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January 01, 2021
Prof. Dr. Aytekin ISMAN
Sakarya University

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A NOVEL ACTIVATED CARBON FROM NON LIVING LICHEN CETRARIA ISLANDICA (L.) ACH

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ABSTRACT
Activated carbons obtained from different sources are used for a wide variety of purposes. For example, they are frequently used in wastewater treatment, energy storage, gas purification, catalysis support materials and removal of environmental pollutants. As far as we know, lichens are rarely used in activated carbon production. However, it is more economical and sustainable to produce activated carbon from lichens. Lichens, which can be found in many regions of the world and have a wide variety of species, are organisms consisting of symbiotic combination of fungi and algae. In this study, activated carbon was produced using *Cetraria islandica* (L.) Ach. lichen (LCI) collected from Çankırı region in Turkey. Chemical activation was performed with $ZnCl_2$. Carbonization was carried out in an ash furnace under nitrogen atmosphere at 768 ºC for 1 hour. The surface area and pore size distribution of the ACCI and LCI were determined by BET analysis. Physicochemical properties of both the ACCI and LCI were examined by FTIR and TGA analysis. Morphological properties were analysed by XRD and SEM techniques. The BET surface area of the ACCI and LCI was found as 394.417 m^2g^{-1} and 1.103 m^2g^{-1}, respectively. While the LCI had a heterogeneous surface morphology, the synthesized ACCI had a homogeneous and porous surface structure. It was found that activation and carbonization processes caused very significant changes in the LCI molecular structure and surface morphology. As a result, a novel activated carbon with relatively high surface area was successfully synthesized.

Keywords: Activated carbon, Lichen, chemical activation

Introduction

An activated carbon can be defined as a carbonaceous material with increased surface area and pore volume by physical or chemical activation of substances with a high content of carbon. It is known that the most important parameter for activated carbon is the surface area (Yagmur, 2008). In order to determine the surface area, the BET method, in which the physical adsorption of nitrogen gas on the activated carbon, is generally applied and the surface is expressed as the BET surface area (m^2g^{-1}). Another important feature is porosity. IUPAC classified the adsorbents according to their pore size radii as follows: Macro (r> 25 nm), mezo (25 nm> 1 nm), micro (1 nm> r> 0.4 nm) and submicro (0.4 nm> r) (Dolas, 2011). The pore structure is effective in determining the adsorption capacity, and the active regions and functional groups on the surface determine whether the adsorption will be feasible or not. Carbonization and activation (physical or chemical) processes are performed to increase the volume and radius of the pores and to create new pores (Rafatullah, 2010). Since the chemical activation process is carried out at a lower temperature and in a shorter time, it is more preferred than physical activation. Zinc chloride is also a frequently preferred activation chemical in chemical activation processes

Of course, most substances with sufficient carbon content, easily available and low cost can be used to produce activated carbon. However, the raw material used in the production of activated carbon significantly affects the chemical and physical properties of the produced activated carbon. In recent years, some biological materials such as agricultural waste, some plants, fruit peels are preferred to produce low cost activated carbons by the researchers (Danish, 2018, Chieng, 2015, Ioannidou, 2007, Jain, 2003, Koyuncu, 2020). Cetraria islandica (L.) Ach. (LCI) which is a kind of lichens species, occurs in damp places such as coastal plains, lichen woodlands, bogs and tundra, usually on rocks or the conifer-hardwood trees (Meli, 2018, Crawford, 2015, Koyuncu, 2020). To the best of our knowledge, the production of activated carbon from LCI has not been investigated (Koyuncu, 2020). In this study, a novel activated carbon (ACCI) was obtained from LCI, and characterizations of both the ACCI and the LCI were examined by Brauner-Emmett-Teller surface area (BET), X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) techniques at the first time (Koyuncu, 2020).

Materials and Methods

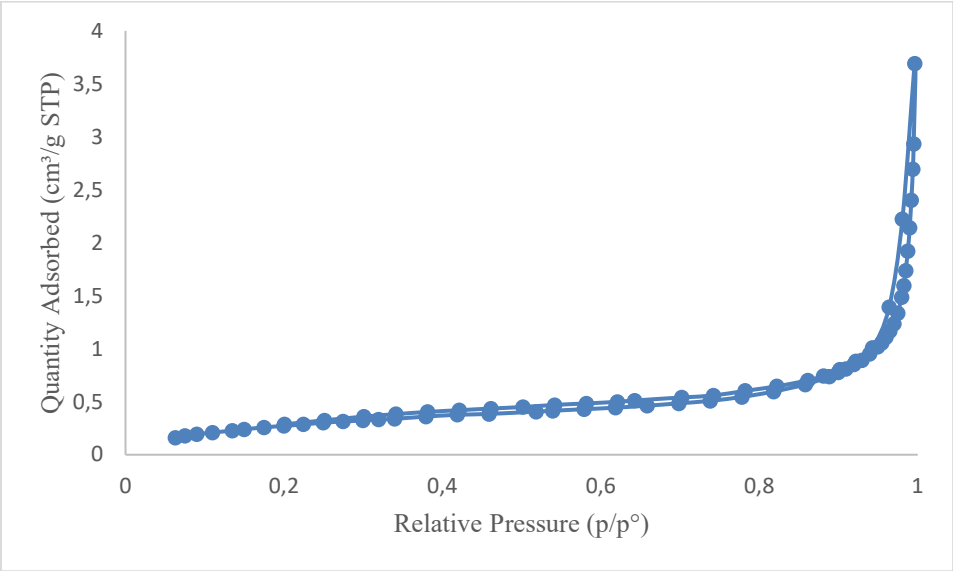
Firstly, the LCI samples were collected from Yapraklı Forest in Çankırı (Turkey). Then non-lichen foreign materials were carefully removed manually under the microscope and the samples were washed several times with

distilled water to remove soil, dust and some salts (Koyuncu, 2020). The biomass sample was dried in an oven at 105 ºC for 24 hours and ground in agate mortar using liquid nitrogen. Then it was sieved through a 230 mesh sieve and chemically activated with zinc chloride at a 1/1 (w/w) impregnation ratio. The mixture was dried and carbonized in an ash furnace under nitrogen atmosphere at 768 ºC for 1 hour. Chloride and zinc ions were removed by washing and filtration processes, and the sample was dried and sieved again (Koyuncu, 2020).

The synthesized ACCI and the LCI were characterized by using BET (Micrometrics-Tristar II), FT-IR (Nicolet-IS50), XRD (Bruker AXS/Discovery), TGA (TA/SDT650) and SEM/EDX (Zeiss GeminiSEM 300) (Koyuncu, 2020).

Results and Discussion

According to the IUPAC (International Union of Pure and Applied Chemistry) classification, the LCI complies with type III isotherm and the ACCI complies with type I isotherm (Figure 1) (Koyuncu, 2020). It is known that the pore size distribution is predominantly in the micropore region in materials fit the type I isotherm. As shown in Figure 1, the pore size distribution of the ACCI was in the micropore region, whereas, it was in mesopore region for the LCI (Koyuncu, 2020, Koyuncu, 2014). Besides, the BET surface area, Barrett-Joyner-Helenda (BJH) adsorption total volume of pores and BJH adsorption average pore diameter of the LCI and ACCI were determined as 1.103 m^2g^{-1} and 394.417 m^2g^{-1}, 0.0044 cm^3g^{-1} and 0.1216 cm^3g^{-1}, 140.18 Å (14.02 nm) and 12.768 Å (1.28 nm), respectively (Koyuncu, 2020).



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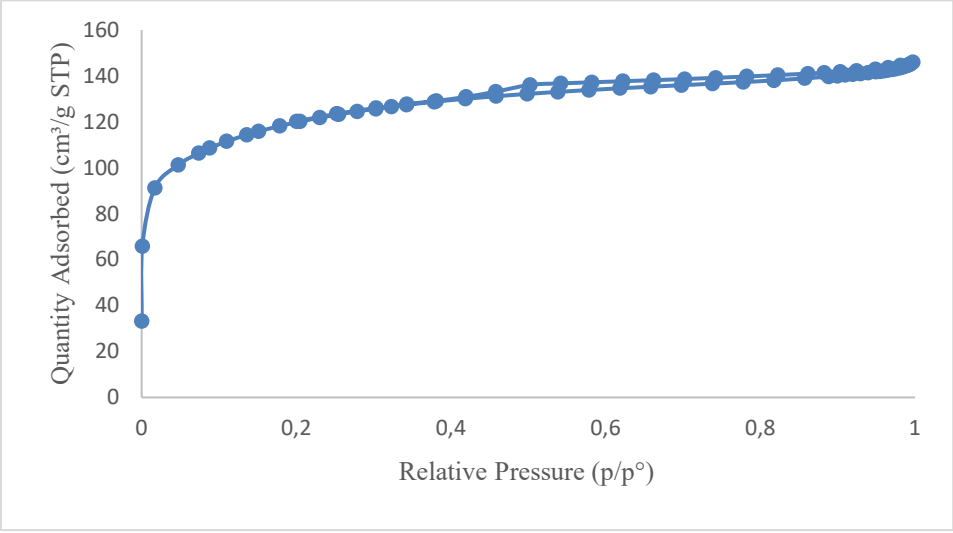

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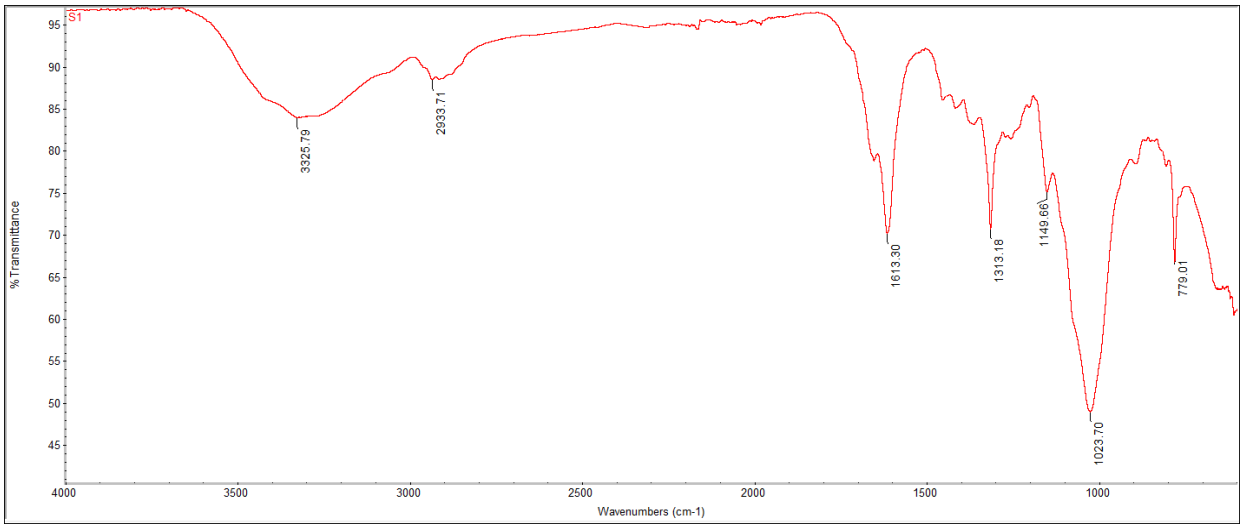
Figure 1. BET isotherms of the LCI (a) and ACCI (b).



