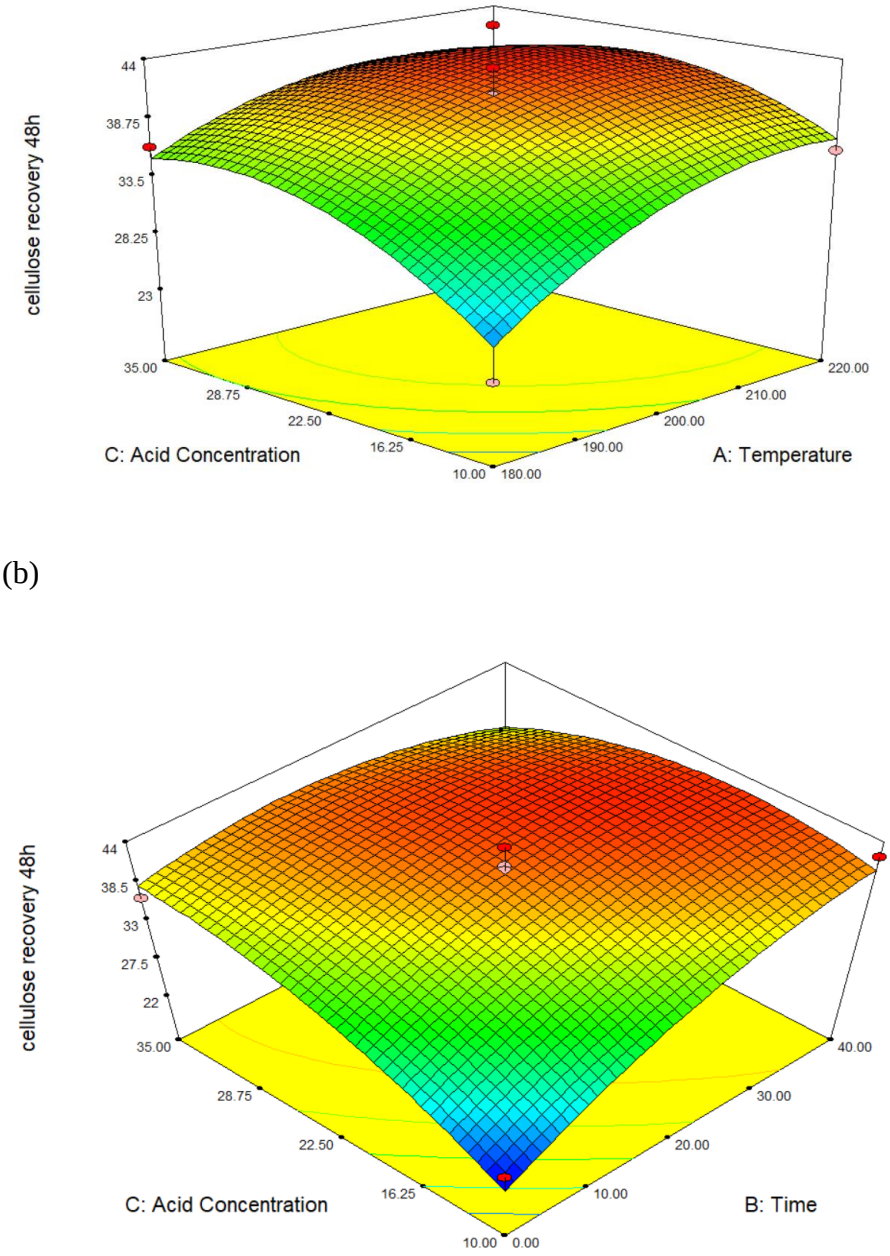


Figure 6.31. Cellulose Enzymatic Digestibility expressed as enzymatic hydrolysis Glucose values, resulting after 48 h enzymatic treatment of the acid hydrolysis cellulosic solid residue, vs. (a) Temperature and Time of acid hydrolysis pretreatment, (b) Temperature (c) Time and Sulfuric Acid Concentration of the acid hydrolysis pretreatment.