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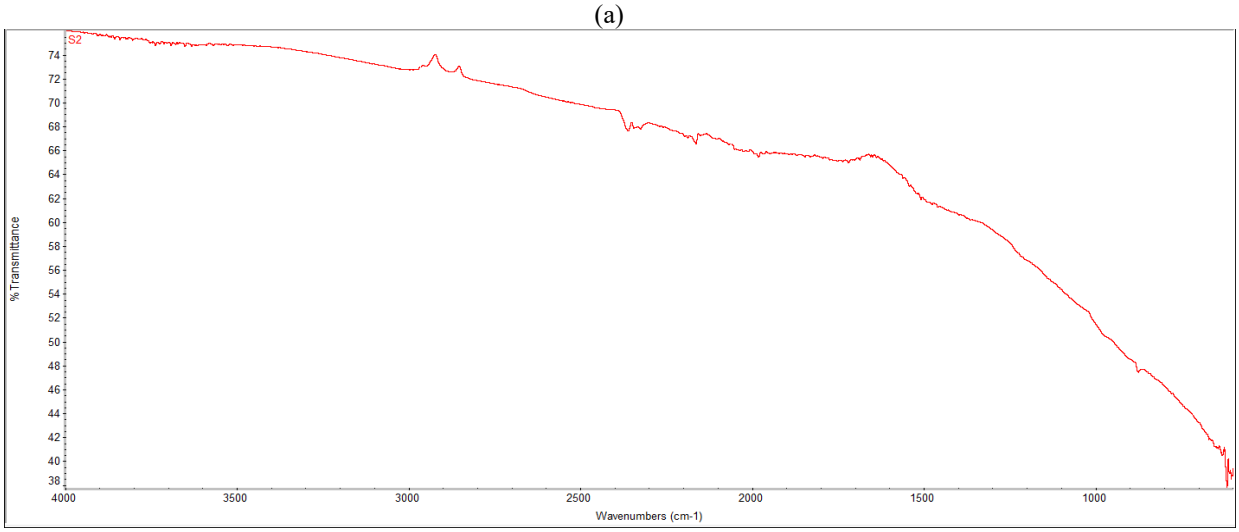
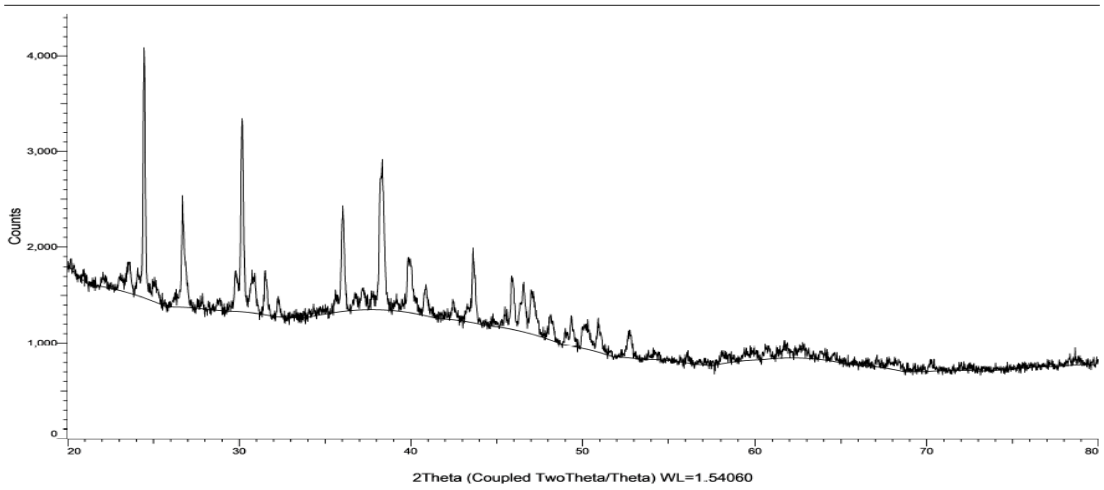


(b)

Figure 2. FTIR curves of the LCI (a) and ACCI (b).

The FT-IR ATR spectrums of the LCI and ACCI were shown in Figure 2 (a, b) (Koyuncu, 2020). The wide band around 3300 cm^{-1} was due to stretching vibrations of –OH groups (Koyuncu, 2020). The peaks at about 2933 cm^{-1} and 1610 cm^{-1} was related to aliphatic C–H, and aromatic –C=O and –C=C bonds stretching, respectively. The peaks at 1155 $cm^{-1}$and 1294 cm^{-1} were from stretching vibrations of the ester group and symmetrical vibration of –COO bond, respectively (Koyuncu, 2020). The peak observed at 1023 cm^{-1} was assigned to stretching vibration of C–O bonds. As can be seen from the Figure 2b, there was a significant change in functional groups in the structure with the effect of the chemical activation and carbonization processes (Koyuncu, 2020). In addition, the results of these effects on the molecular and crystalline structure of the LCI biomass are shown in XRD diffractograms (Figure 3 a,b). We can say that the ACCI contains sharp peaks indicating more crystalline structure, and the peaks at $2\theta = 31.8^{o}$, 34.5^{o}, 36.5^{o} belong to activated carbon (Koyuncu, 2020).



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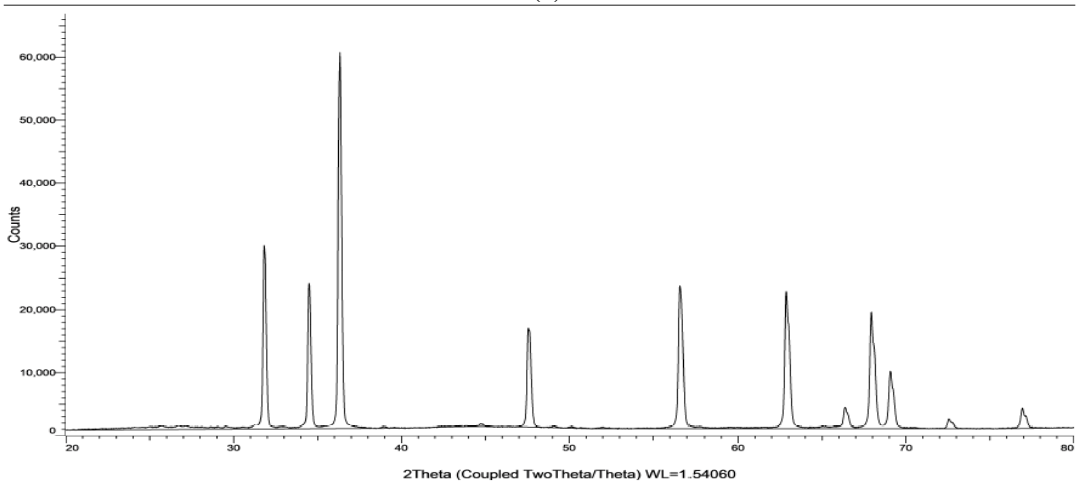
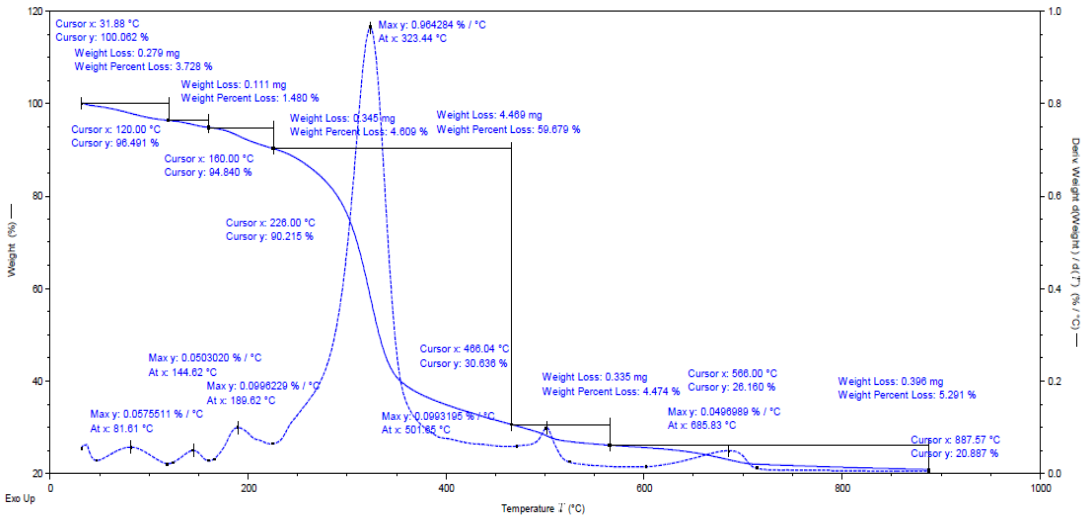


(b)

Figure 3. XRD patterns of the LCI (a) and ACCI (b).

Thermogravimetric analysis results of the LCI and ACCI were shown in Figure 4. Except the initial moisture loss, no significant degradation of the LCI was observed up to 350ºC (Figure 4a) (Koyuncu, 2020). However, the ACCI showed very stable temperature profile, and almost no degradation was observed until 750ºC (Figure 4b) (Koyuncu, 2020).



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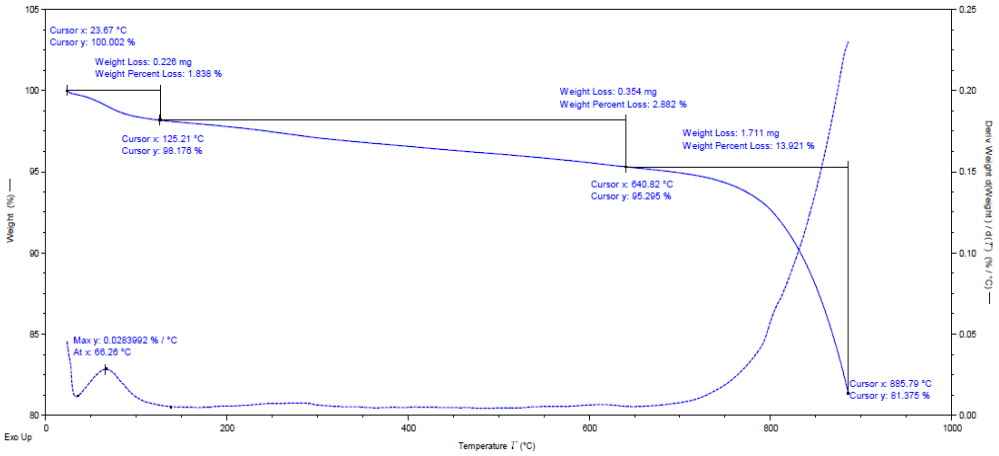
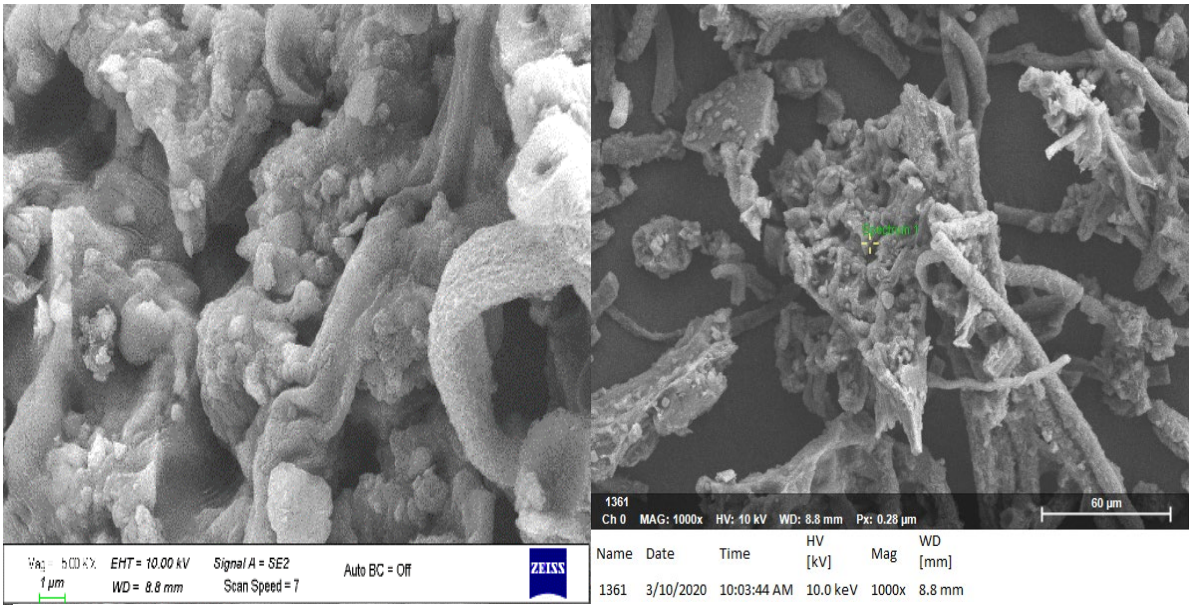


(b)

Figure 4. TGA curves of the LCI (a) and ACCI (b).