The dilute acid pretreatment followed by enzymatic hydrolysis of medical paper waste was investigated. Glucose and Total sugars were produced in the liquid phase, while cellulose recovered in the solid fraction converted to glucose via enzymatic hydrolysis. The enzymatic hydrolysis of pretreated MPW showed that it can become a recycled, sterilized product with increased output of glucose fermentable to bioethanol

compared to untreated material. The results showed that acid hydrolysis pretreatment of MPW can significantly enhance the cellulose enzymatic digestibility of the acid hydrolysis solid residue up to 43.2%, compared to 21.8% of the untreated one, and consequently increase the glucose total yield of the combined two-step process. According to the Response Surface Methodology, the optimal acid hydrolysis conditions to maximize the Cellulose Enzymatic Digestibility were 209 ^{o}C, 21 min isothermal time, and 25 mM SA, resulting to cellulose enzymatic digestibility up to 42.7%. The optimal Combined Severity Factor was $\log R_0$*=2.78. The use of solid waste to produce renewable liquid fuels is related to the bioeconomy/biobased economy under the concept of industrial ecology/symbiosis and zero-waste circular economy.

Dey et al. (2021), examined a combined fermentation procedure for effective transformation of pulp and paper slurry substance to bioethanol. They showed the possible application of pulp and paper slurry waste as feedstock for ethanol production, which can be embraced by industries as a green alternative to common solid waste management.

In accordance with Al-Battashi et al. (2019), worldwide need of bioplastic particularly polyhydroxyalkanoate have been increased in the last decades as an alternative to petrochemical-based plastic. Utilization of wastepaper, the main component of urban solid waste, as a carbon resource for polyhydroxybutyrate production is not just an unconventional, green route of waste management but also improves the waste valorization.

According to Michelin et al. (2020), growing environmental and sustainability worries, have encouraged a rising utilization of renewable bio-resources such as nanocellulose which has numerous striking features like non-toxic nature, biocompatibility, and biodegradability, related to its mechanical properties and those connected to its nanoscale, developing as a hopeful material in various sectors, like packaging, reformative medicine, and electronics, amongst others. Nanofibers and nanocrystals, derived from cellulose sources, have been mainly manufactured by mechanical and chemical treatments; however, using cellulases to acquire nanocellulose attracted considerable attention since it is environmentally friendly. Particularly, enzymatic hydrolysis using cellulases and utilizing of the pulp and paper industry residues are important regarding nanocellulose production. Combined process to produce nanocellulose and other high-value goods out of enzymatic hydrolysis are of great interest. This varies considering its properties, possible applications, and future perceptions when using enzymatic hydrolysis as a pretreatment in the scale-up of nanocellulose production.

Moreover, Kumar et al. (2020) examined the preparation of nanocellulose when wastepaper's cellulose was used to support the solid waste management under an economic environment protection attempt.

Annamalai et al. (2020), studied the effect of several pretreatments for effective hydrolysis of waste office paper and newspaper into sugars suitable for bioethanol through fermentation. The improved pretreatment and consequent ethanol production yields proposed that wastepaper could become a hopeful feedstock for bioethanol production.

Di Fidio et al. (2020), discovered that single cell oil signifies an excellent replacement of fossil resources and vegetable oils from food crops waste. They caried out a two-step process for the transformation of cellulosic paper mill waste into single cell oil. Hydrolysates including glucose and xylose were created by enzymatic hydrolysis of raw waste. The oil gained from a negative value industrial waste, was a promising platform chemical to generate biodiesel, biosurfactants, animal food and biobased plastics.

Enzymatic hydrolysis in bioethanol production presents an essential step, where sugars that are fermented, are acquired in the final fermentation step. Regarding enzymatic hydrolysis, many new efficient enzymes is found that ensure a further cost-effective process. There are various enzyme strategies applied in hydrolysis procedures, where several lignocellulosic biomasses, like wood feedstocks, various agricultural wastes, and marine algae are being used as substrates for an effective bioethanol production (Vasić et al. 2021).