Name	Date	Time	HV [kV]	Mag	WD [mm]
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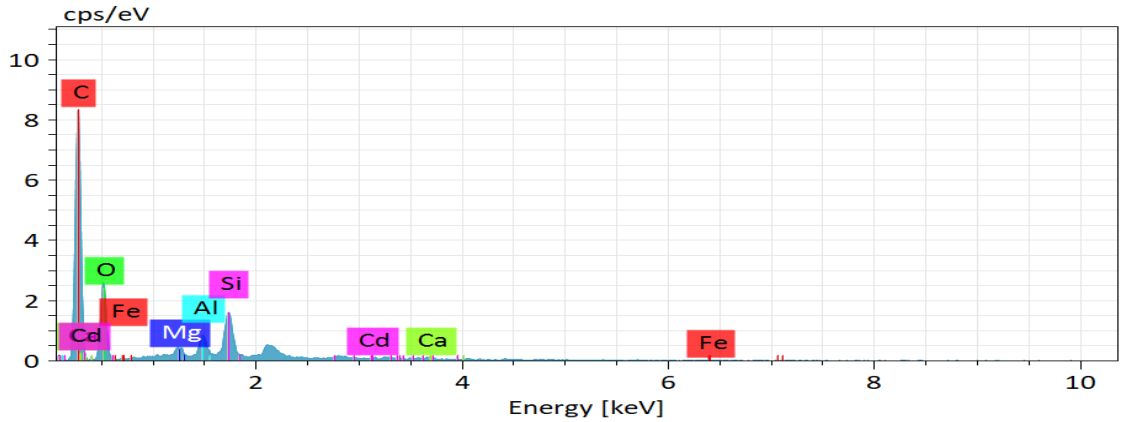
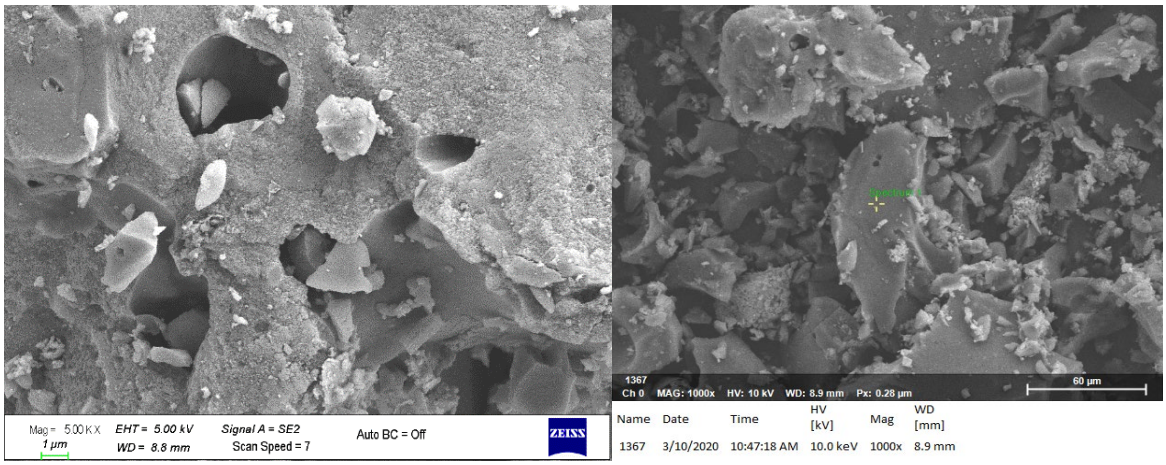
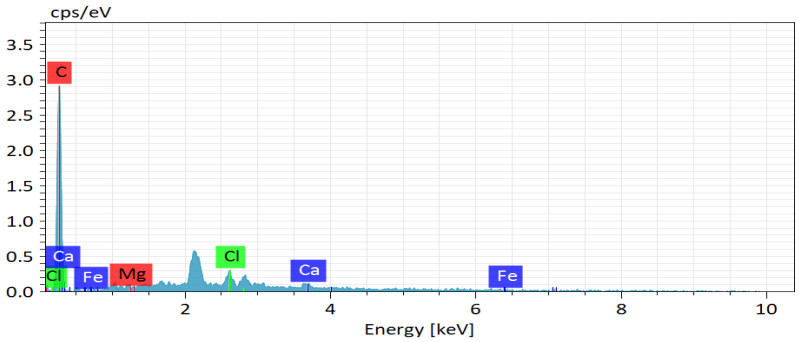


Spectrum	Carbon	Oxygen	Magnesium	Aluminium	Silicon	Calcium	Iron	Cadmium
Spectrum 1	61.66	25.95	0.91	2.24	7.48	0.79	0.73	0.25

(a)





Spectrum	Carbon	Magnesium	Chlorine	Calcium	Iron
Spectrum 1	86.64	0.39	4.88	4.50	3.60

(b)

Figure 4. SEM/EDX results of the LCI (a) and ACCI (b).

SEM images and EDX results of the LCI and ACCI were given in Figure 4 (Koyuncu, 2020). As can be seen from the Figure 5a, the LCI has heterogeneous surface, and the elemental compositions of the LCI surface consist of 61.66% carbon, 25.95% oxygen, 0.91% magnesium, 2.24% aluminium, 7.48% silicon, 0.79% calcium, 0.73% iron and 0.25% cadmium. It should also be noted that the chemical composition is not the same at all points for heterogeneous surfaces.

The carbonization and the chemical activation processes led to have a more homogeneous and porous surface of the ACCI (Figure 4b) (Koyuncu, 2020). The elemental compositions of the ACCI surface are determined with EDX analysis, and found as 86.64% carbon, 0.39% magnesium, 4.88% chlorine, 4.50% calcium and 3.60% iron. As a result, the carbon composition (in percent) of the ACCI was increased from 61.66% to 86.64% by the activation and carbonization processes.

Conclusion

A novel activated carbon was produced from the non-living LCI for the first time, and the physicochemical and morphological properties were characterized. The BET surface area of the ACCI was determined as 394.417 m^2 g^{-1}. The pore size distribution of the ACCI was in the micropore region, and the pore diameter found as 1.28 nm.

The effects of chemical activation and carbonization processes on the surface were evaluated using different analysis techniques. Summarizing, we can say that the ACCI surface was more crystalline structure, more stable temperature profile and more porous and homogeneous surface than that of the LCI surface.

As a result, we think that the ACCI with high surface area can be utilized in many industrial fields as an effective biosorbent.

Acknowledgements

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AN EXPERIENCE OF IMPLEMENTING ICONIX, A SOFTWARE DEVELOPMENT METHODOLOGY, IN A SOFTWARE DEVELOPMENT CLASS DICTATED IN A PRIVATELY MANAGED UNIVERSITY FROM ARGENTINA, VIRTUALLY, DUE TO THE QUARANTINE

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ABSTRACT
Due to the mandatory quarantine implemented in most countries, and especially where this investigation is taking place, Argentina, most Academic organizations, either public or privately managed, needed to reinvent themselves in order to be able to teach courses in a completely remote environment. In this context, one class, which has the objective of develop a specific software and where this research took place, will use ICONIX, a software development methodology that is one of the latest technology standards used in the software industry, and flipped classroom, where instead of professors teaching students, they provide them with all the necessary information so they can study them before the class takes place. Given that this class has been always taught face-to-face and under other software development methodologies, the purpose of this paper is to evaluate the experience and take relevant data, measurable, about the degree of acceptance of both students and professors, in order to conclude if this virtual experience can be replicated after the quarantine period ends, replacing, if possible, the classroom teaching for a more up-to-date approach, taking advantage of the latest tools that have been developed for communicating, creating, distributing, grading assignments and sharing files and knowledge between teachers and students.

Introduction

As cited in [1], “during history nothing has caused more human deaths than infectious diseases". COVID-19, as of today, has shown us how vulnerable we still are to these invisible and unknown threats. Also known as “Coronavirus”, COVID-19 is an infectious disease caused by the SARS-CoV-2 virus strain (Severe acute respiratory syndrome Coronavirus 2) and it was identified at the end of 2019, by December, in Wuhan, capital of Hubei, a province in China. Since that moment, its spread has not stopped, resulting in the COVID Pandemic we stand now. As of today, more than 32 million cases have been reported in more than 210 countries, with over 990000 deaths around the globe. On the other hand, luckily, more than 22 million people have recovered from it. COVID-19 was declared a pandemic by the World Health Organization (OMS) on March 11th because of its alarming rates of propagation and severity. The term “Pandemic” is used when a new disease is spread worldwide, where most of the persons do not have immunity for it [2]. The first case in Argentina was detected in a 43 year old man that had been in Italy recently, this also made this the first imported case of COVID-19. By March 4th, the number of suspected cases due to suspicious symptoms was around 10. On March 5th, the second case was officialized in Argentina, a 23 year old young man that also had been abroad. On March 6th, Argentina officialized 8 COVID-19 cases. Unfortunately, by March 7th, Argentina had the first disease due to the infection. Days passed by and the number of infected and diseased people increased. Therefore, the Argentinian President, through the decree 297/2020 in March 18th officialized the quarantine, which was called “Preventive and mandatory social isolation”, in order to protect public health and prepare hospitals to be able to handle severe cases. During its validity, people must remain in their residences, abstaining themselves from attending their workplaces, without being able to drive in public ways, lanes and public places, with the final purpose of reducing the circulation of

people and the possibilities of getting infected with COVID-19. Because of this disposition, educational entities and institutes, in all educational levels, were forced to close their physical buildings and started the process of "digital transformation". This means that courses had to be migrated to a virtual format.

High education institutes and universities, like for example UTN BA (National Technological University from Buenos Aires), through one of its internal organism "EAD" (Distance Education Directorate), had been working, taking several orientational actions, support and training, in order to be able to dictate courses, virtually, across all careers [3]. Virtual classrooms were implemented using their internal software, already in place, which is also used to manage classes, classrooms, information, communication and several more functionalities, for both students and professors. The main challenge for the University was reaching all classes and careers in a short period of time and measuring the teaching learning process exclusively using their internal tools. The UNR (National University from Rosario, Santa Fe, Argentina) has implemented virtual classrooms to assure the academic year. In the case of the UBA (University from Buenos Aires) has decided to reschedule their academic calendar. This was decided to guarantee that students take classes in person without exposing them to a possible contagion. Given the size of the UBA (over 300000 students), is that some of their Faculties made exceptions, like the Faculty of Exact Sciences where some of their careers are using virtual methods to assure courses and classes are given [5, 6]. The Austral University (Privately managed University) has made available to students and professors the "Plan de continuidad de actividades académicas COVID-19" (COVID-19 Academic Activities Continuity Plan) [7], with the intention of assuring that all academic activities take place. This, basically, establishes guidelines of how classes will take place, which tools are going to use, general rules and code of conduct.

Institutional Situation

The privately managed educational institution from Rosario, Argentina, where this work took place, was ready, partially, to face the challenges of virtual education. From one side, they had already started with blended education, four assignments are dictated using that methodology, with a remote percentage of classes, up to 50%. This proposal finds its foundations, first, in the article "Educación Superior y Tecnología: la propuesta de Educación A Distancia en Argentina y su marco legal" from Ana Carolina Ezeiza-Pohl [8], that describes the remote education proposal and its legal framework; and the legal resolution 1717/2004 from the Science, Technology and Education Ministry [9]. This resolution describes the general dispositions of remote education. Also, the University already had a contingency protocol in cases where, due to extreme circumstances, this needs to remain closed and virtual classes are implemented. That is why, with the spread of COVID-19 in Argentina and the strict quarantine that was decreed in March the 20th, the University was forced to close their physical doors of all its dependencies and execute their contingency protocol.

The University had to reorganize itself like other institutes have done. All professors had to be trained to be able to adapt their classes to the new virtual methodology. Also, all study materials along with plans and all the information that is relevant for courses and classes had to be digitized to be shared with students. To simplify some of the processes of adapting to the new tools, several professors have recorded videos and uploaded them, and thus made them available when both students and professors need it. It should be noted that several professors already have the necessary experience to carry out virtual classes, and that much of the documents were already digitized, facilitating some of the adaptation processes to this new situation. Students accustomed to studying and attending to presential classes within the University, are also in an exceptional adaptation process, which is happening not only in Argentina, but worldwide.

In this research work, quantitative information was collected, which serves to evaluate the adoption level of a group of students facing this new virtual education system, in one class, and finally, to conclude if it is possible and potentially fruitful the implementation, in the long term, of the virtual education system, even after the COVID-19 pandemic ends. Also, through surveys, professors presented their conclusions after the beginning of the first semester, concluding with an assessment of the viability for the implementation of a virtual educational system once the quarantine has been lifted and the face-to-face courses are reinstituted in the University.

Iconix

Iconix [10] is a minimalistic process of practical software development. It's a simplified and more traditional methodology that unifies a set of object oriented methods in order to have strict control over the entire development life cycle of the product that's been made, and has a sequence of steps that must be followed that clearly determines the activities to be carried out at each stage of the life cycle of the project that uses it. Iconix derives directly from RUP (Rational Unified Process, standard object-oriented software development methodology, with its analysis and documentation) and its foundation is the fact that 80% of cases can be solved with only 20% use of UML (Unified Modeling Language, standard for the visual representation of objects, states and processes within the system that's being developed) which greatly simplifies the process without losing documentation by leaving only

what is necessary. This implies a dynamic use of UML in such a way that other diagrams can be used in addition to the ones already stipulated if it is convenient. Iconix is guided using "Use Cases" and follows an incremental and iterative life cycle. The end goal is that the final version of the software that is being developed is obtained from the Use Cases. The Iconix process is divided into dynamic and static workflows, which are highly interactive. It may happen that you have to go from one iteration of the entire development process to a small number of Use Cases. The Iconix process is suitable for Agile projects where quick reaction is necessary when it comes to factors such as requirements, design, and estimates.

Iconix has the following key features:

- Rationalized use of UML
  - Minimalist approach.
  - Small amounts of steps to succeed.
- Traceability
  - In any stage a line can be traced to the system requirements.
  - Objects follow up as they evolve.
- Iterative and incremental
  - Between domain modeling and Use case analysis.
  - Iterations over the dynamic model that refine the static model.

To simplify, Iconix process consists of the following stages:

- *Requirements*: where functional requirements definition happens, the development domain is modeled, the behavior requirements are defined and as a closure for this stage, use cases need to fit the client's expectations.
- *Analysis and preliminary design*: robustness diagrams design (this are graphical representation of the steps of one use case), while use cases are rewritten, if necessary; updating the domain model, determining the controllers needed to run use cases and rewriting use case sketches.
- *Preliminary design revision*
- *Detailed design:* sequence diagrams design, domain model update as the sequence diagrams are developed and static model cleanse.
- *Critical design revision*
- *Implementation:* unity testing, integration testing, revised code execution and an update model to be ready for the next stage of work development.

In **Table 1**, we are comparing the process models in terms of the characteristics of the project, and analyzing the size of the process, equipment, and problem complexity for each model. We can highlight that with a small development team, large, highly complex projects can be carried out; in the case of XP and SCRUM [12].

Process model	Process size	Team size	Problem complexity
RUP	Medium/Extensive	Medium/Extensive	Medium/High
ICONIX	Small/Medium	Small/Medium	Small/Medium
XP	Small/Medium	Small	Medium/High
SCRUM	Small/Medium	Small	Medium/High

Table 1: Process models comparison.

In **Table 2** we can observe, with respect to learning curves, that Agile models offer greater advantage, but with certain limitations, since they have not yet been exploited on a large scale as, for instance, RUP, that is has high support and comprehensive tools that guides through it, facilitating the application of this methodology more effectively, allowing to make the most of it [12].

Process model	Learning curve	Integration tools	Extern support
RUP	Slow	High support	High support
ICONIX	Fast	Some support	Some support
XP	Fast	Not specified	Some support
SCRUM	Fast	Not specified	Some support

Table 2: Process models comparison, learning curve perspective.

Among the advantages of Iconix we can name that it's a process that has certain similarities to Agile methodologies to carry out software development, and that it's focused on the construction of management systems of small and medium complexity with the participation of end users. Among its disadvantages, we can mention that this methodology needs fast and precise information on the requirements, of the design and the estimates; also, this methodology should not be used in long term projects given its characteristics. From a work force point of view, in Rosario (Santa Fe state, Argentina) most development and sourcing companies that are focused in developing custom software mostly use Agile alternatives like Scrum, Kanban or hybrids, none of them use Iconix.

Description Of The Course Selected To Carry Out This Research Work

The course selected to carry out this work has the final purpose of developing custom-made software, in this case, a "Security module", this is a set of functionalities whose main objective is to regulate and organize, though groups and permissions over forms, the users who may or may not interact with a software and its functionalities. Students are requested to develop (source code and working application) and documentation, following certain guidelines. This course is from the third year from the Systems Engineering degree career and is based basically on all the knowledge that has been gathered in previous years, where all the necessary concepts to design and develop were addressed. Among those important materials that students need to have in order to go through the course with no inconvenience we can name: system analysis, programming, object-oriented programming, development methodologies, domain modeling, design, and database management. Historically, this subject was carried out using the Unified Process methodology alternating with more agile models such as Iconix.

During 2019, the course used a complete "Agile" approach, implementing Scrum as software development and work methodology with all its ceremonies, artefacts, roles, and requirements. The experience was positive, for both students and professor, and the results were favorable. A more Agile approach and mindset and expertise lay the foundations for a more in-depth approach and given that, during 2020, the course is using Iconix, it serves as a contrast with what was done in previous years. 2019 course with a more "Agile" approach was done using and following steps:

1 All the work was done by the entire class as one group, the professor played as "Product Owner" and a group of students served as "Scrum masters".
2 Stages where aligned with Scrum:
   a) All ceremonies were performed, planning daily stand ups, retrospective meetings, and project progress review meeting at the end of the Sprint (mostly called "Demo meeting")
   b) User stories were used as a tool for documenting requirements.
   c) An agile Management tool was used to properly manage sprints, backlogs, and tasks.
3 The development served the same characteristics as it was described previously (a Security module essentially).
4 Even though all the work was executed as a whole team, each student needed to defend the work that the whole team did, individually. This was a way to ensure that the students learned, and they can approve the course.

Applying Iconix in the Selected Course

The course selected for the purpose of this work, which was detailed previously, has as final goal, the development of a "Security module". This course is mainly enriched by the classroom experience, the contact with the professor and the teamwork, but given the current social context, it has been forced to implement the necessary tools so that this experience is not lost, classes can be carried out and students can finally learn. The professor has the necessary experience to be able to carry out the virtual teaching of his course, and most of the study material is digitized, simplifying the adaptation to the virtual learning model.

For the development of the "Security module", "Iconix" was used as a development methodology. This "Security module" must meet certain functional and non-functional requirements. Among the functional requirements we can name: login, logout, password change and reset, profiles and groups management, and an audit module to be able to view data traceability. It was also necessary for the student, during the design and analysis stages, to document requirements and, using UML, to develop all diagrams (all required by Iconix).

The software tools chosen for this course were: Zoom (at the beginning), Blackboard and Google Classroom. For Documentation and programming, students were able to choose the tool with which he felt more comfortable, although with certain restrictions, for instance, the programming language must be object oriented, Databases must be relational and Iconix guidelines must be followed at all times.

Course schedule and classes:

Date		Lesson
7/4/2019	Unit 1	The process of creating software
14/4/2019	Unit 1	The process of creating software
21/4/2019	Unit 2	Security module analysis and design
28/4/2019	Unit 2	Security module analysis and design
5/5/2019	Unit 3	Metrics
12/5/2019	Unit 3	Metrics
19/5/2019	Unit 4	Risk and quality management
26/5/2019	Unit 4	Risk and quality management
2/6/2019	Unit 5	Design patterns
9/6/2019	Unit 5	Design patterns
16/6/2019	Unit 5	Design patterns
23/6/2019	Unit 5	Design patterns
30/6/2019	Unit 5	Design patterns
7/7/2019	Unit 6	Software testing
14/7/2019	Unit 6	Software testing
21/7/2019	Unit 6	Software testing

Table 3: Detailed schedule of the course.

The course was dictated once a week, on Tuesdays, in two separate blocks, both of 80 minutes each, with a 20 minutes break between them. The course is programmed as follows, the first block, will review lessons detailed in Table 3 and using the "flipped classroom" methodology, which is a semi-face-to-face or virtual learning methodology, a different way of learning and teaching. Using this methodology, prior to the beginning of the course, all the information needed on the topics to be discussed, along with a short evaluation, which serves as a review of the topics discussed, will be shared by the professor. This evaluation will be relevant also at the moment of identifying the acceptance by the students of this learning methodology. The professor and the group of students review the concepts in search of queries or doubts in this regard. Once this first block was finished, it was considered that the concepts were assimilated correctly by the students.

The second part of the course is of a purely practical approach, where the practical implementation of the theoretical concepts (revised during the first block) about the work that the students must carry out, the "Security module".

The articulation between the course and Iconix occurs in the following way: given that this process has defined phases, the subject was presented following the corresponding model. These are:

1 Requirement analysis: during the first classes, an exhaustive study of functional and non-functional requirements of the Security module was carried out, concluding this first stage with the following deliverables: Use case model, Domain model, preliminary design and Detailed use cases.
2 Preliminary design analysis: focused on discovering the objects and got deeper in the domain model, finishing with a preliminary technical architecture and has as deliverable the Robustness diagram, which will be used in the next phase as the skeleton of the Sequence diagrams.
3 Once the preliminary design phase concludes, the detailed design phase is immediately continued, which focus on a deep review of the preliminary design and has the Sequence diagrams and the Class diagrams as deliverables.
4 After the detailed design stage, the implementation phase is started, which consists of testing and subsequent programming.

All information necessary to carry out all previously mentioned phases proposed by Iconix could be found within a collaborative tool, Google Classroom. To carry out the courses and dictation, at the beginning Zoom was used, and then, Blackboard Collaborate was used. Beyond the work needed to approve the course, students must comply with two partial examinations, which consisted of partial deliveries of their work with its defense, and also, a research request, which consisted of the application of Design patterns in their project, responding to functional and non-functional requirements. Unlike other years, as we mentioned earlier, the work was carried out individually, and since the courses will be in a virtual mode, the students were responsible for the partial and final deliveries to be made in a fixed schedule. Requirement changes will be introduced throughout the semester to force students to carry out research tasks, and to review the best approach to implement those changes to their solutions.

During the second semester, the same experience will be carried out, but instead of using Iconix, Scrum will be used, this will be evaluated in a separate investigation work.

Proposal Acceptance Indicators

In order to be able to qualify the acceptance degree (or not) of both, the students and professors, of the proposed methodology used during the time the course took place, the following indicators have been taken into account.

- *Attendance*: student attendance was relieved in all classes. As the course is done in two parts, the assistance will be taken in both parts, and thus, evaluate desertion degree and interest.
- *Students participation*: we measured the number of questions and querying students asked during classed. With this indicator, the higher the number, the higher the interest students had of topics and subjects that are covered in the classes.

Adherence to Iconix practices and progress in student work

- Progress in student's work: the progress of the work each student needed to do was evaluated in each partial delivery that the professor requested. This way, we were able to obtain a global progress metric in terms of the development of the work and the adherence to Iconix, as development methodology.
- Adherence and acceptance of Iconix as a development methodology, through the analysis of self-assessments included in each class.
- Previous knowledge of Software methodologies: the starting point of the students in terms of software methodologies was surveyed, to understand their previous experience, both in working environments and in educational matters in relation to Agile methodologies, requirements engineering and domain modeling, among others.
- At the end of the semester, the knowledge acquired about Software Process Methodologies will be relieved to have an overview of the learning curve in this matter.
- Periodical interviews with the professor to understand his point of view regarding the use the students are giving to the virtual work methodology and the learning context.