The industrial production of sugar syrups from lignocellulosic materials requires the conduction of the enzymatic hydrolysis step at high-solids loadings. Such conditions result in sugar syrups with improved concentrations and in improvements in both capital and operational costs, making the process more economically feasible. This method has numerous technical problems that affect the procedure effectiveness, recognized as the "high-solids effect" (da Silva et al. 2020).

Nair et al (2020) utilized waste office paper as a feedstock for microbial lipid production using dilute SA pretreatment to boost the cellulose substance of wastepaper. Additionally, the lipid outlining of the acquired fatty acid methyl esters showed great similarities to vegetable oil, while the formed biodiesel properties were corresponding to the global specifications.

7. Conclusions

MWTTs can be separated to large scale and lab scale MWTTs. Incineration, pyrolysis, rotary kiln treatment, microwave/steam sterilization, and plasma gasification/melting form the large-scale technologies, while acid hydrolysis, combined acid and enzymatic hydrolysis, anaerobic digestion, autoclaving, enzymatic oxidation, hydrothermal carbonization/treatment, sulfonation, batch reactor thermal cracking, and torrefaction form the lab scale technologies. Large scale technologies find application in the total volume of MW as a whole or to majority of MW segregated fractions such as plastics and lignocellulose.

Laboratory scale MWTTs on their majority are on experimental stage. Their focus is to use MW fractions as feedstock to produce fuels (gas, liquid, solid) and materials. Such materials are cotton, paper, cardboard, textiles.

Among lab scale technologies, torrefaction, acid hydrolysis and sequential acid and enzymatic hydrolysis pretreatment were experimentally investigated thoroughly in this work.

As regards the experimental design, RSM via Box-behnken, and CSF were successfully applied to examine the behavior of MCW and MPW on the selected pretreatment conditions. The methodology and the selected pretreatment conditions used found to be appropriate for the above experiments. Graphs show that the optimal conditions of each set of experiments are in intermediate conditions and the desirability percentage very high.

The kinetics models applied found to have good fitting with the experimental results which proves that they were correctly chosen. As it was analyzed in the discussion of each experiment, the results found to match literature and are comparable with other materials pretreated likewise.

Torrefied MCW showed improvement regarding its HHV and adsorbance. More specifically, torrefied medical cotton became sterilized and had 20,6 MJ/kg HHV, 26% greater compared to raw medical cotton. Regarding its adsorbency ability, torrefied MCW showed great increase compared to raw cotton. The severest conditions maximized adsorbency of MCW when removing MB from wastewater. The increase was from 0.456 mg/g of raw MC up to 2.57mg/g. Mild conditions though, provided similar, to

intense conditions, results (2.36 mg/g) with lower solubilization. Torrefied MCW in both cases showed that it responds well as a heating material, or as an adsorbent compared to untreated medical cotton. Moreover, MCW after pretreatment is considered a sterilized recycled material.

Acid hydrolysis was also examined for its capability of making MCW a potential heating material or a low-cost adsorbent. When HHV was examined, the results showed that most tense conditions lead to greater solubilization and thermal energy output. The difference between acid hydrolyzed MCW and raw MCW was 53% with HHV reaching, 24.9 MJ/kg. The experimental design used to examine acid hydrolysis effect to MCW gave the following results regarding adsorbance. Adsorbance reached 3,609mg MB per g of MCW compared to 0.456 mg/g of the untreated material. This increase concludes that acid hydrolyzed MCW could be used as a low-cost adsorbent for the removal of basic dyes and other types of pollutants from wastewater.

Another approach applied was the sequential acid and enzymatic hydrolysis of MCW and MPW to produce fermentable glucose for multi purposes. MCW gave its maximum efficiency of both % SRY, % GRL, and % ED-48h values at the proposed conditions of RSM (200 ^{o}C, 0 min, 35 mM). MCWs' solid fraction reached 95.6% cellulose conversion to glucose when treated at 220 ^{o}C, for 0 min using 22.5 mM SA. Enzymatic digestibility of pure cotton showed comparable results to MCW-S when both were pretreated at same conditions. This results to the simultaneous sterilization and recycling of MCW alongside with converting it into fermentable glucose with considerable yield.