Proposal Acceptance Evaluation

We emphasize that at the time this work was presented, the percentage of student attendance is vastly higher than when classes took place in premises, as can be seen in Figure 1. Attendance was never below 88,88%. Also, given the characteristics of this course, consisting in two modules, we can see that the attendance percentage is still high, and with few dropouts, with an average attendance of 90,74%.

Regarding class duration, please note that this is adjusted to the needs of the professor and the students. We can see in Figure 2 that, except for the first class, on April 7th where Zoom was used (with it's 40 minutes limitation), the rest of the classes remained above 60 minutes, which corresponds to 75% of the estimated course duration. The second part of the course, which is also 80 minutes long, has a good record also, in average, the total was about 75% of respected duration.

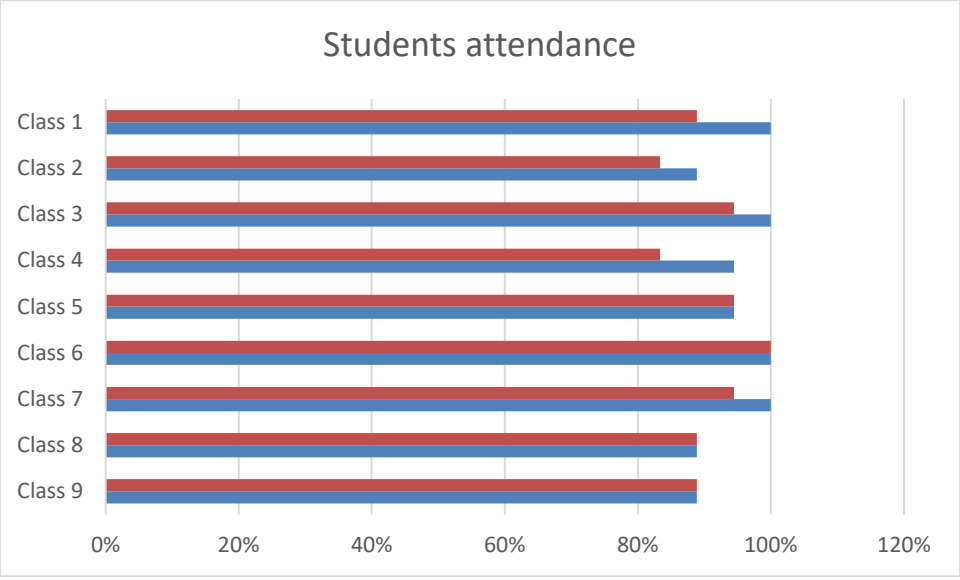

Figure 1: Students attendance during class, first part of the class represented in blue, the second part, in red.

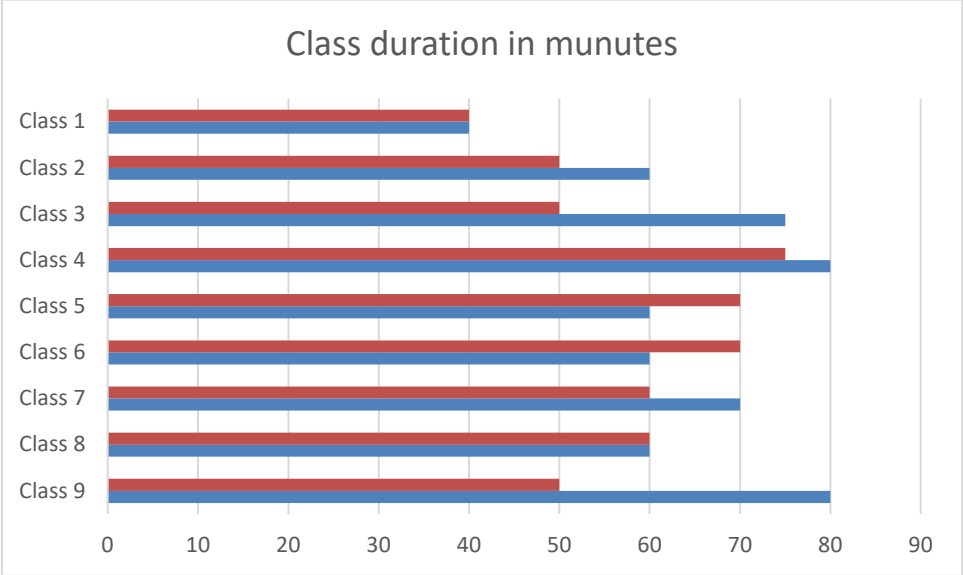

Figure 2: Class duration record, expressed in minutes. In Blue, the first part of the course is represented, in red, the second part.

Of the indicators selected to evaluate the student's experience, the most relevant that we used to measure was the participation in classes. After talking with the professor, we noticed that the participation is normal due to the course characteristics and past years, and, on average, the questioning and querying from the students surround doubts regarding functional requirements, characteristics of the practical work to be carried out and technical specifications over some diagrams requested by Iconix (like, for example, Robustness and Sequence diagrams).

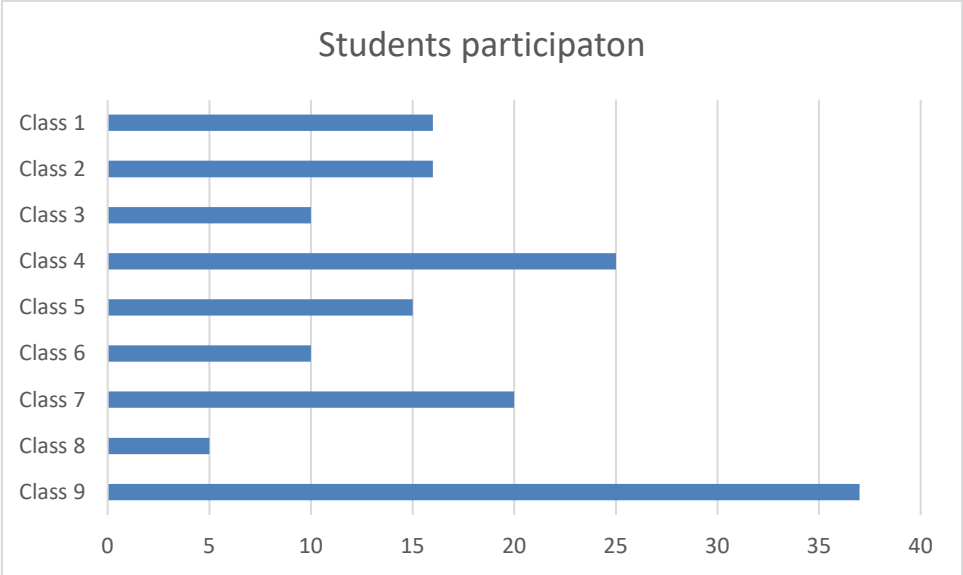

Figure 3: Number of questions and querying made by students in the classes. A note must be made, in class 8 there was an examination instance and that is the reason behind the considerable drop in participation.

Adherence to Iconix practices and progress in student work

By the time this work took place, we can define that, based on what was reported by the professor, from 17 students that formed the students group, only two students did not pass the first partial examination that took place in class 8 and only 1 student was absent. Consequently, 82% of all students passed the first partial instance, which is an excellent indicator of their progress. Using as a reference the weekly evaluations sent by the professor within the context of "flipped learning" applied during the course, in the 9 classes that have been surveyed at the moment this work took place, there were approximately 65% deliveries, with good results. From the information obtained at the beginning of the semester through the knowledge of software process model evaluation that was sent, most of the students had academic knowledge of Agile methodologies (Figure 4) and requirement engineering (Figure 5), they consider themselves able to conceptualize requirements.

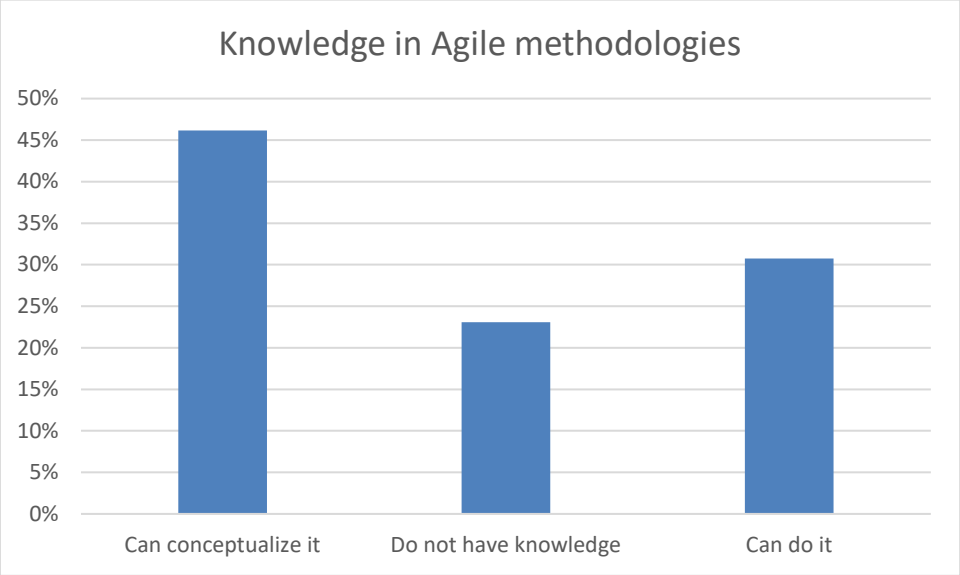

Figure 4: Students that had responded to the Development process knowledge survey regarding Agile methodologies knowledge.

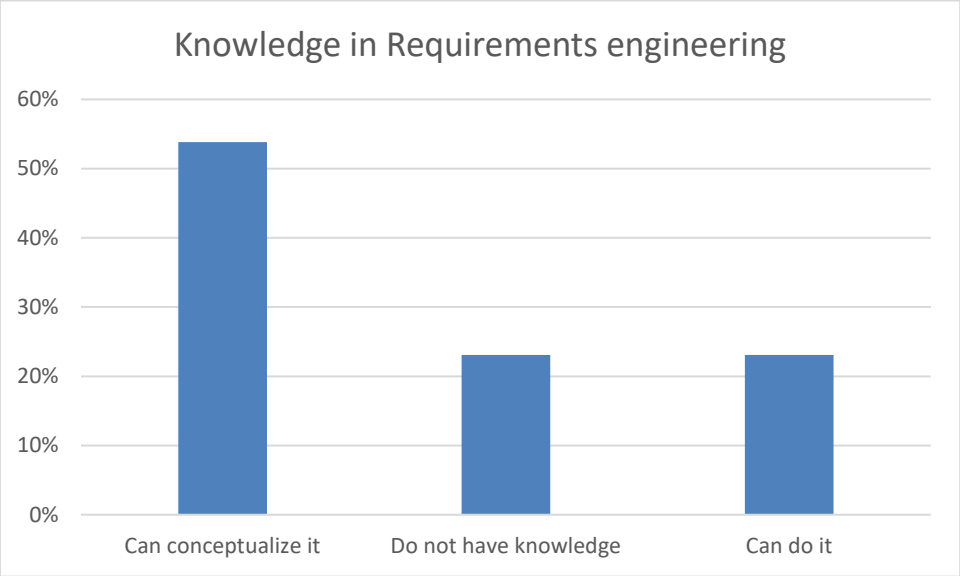

Figure 4: Students that had responded to the Development process knowledge survey regarding requirements engineering knowledge.

Finally, and based on the interviews that took place with the professor, we conclude that, although Iconix is an excellent development methodology for the pedagogical field, it is not within the standards of the labor market, distancing students from it. On the other hand, the virtual methodology used during course with an inverted learning methodology like "flipped classroom", although favorable for the empowerment of the students, finds its weakness first in the absence of face-to-face contact and secondly, the large amount of time it take professors to prepare every class, class by class, in advance.

Conclusions

Being able to generate the proper environment for that the teaching-education process happened in a timely manner in times of isolation was not an easy task. The main challenge was to find the intersection between students, professors, communication tools, pedagogical tools, and the technology to generate synergy and thus, being able to go through the first semester in harmony.

The course that was selected to carry out this work has special characteristics compared to others, for example, applies Agile-type work methodologies, it is focused on analysis, design and development of special software and

all the work needed to be carried out individually. To face and overcome this challenge, several factors needed to happen. In the first instance, the University had provided the course with all necessary tools so that the virtual dictation of courses was as similar as a face-to-face interaction, and in order for this to happen, Blackboard and Classroom where implemented as communication and collaboration tools, between professors and students. Human factor in this experience is crucial. Over its history, the University has a more traditional approach for courses and classes, on premises. In recent years, only a few subjects implemented semi-presence, up to 50% but these are only a few examples. As a result of the quarantine, students and professors were forced to migrate to the virtual modality, altering the status quo.

In the course selected for this work to happen, the attendance and punctuality of students improve considerable, participation during classes has not been affected due to the need of first interacting with the tool and then being able to do the querying, finally, in the course selected for this work to happen, in comparison with previous years, no desertion or drop out was registered. Regarding the methodology used to carry out the development of the Security module, the information collected through the surveys and interviews informs us that, unlike previous years, a great deal of the students had a great percentage of progress in the work they are carrying out most of them, with their partial examinations approved; always taking in consideration that, from our initial survey, most of them did not had great experience working with development methodologies. Flipped learning also served its purpose, students took the time and the necessary work to study the material provided by the professor and then complete the self-assessments. In this regard, on average, 60% of students completed the self-assessments class by class. Finally, based on the interviews carried out with the course professor, although he considered that the students have adopted the Iconix practices, he also expressed that the completely virtual methodology is not the most appropriate one for courses like this one, referencing the need for semi-presence due to the lack of contact with and between students, and, on the other hand, although Iconix is a very good pedagogical methodology, currently, on the labor market, is not used as a developing framework in the software industry. Considering the partial results obtained in the course, during this semester, from the professor and students point of view, we can conclude as follows: Iconix, a development methodology, although with great academic application, but not used in the software industry, accomplished its objective moderately during the first semester. The group of students made good use of the tools available for teaching and complied in a timely manner with their deliveries with a moderate to normal participation during classes. Finally, and given the special characteristics of this course, although the completely virtual model is fulfilling its objective, at the same time, it is very demanding for the professor in the absence of presence to be able to interact directly with students.

Using 2019 as reference, we consider that, based on the possibilities of extended isolation in Argentina with the continuity of the virtual model, it is necessary to apply a different work methodology, which is adjusted to the current software industry situation, that trains students in the latest technological standards and simplifies teaching work. The proposal is focused on the use of Scrum as a working framework with the use of project management tools and the support of students and professors for this to be successful.

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EFFECT ON BENDING RIGIDITY OF TOWEL SAMPLES WITH DIFFERENT FIBER CONTENT

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ABSTRACT
Recently, there have been significant developments in investigating the quality perception and aesthetic behavior of the towel fabrics due to the developments in objective evaluation techniques in parallel with the technology. When bending properties are evaluated especially in terms of towel fabric comfort and towel quality perception, it is the main parameter that affects the selection of raw material, design and appearance of the textile material. In this study, towel samples with different fiber content (cotton, modal, bamboo, tencel, polyester etc.), yarn structure (carded, combed, open-end), yarn count, pile height, weight values were collected. By measuring the bending rigidity of towel samples, the effects of towel samples with different fiber content on both quality perception and bending rigidity were investigated.
Keywords: towel, towel comfort, towel quality, towel quality perception, bending rigidity.

Introduction

Today there is a growing interest in the interaction between textile materials and human beings. Mental as well as physical comfort has become much more important for the consumers in the past few years [1, 2]. Since fabric comfort and fabric quality perception are sensitively perceived by the human body, subjective evaluations should be made first and supported with objective measurements in order to produce similar fabrics in terms of their handle and ensure their continuity [3, 4, 5].

Although fabric comfort and fabric quality perception properties are generally evaluated according to subjective assessment methods, it has been proved in previous studies that there is a correlation between some physical properties of the fabric that can be measured objectively [6]-[12]. For this purpose; simple and advanced technology measurement systems (e.g. Kawabata Evaluation System) have been developed in which properties such as bending rigidity, smoothness, softness, stiffness and thickness can be measured with numerical values, which closely concern fabric comfort and quality [1],[6],[8],[12]-[17]. Due to the expense of the Kawabata equipment and maintenance difficulties, for determining the comfort and quality properties of fabrics, mostly in Turkey, bending length, devices measuring physical properties such as stiffness and fabric stiffness is used. The bending length is the deviation of the fabric fixed at one end by its own weight from the horizontal. Bending rigidity is the resistance of the fabric against bending. Fabric stiffness is the resistance of the fabric against bending like rigidity. The fact that these values are high indicates that the fabric has a hard handle and affects the fabric quality perception significantly [8].

The comfort and quality perception features of the fabrics are influenced by various factors such as fiber type, weight, yarn density and yarn count [8], [18]-[19]. It is known that the fibers form the yarns, that yarns also form the fabric, therefore the fiber properties have great importance in terms of fabric properties. Many fibers obtained naturally or chemically are being used in textile to obtain textile fabrics with different properties [19]. When it comes to towel fabrics, cotton, which is a natural fiber, comes first, followed by blends of cotton with fibers such as bamboo, modal and tencel.

In recent years, with the development of objective measurement techniques, the importance of quality and comfort of towel fabrics has increased. Bending rigidity is among the most important appearance and mechanical properties of towel fabric. Traditional methods, which are used for the measurement of these features and have not changed much since the 1930s, have contributed in parallel with the development of technology, especially in recent years [20]. As long as the perceptions of quality and comfort are reshaped over time, bending properties of towel fabrics will continue to attract researchers.

Denizli is one of the most important towel production location in the world. Different towel manufacturers have been visited in Denizli because it is very easy to access a wide variety of towel samples with a wide range of production parameters. In this study, physical test measurement results were used to evaluate the quality perception

features of towel fabrics with different fiber content, yarn structure, yarn count, pile height and weight values. By measuring the bending rigidity of the towel samples with physical testing, the effects of the towel samples with different fiber content on both quality perceptions and bending rigidity were investigated. The data obtained were interpreted in terms of parameters such as fiber type, yarn count, pile height and weight, which affect the quality and comfort. The results obtained from the study are thought to offer a new viewpoint for the innovative product development compatible with the needs of the consumer in the towel industry and in this context it is considered to be important in terms of the absence of a study on towel fabrics.

MATERIAL-METHOD

Material

The properties of 15 different towels for the analysis of towel fabrics are given in Table 1. The samples were cut on a laser machine 10x10 cm and 10x20 cm in size. Standart atmospheric conditioning was carried out for the towel samples for 24 h with temperature 20 ± 2 °C and relative humidity 65 ± 2% prior to the studies.

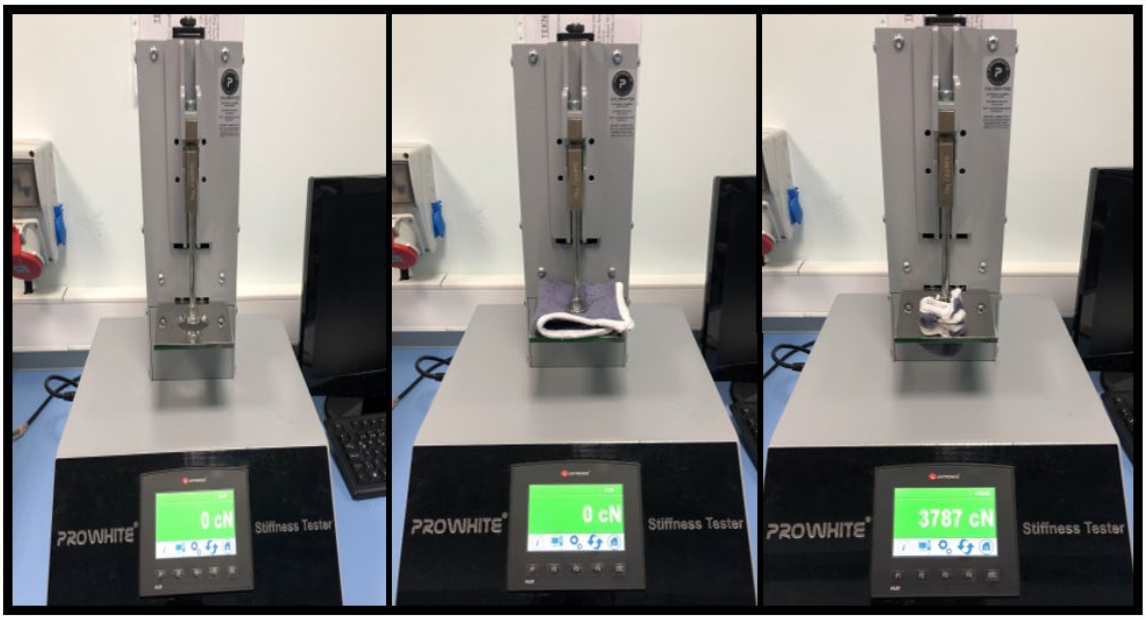
Table 1. The properties of the towel samples

Sample number	Fiber content	Yarn count (Ne)	Pile height (mm)	Weight (gr/m^2)
1	100% Cotton	Pile: 20/2 Carded yarn Ground: 24/2 Carded yarn Weft: 16/1 Carded yarn	5.1	550
2	100% Cotton	Pile: 20/2 Carded yarn Ground: 24/2 Carded yarn Weft: 16/1 Carded yarn	6.25	550
3	100% Cotton	Pile: 20/2 Carded yarn Ground: 24/2 Carded yarn Weft: 16/1 Carded yarn	5.25	550
4	21% Modal - 79% Cotton	Pile: 12/1 Combed yarn Ground: 20/2 Combed yarn Weft: 14/1 Combed yarn	8.1	700
5	75% Cotton - 25% Modal	Pile: 16/1 Cotton-Modal Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	9.75	650
6	95% Cotton - 5% Silk	Pile: 13/1 Cotton-Silk Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	6.9	725
7	95% Cotton - %5 Cashmere	Pile: 14/1 Cotton-Cashmere Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	8.22	635
8	50% Modal - 50%Cotton	Pile: 16/1 Modal-Cotton Ground: 20/2 Open end Weft: 20/2+16/1 Carded yarn	7.6	600
9	34% Modal - 66% Cotton	Pile: 12/1 Combed yarn Ground: 20/2 Combed yarn Weft: 12/1 Combed yarn	8	650
10	60% Bamboo - 40% Cotton	Pile: 16/1 Bamboo-Cotton Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	7.4	550
11	70% Modal - 30% Cotton	Pile: 16/1 Modal-Cotton Ground: 20/2 Carded yarn Weft: 16/1 Open end	8.25	544
12	60% Cotton - 40% Bamboo	Pile: 16/1 Cotton-Bamboo Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	8.7	580
13	85% PES - 15% Cotton	Hav: Ne 20/2 (%85 PES - %15 Cotton) Zemin: Ne 18/2 (%100 PES staple fiber) Atkı: Ne 18/2 (%100 PES staple fiber)	8.1	564
14	50% Cotton - 50% Tencel	Pile: 16/1 (50% Combed Cotton-50% Tencel) Ground: 20/2 Carded yarn Weft: 16/1 Carded yarn	6.8	550

15	85% PES - 15% Cotton	Hav: Ne 20/2 (%85 PES - %15 Cotton) Zemin: Ne 18/2 (%100 PES staple fiber) Atkı: Ne 18/2 (%100 PES staple fiber)	8.55	587

Method

Samples cut in 10x20 cm dimensions were folded in half and measured in the Prowhite Stiffness Tester Unitronics device. The measurement device, the placement of the sample in the device and its image at the time of measurement are given in Figure 1.



Şekil 1. Bending rigidity test measuring device

Samples cut in 10x10 cm dimensions were used to determine the pile height. Pile height values of the samples were determined according to TS 629. 10 yarns were drawn from the warp direction of each towel sample of 10x10 cm size. The value obtained by dividing the sum of the corrected lengths of the yarns removed from the fabric by 100 is defined as the pile height of that towel.

Results And Discussion

The bending rigidity test results measured on the Prowhite Stiffness Tester Unitronics are shown in Table 2. Measurements were made 5 times for each sample and their average values were calculated.