MPW was also treated likewise. The results demonstrated that acid hydrolyzed MPW can considerably improve the solid residues enzymatic digestibility up to 43.2%, compared to 21.8% of raw MPW, and therefore improve the glucose total output of the combined two-step process. Response Surface Methodology proposed the optimal conditions that enhance enzymatic digestibility (209^{o}C, 21 min isothermal time, and 25 mM SA).

As regards suggestions for further research, MPW adsorbance and HHV capabilities are expected to be studied in the near future. A matter of significant interest would

be the of co-processing of MW plastic and/or cellulosic/lignocellulosic fractions with similar municipal/industrial solid waste and/or agricultural/forest lignocellulosic fractions aimed for industrial fuels/materials production.

Moreover, to make the step from laboratory scale MWTTs to full scale facilities, further research is needed to achieve increased energy efficiency, enhanced materials production, sufficient financial viability, and sustainability within the zero-waste circular economy concept. More work must be done as regards the MW segregation redesign

providing easier access to MW fractions that can be used as potential recyclable materials. This would have a great benefit on cost reduction to make MWTTs' processes financially sustainable. The sustainable function of an MWM system needs effective MW logistics and sense of balance among MWG locations and MWT facilities. Simulation and optimization could be performed to investigate the economic feasibility of torrefaction, acid hydrolysis and enzymatic hydrolysis technologies. The application of sensitivity and uncertainty analysis would indicate the effects of various technical and financial factors, like MWFs availability, quality, transportation cost, and workers' wages, on production costs.

Another topic appropriate for experimental future research, considering the relative literature, is the DoE to examine the suitability of fruit pits and other food waste collected from MW, as heating materials and adsorbents. This could lead into a wider range of MW exploitation than the examined herein. Similar experiments could be also extended to include cardboards and fabrics that are lignocellulosic materials within the idea of co-processing them as lignocellulosic MW.

A recent matter of interest for future research, is the study of the above examined or mentioned fractions as regards their feasibility as a resource of nanocellulose/cellulose nanocrystals production. Nanocellulose production from such resources seems to arise via acid hydrolysis with high efficiency. Nanocellulose is high added value material that can find application in many purposes of the modern era such as using it as a strengthening agent in paper and cardboard production. It can also be used as Kevlar or carbon substitute and in the design of flexible OLED displays.

Abbreviations

MW: Medical Waste

MWG: Medical Waste Generation

MWC: Medical Waste Classification

MWT: Medical Waste Treatment

MWTT: Medical Waste Treatment Technology

MWD: Medical Waste Disposal

MWF: Medical Waste Fractions

MWM: Medical Waste Management

MCW: Medical Cotton Waste

MPW: Medical Paper Waste

MCW-S: Medical Cotton Waste Substitute

MWGR: Medical Waste Generation Rate

CED: Cellulose Enzymatic Digestibility

CE: Circular Economy

DoE: Design of Experiments

DNS: Dinitrosalicylic Acid

EPA: Environmental Protection Agency

ERA: Energy Recovery Analysis

ERE: Energy Recovery Efficiency

ED: Enzymatic Digestibility

GRL: Glucose Recovery from Liquid

LCA: Life Cycle Assessment

LCC: Life Cycle Costing

NLRA: Non-Linear Regression Analysis

NREL: National Renewable Energy Laboratory

HHV: Higher Heating Value

HPLC: High Performance Liquid Chromatography

QS: Quantitative saccharification

SEE: Standard Error Estimate

CSF: Combined Severity Factor

SF: Severity Factor

SA: Sulfuric acid

SRY: Solid Residue Yield

WHO: World Health Organization

XRD: X-Ray Diffraction

HMW: Hazardous Medical Waste

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