Tablo 2. Bending rigidity test results of towel samples

Sample number	Fiber content	Bending rigidity (CN)
1	100% Cotton	3708
2	100% Cotton	5192
3	100% Cotton	3536.2
4	21% Modal - 79% Cotton	5300.8
5	75% Cotton - 25% Modal	4525.4
6	95% Cotton - 5% Silk	4129
7	95% Cotton - %5 Cashmere	3805.2
8	50%Modal - 50%Cotton	3579.4
9	34% Modal - 66% Cotton	3001
10	60% Bamboo - 40% Cotton	1906.4
11	70% Modal - 30% Cotton	1786.4
12	60% Cotton - 40% Bamboo	1721

13	85% PES - 15% Cotton	1564.4
14	50% Cotton - 50% Tencel	1278.6
15	85% PES - 15% Cotton	1070.2

While the bending rigidity values generally increase as the grammage and pile height value increase, when examined in terms of yarn count factor, is observed that the resistance against bending in thinner numbers decreases. When analyzed also as fiber content, it can be stated that as the use of regenerated and synthetic fiber increases, the samples tend to have a soft handle than others. The high bending rigidity values indicate that the towel sample has a hard handle. Singh, Behera and Matsudaire (2014) point out the perception of softness ın the description of the quality perception of good towel fabric.

Conclusion

In this study; by measuring the bending rigidity of towel samples with different fiber content, yarn structure, yarn count, pile height and weight values, the effect of towel samples with different fiber content on both quality perceptions and bending rigidity was investigated. In the results obtained from the study, high bending rigidity values indicate that the towel sample has a hard handle. As one of the towel properties that best expresses the towel quality perception is the softness parameter, it was observed that the ratio of regenerated and synthetic fibers increased in samples with low bending rigidity.

As a doctoral thesis, with this study, which is a part of the research conducted within the scope of ‘’Determination and Development of Objective/Subjective Evaluation Criteria of Quality Perception in Towel Structures’’; it is expected that by comparing the production parameters that affect the quality and comfort characteristics by determining the bending rigidity of towel fabrics, which is one of the physical test methods, it is expected to provide benefits to towel fabric manufacturers in determining how different production parameters affect consumer preferences and directing their product development activities within the framework of these parameters.

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ON THE CONCEPT OF TIME IN EVERYDAY LIFE AND BETWEEN PHYSICS AND MATHEMATICS

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ABSTRACT
In this paper I consider the concept of time in a general way as daily human time and then within physics with relation to mathematics. I consider the arrow of time and then focus the attention on quantum mechanics, with its particular peculiarities, examining important concepts like temporal asymmetry, complexity, decoherence, irreversibility, information theory, chaos theory. In conclusion I consider the notion of time connected to a new theory in progress, called "Superfluid Dynamic Space" theory, based on a time-invariant universe that overcomes the Big Bang model and is connected on the so called "bijective physics".
Keywords: Time, Modern Physics, Irreversibility, Decoherence, Symmetry/Asymmetry, Entanglement, Complexity, Superfluid Dynamic Space (SDS), Education.

Introduction

The problem of time is one of the fundamental problems of human existence; even before being the subject of philosophical investigation, it constitutes the man's ever-present problem, since even in an unconscious way it is intrinsically linked to our life. From the viewpoint of existential philosophy, it also involves the problem of the destiny of man, considered only indirectly by mathematical and naturalist philosophy. It is in fact over time that the destiny of human existence is realized.

A double meaning is linked to the time: on a hand we have the fear, the worry, which temporalize the being, on the other hand the hope, the change produced by creative activity. This dualism is intrinsic in the structure of the person, in the sense of union between the changeable and the immutable. Time is therefore a change in two distinct meanings: as development of life and as death.

The man's destiny is fulfilled in time, in the past and in the future; but this past and this future exist only in the present. Furthermore, the past can be considered under a double aspect: the past that has existed and is now over, and the past that still lasts in the present and which exists in the present memory as a transfigured past.

The relation between the three dimensions of time involves another very important existential aspect: how to act so that a painful past no longer exists and so that a beloved present continues to exist and does not die in the past.

Time is for some aspects an evil and its passing can be sad. This evil consists in the impossibility of savoring the present in all its fullness, due to the impossibility of completely freeing yourself by the sadness of the past and the fear of the future.

The joy of living the present moment as total fullness is always denied by the elapse of time. Without the loss of many things of the past, the man should not be able to live; a total memory would destroy him. This need to forget the past denotes an evil of time.

The temporal dualism becomes evident in the present moment. The instant can be seen as a small fraction of time, an infinitesimal fraction between the past and the future; but we can also see it as not belonging to time, as instant that cannot be divided into past and future. This problem has evident links to our age, dominated by technology and by speed.

The value of the instant is lost in it, which becomes only a means for the following instant. Time becomes thus an accelerated time, where the man is leaning towards the future and his ego decomposes in this temporal speed, losing the unity that is instead deeply connected to the unity of the indivisible moment.

The time-man relation is for some aspects paradoxical: on a hand the person is change, realization over time, on the other hand she/he is immutability, unity through the change, and therefore is damaged by time.

Another fundamental problem closely connected with time is the problem of death. Death occurs in time, resides in life and is its end. In the relation between time and infinity, we can consider two meanings: a quantitative and a qualitative one. Time seen as quantitative infinite brings death with it; on the other hand, victory over death and

healing from the evil of time is linked to the meaning of qualitative infinity of time or eternity (Di Sia, 2015).

The intensity of our inner life can change the character of time; time that can accelerate or slow down in relation to the richness of life has no mathematical character (Di Sia, 2018[a]). Two of man's greatest problems, i.e. the problem of the foundation and that of the future, are both inseparably linked to time and reveal time as the intimate destiny of man. The human existence is immersed in time; its origin and conclusion seem to go beyond it.

The notion of time is present in all areas of thought that reflect and study the reality and the human being, from mathematics to physics, from philosophy to neurosciences. The problem of time escapes our senses and mathematics and physics often lead to results that are logically far from ordinary human thinking.

Mathematically, time is indicated as a variable t present in the equations; time flows and the term t defines some dynamics. Time can be defined on an oriented line, each instant is in one-to-one correspondence with a point of this line. When we graphically represent a movement in space, time is considered as if it were another spatial dimension. This is a static way of interpreting time, there is also the dynamic way, related to the flow of time (Di Sia, 2017).

In particle physics, space-time is flat, rigid and static; in general relativity it is curved, flexible and dynamic; they are two different conceptions of time. The canonical scientific theories developed to date use different notions of time (differentiable time, time in different dimensions, non-continuous time) and there are also time-independent theories (Fiscaletti, & Šorli, 2015; Di Sia, 2015[b]).

The subjective time, as memory of every moment of the present of our consciousness, has an asymmetrical structure and is elastic. The past seems written, frozen; we can remember it, but we can no longer hear that it runs. The future appears uncertain, not firmly attached to reality. In everyday life, past and future are not equivalent; there is a relative condition due to our consciousness (Šorli, 2019[a]).

Time flows constantly, even if our perception of its flow varies according to our emotional state; when we say that time runs quickly, we imagine something flowing at an increasing speed. This something is not actually time, it is the different way in which we emotionally experience the running reality (Fraisse, 1963).

To date, it has been not fully possible to demonstrate, on a scientific level, that time exists and flows from a past to a future. The human being appeals to basic personal feelings, to the fact that we are witnessing our aging, to the fact that disorder, in a closed system, spontaneously grows (Schroeder, 1999).

In relation to irreversibility, the concept of arrows of time has been studied. It seems difficult to be able to untie the concepts of change and invariance, two contradictory but inseparable components in the human effort to understand reality; it seems not possible to fully explain the change without referring to the invariance, and vice versa.

Within physics and science in general, there are different times, reflections on cosmological, thermodynamic, gravitational, biological arrows of time; each of them is based on different principles, and it is difficult to determine whether one is more fundamental than the others (McGucken, 2017; Mersini-Houghton, & Vaas, 2012; Savitt, 1997).

Mathematics has been studied and used since ancient times; however, it is starting by Descartes, Galileo and Newton that the mathematical language has been elevated to the rank of true language of Nature, allowing to talk about phenomena and make predictions.

In some cases it is possible to create, starting by differential equations with respect to time, solutions in which the parameter t is completely eliminated; as example, from the time-dependent solutions of Newton's equations for an orbital motion, $r(t)$ and $\alpha(t)$, one can build time-independent solutions $r(\alpha)$. The motions in the universe could be replaced by timeless trajectories in a larger space of configurations. This is an interesting theme, because it demonstrates how the interpretation of the t parameter can present many more aspects than we think, and also, in some sense, leads to the elimination of a generic absolute time.

The mathematized time of physics does not exhaust the sense of lived time, not more than lived time gives the intuition of all aspects of physical time. The simplest scheme adopted by science consists of a homogeneous one-dimensional (1D) time, composed of instants that follow one by another in an identical way. According to the thinking of some authors, it would not grasp the essential nature of the duration of the true time of life, which is

continuous invention, continuous emergence of novelty (Canales, 2016). A current line of research considers a time-invariant flat universe, which goes beyond the Big Bang model and refers to the two concepts of "fundamental time" and "emergent time" (Di Sia, & Šorli, 2020[a]).

Time and irreversibility

The theme of the time irreversibility of physical theories has been the protagonist of heated debates over years in classical and quantum physics. Problems arose with the birth of thermodynamics, in particular in relation to the principle of growth of the entropy in a closed system, having found a temporally asymmetric fundamental law.

The temporal asymmetry of the reality surrounding us seems to be quite evident. We are witnesses of irreversible phenomena and we feel that there is a substantial difference between past and future. This evident asymmetry of Nature is in contrast with the laws of classical dynamics, symmetrical by time inversion, namely invariant with respect to the change of the time variable "t" into "- t".

The attempt to reconcile classical mechanics with thermodynamics began with Boltzmann's work. He noted that the microstates, that became states with higher entropy after a time evolution, were much more probable than those that became states with lower entropy. In essence, the time reversibility of the Newtonian law of evolution leads to the conclusion that entropy should increase towards the future and, symmetrically, also towards the past (Darrigol, 2018).

Over years, various solutions have been sought for this problem, from the treatment of entropy as a function of probability distributions to the question of special initial conditions, resorting to the use of asymmetric temporal boundary conditions. This led to the question of why the macroscopic world, which should spring from the microscopic one, regulated by quantum laws, shows evident signs of temporal asymmetry, i.e. of irreversibility.
In physics, irreversible phenomena often occur, to the point of having created cases of hypothetical arrows of time in various physical disciplines. We can think, as example:

- to the phenomenon of electromagnetic radiation, in which there are delayed and advanced solutions, although only the first ones seem to occur in Nature;
- to the self-organization of matter, in physical and biological processes, which has been of enormous importance in Prigogine's reflections. It is known that global entropy, when the surrounding environment is considered, always grows in harmony with the second law of thermodynamics, but in relation to the single system (for example a cell) we can witness an entropic decrease (Kondepudi, Petrosky, & Pojman, 2017);
- to the law of exponential decay, concerning unstable physical systems;
- to gravity, although its time direction may be linked to a question of initial conditions; gravity describes an attraction in both time directions, since Newton's equations are of second order with respect to time.

Superposition and entanglement

The superposition of quantum states represents an anomaly compared to what happens in classical physics; this derives by the fact that quantum mechanics is governed by a linear differential equation, so if two wave-functions ψ_1 and ψ_2 are solutions of the Schrödinger equation, even their superposition (a linear combination) is a solution (Griffiths, & Schroeter, 2018). This fact is incredible in the sense of the common logic, i.e. to think for example to an electron in a state of spin up and down simultaneously. It is difficult to put into words what mathematics indicates as possible. The collapse of the wave-function leads to the cancellation of the initial superposition (Di Sia, 2018[b]).

One might think that superposition is a simple mathematical tool, useful exclusively to calculate the probabilities related to each single eigenstate, but macroscopic superpositions have been observed in very sophisticated experiments; they are not impossible to see and, therefore, must not be considered non-existent (Mari, De Palma, & Giovannetti, 2016). If superpositions really exist, why does it seem so difficult to see them? An answer to this question has been provided by the decoherence theory and the continuous elimination of the superposition of states could provide a time direction (Zeh, 2002).

Entanglement is an extremely interesting and peculiar aspect of quantum mechanics; it provides that the states of two or more objects can be described in relation to each other, even if they are separated by enormous spatial distances, leading to an immediate action that contradicts the fact that the speed with which the signals are transmitted can not exceed the speed of light, i.e. $3 \cdot 10^8$ m/s in vacuum.

Quantum entanglement leads to holistic visions of Nature, in the sense that, assuming that everything began with a space-time singularity called Big Bang, but even without a hypothetical initial Big Bang, every single element of the universe would be in correlation with any other, in a global interconnection network; a measurement on an

object would have repercussions on all the others, independently by distances (Di Sia, & Bhadra, 2020[a]; Di Sia, & Bhadra, 2020[b]).

An experiment on a system "here and now" would have repercussions on all systems throughout the universe; as a consequence, at the level of analysis of the temporal flow, the collapse of the wave-function, due to a measurement that can provide irreversibility resulting by a time direction, would automatically be accompanied by innumerable other collapses, due to total entanglement, leading to a universal time direction and to the natural disappearance of the superposition of states (Kiefer, & Joos, 1998; Zurek, 2003; Di Sia, 2020[a]).

Quantum mechanics between innovation and complexity

The theme of irreversibility plays a central role in the debate on the challenge of complexity that led to talk of complex sciences in recent decades. One of the focal points characterizing the reflection on complexity concerns the importance of the temporality of physical, biological and social processes. This temporality has often been ignored in favor of static visions, in which the flow of time is conceived as a simple manifestation of a timeless necessity (Ali, *et al.*, 2020).

It was a sort of separation between "observer" and "observed system"; the idea that the run of time is a disturbance led to the creation of experimental situations that remove any observer influences as much as possible, considering processes that could be described through symmetrical equations by time inversion.

Thinking the macroscopic irreversibility as governed by more fundamental microscopic laws, implies an assumption that there would be a hierarchy of levels of reality, the first of which is the smallest; all this has been challenged by reflections on complexity (Rueger, & McGivern, 2010).

As far as physical laws are concerned, we are seeing that a clear division between "observer" and "system" cannot be made, with the need for a physics that integrates within itself the strength of a historical description; the historicity of the laws of physics follows from the request not to neglect the observer through temporal processes, and therefore he cannot ignore them. The observer, with his actions, modifies the reality surrounding him.

Concerning the hierarchy of levels of reality, the complex thinking has questioned the reductionist thought between disciplines and within them, rejecting the idea that different aspects of reality could be described by a single point of view, more fundamental than others (Gallagher, *et al.*, 1999).

Prigogine's approach does not replace classical and quantum mechanics with a temporal reformulation of physics, but joins traditional physics, trying to reach previously inaccessible problems and to explain new phenomena. On a hand, Prigogine sought an irreversibility independent by the observer, on the other one he wanted to formulate a more human physics, in the sense that time, i.e. history, could be inscribed in the physical descriptions provided by theories. However, these are two goals in some sense in contrast one with the other, since it is difficult to distance the observer from the theory for making it more human. Prigogine emphasized also the delicacy of the concept of environment, in relation to who establishes the distinction between an object and its environment, questions that often goes back to the analysis of the problem of decoherence (Prigogine, & Stengers, 1984; Prigogine, 1997).

The irreversibility of quantum mechanics is manifested in the probabilistic nature of its predictions. The constraint as a possibility, fundamental idea of complex thought, is strongly present in quantum theory, helped by chaos theory as a representative theory of complex sciences.

Compared to chaos theory, quantum mechanics has less orthodox characteristics (in the sense of classical physics). Chaos theory describes a basic determinism, which however does not lead to some predictions after a more or less long time, due to the strong sensitivity to the initial conditions. Quantum mechanics instead moves away from determinism in a deeper and more fundamental way; it is intrinsically probabilistic, even in the interpretations in which it has tried to restore determinism, not simply tied to the basic equations of the theory (Butterfield, & Pagonis, 2010).

In the context of standard quantum mechanics, the "measurement" opens the system to the potential possibilities it carries, to the personal decision to measure some variables and the actual implementation of this measurement; it is an incredibly innovative theory from this point of view (Becker, 2019).

The indeterminism it describes is not an exclusively mathematical fact; the possibility of knowing the probabilities of the measurement outcomes through the knowledge of the square modules of coefficients in the development of

the wave-function in the eigenstates of the observable, it is not a question linked only to formalism. These probabilities become current after a measurement process.

In classical physics it does not happen; the system assumes all values described by the equations of motion in well-defined times, and speaking of measurement is therefore superfluous. The measurement is necessary to physically know the value already predicted by the equations.

With quantum theory we cannot speak on a measurement result if we do not associate the measurement itself; there can be no knowledge of the system if there is no act that physically makes man interacting with it. Also for this reason it is a complex vision of Nature, which detaches itself from the paradigms of classical physics and which has inscribed in its essence the need for the presence of the observer to define the values that an observable of the system can assume.

For classical physics, that is essentially mechanistic, time does not have a decisive importance, because it reflects a mechanical nature, independent by time; for quantum mechanics it is more difficult to evade the importance of the time direction. But the quantum flow of time is linked to the choices and physical acts that the observer performs, so it is possible to consider time as a psychological element, an illusion, as Einstein argued (Šorli, & Di Sia, 2020). Time, read through the eyes of quantum theory, becomes inevitably linked to the human action and, conversely, our action develops over time, in a continuous choice between different possibilities.

Even in the past (we can think for example to the work of St. Augustine), man had admirably emphasized that time is experienced, it is not "a priori" defined; for this reason, time and man cannot be divided. Precisely because he lives, man produces a temporal unfolding that leads him to a goal (Saint Augustine, 1961). Quantum mechanics, in its various interpretations, has managed to represent this idea better than classical mechanics, also thanks to its indeterminism closely linked to the act of measurement.

The difference between thermodynamics and quantum mechanics lies in particular, in addition to the domain of application and the different mathematical formalism, in the role that is given to the observer; from an "active role", such as that of the quantum observer, we move to a "more classical role", i.e. non-fundamental, of the thermodynamic observer. These are qualitatively different times.

Our interaction with reality cannot be neglected, and quantum mechanics states it clearly, not only with regard to the inevitable perturbation of systems by the observer, but also more deeply about our personal act of deciding which observable to measure, and therefore how to expand the wave-function (Di Sia, 2020[b]). Therefore, just as the observer must be taken into due consideration for the results of experiments, he must also be taken into consideration with regard to the flow of time.

Information, complexity and arrow of time

The universe tends to degrade into a uniform state of disorder known as "thermal equilibrium". The astronomer and philosopher Sir Arthur Eddington in 1927 cited the progressive dispersion of energy as proof of an irreversible arrow of time. But this arrow of time does not seem to follow the basic laws of physics, that work in the same way both forward and backward in time (Price, 2013). With quantum physics, a more fundamental source for the arrow of time seems to have emerged, due to the way in which elementary particles intertwine when they interact, namely the effect of "quantum entanglement".

A line of research argued that objects reach equilibrium, or a state of uniform distribution of energy, in a finite time and in time scales proportional to their size, becoming quantum mechanically entangled with the surrounding environment (Jost, *et al*., 2009). The history of the arrow of time begins with the idea of quantum mechanics that Nature is intrinsically uncertain. An elementary particle lacks definite physical properties and is only defined by the probability of being in various states. Quantum uncertainty generates entanglement, which could be the source of the arrow of time. When two particles interact, they can no longer be described by themselves; they become entangled components of a more complicated probability distribution describing both particles together.

It is as if particles gradually lose their individual autonomy for becoming elements of a collective state; these correlations ultimately contain all the information, and the individual particles none. The arrow of time would therefore be an arrow of increasing correlations. Advances in quantum computing have over time transformed quantum information theory into one of the most active branches of physics (Nielsen, & Chuang, 2000).

Objects interact with the surrounding environment; as, for example, particles of a liquid in a glass collide with the air, the information of an object is dispersed out of it and we find it spread over the whole environment, a kind of

local loss of information that we find globally in the surrounding environment. Except for rare random fluctuations, its state stops changing over time; consequently, the liquid in the glass, once cooled, does not heat up spontaneously. This statistical improbability would give to the arrow of time the appearance of irreversibility.

The local decrease of information through quantum entanglement brings the liquid into equilibrium with the surrounding room, which balances itself with the external environment, and this latter slowly balances itself with the rest of the universe. The first creators of 19th century thermodynamics interpreted this process as a gradual dispersion of energy that increases the overall entropy, or disorder, of the universe (Belavkin, & Ohya, 2002).

According to the point of view involving the entanglement, information becomes more and more widespread, but does not disappear completely; even if it increases locally, overall in the universe remains constant. The universe as a whole would therefore be in a pure state, but with its individual pieces, which are entangled one with each other, would be in mixtures, therefore not in pure states. This kind of approach could help in understanding the fundamental limitations of quantum computers and also about the ultimate fate of the universe.

When we read a message on a piece of paper, the brain is correlated with it through photons that reach the eyes; only from then on we will be able to remember what the message says. The present can therefore also be defined as the process of becoming related to the environment.

Physics emphasizes that, despite great advances in understanding how changes over time occur, no substantial progress has been made in discovering the deep nature of time and why it looks different, both perceptually and in the equations, with respect to the three dimensions of space.

"Past hypothesis", gravity and arrow of time

An explanation, called "past hypothesis", assumes that the universe began with a particular state of low entropy, and then progressively moved towards a state of greater disorder (*plato.stanford.edu*). According to this hypothesis, the arrow of time can be attributed to a trend in the universe towards greater confusion. But cosmological observations suggest the opposite, namely an evolution from a very disordered state of the past to the well-ordered structures we see today, with galaxies, solar systems, humans, and so on.

A way to reconcile the second law of thermodynamics with observations is to assume that, while matter in the universe appears to have more order, the gravitational field would increase in entropy, compensating the order of matter so that global entropy is increasing. However, attempts to define a notion of entropy for the gravitational field has so far not yielded good results (Chaichian, Oksanen, & Tureanu, 2011).

Furthermore, this hypothesis makes too many unreasonable assumptions about the early universe, stating that we are the result of a statistical fluke or an implausibly special initial conditions of the universe, unsatisfactory explanations from a scientific point of view.

A more satisfying explanation is related to the concept of complexity. The universe is a structure whose complexity is growing; our perception of time could be the result of a law that determines an irreversible increase in complexity. By connecting the arrow of time to the topological properties of the universe, the growth of complexity would be accompanied by a growth of local information and the problem of time is so connected with the theory of information.

If the fundamental laws of Nature are invariant by time reversal, i.e. time is symmetric, then the origin of the thermodynamic asymmetry in time could lie in temporally asymmetric boundary conditions. This conclusion would follow even if the fundamental laws are not invariant by time reversal.

None of the possible studied candidates for a unified theory of Nature seem to involve the thermodynamic arrow: string theory, canonical quantum gravity, quantum field theory, general relativity, all allow solutions without a thermodynamic arrow. So the universe could have a thermodynamic arrow due, in whole or in part, to its temporally asymmetrical boundary conditions.

Recent advances on the concept of time

The Wheeler-deWitt equation and other proposals, as the timeless path integral approach for relativistic quantum mechanics, a fundamental level of physical reality based on an invariant set postulate, and models of a non-dynamical timeless space, suggest a timeless background space of physics, and the fact that the duration of physical events has not a primary existence. The view of time as emergent quantity that measures the numerical order of material changes brings to a interesting unifying re-reading (Šorli, & Di Sia, 2020).

Several authors suggest that the space background of physical processes is timeless, namely time cannot be considered a primary physical reality flowing on its own in the universe. These research suggests that time can be an emergent quantity, that measures the numerical order of physical events (Fiscaletti, & Sorli, 2015). Also Einstein and Gödel considered the idea of a timeless universe at the half of the 20th century.

The time of general relativity and that of quantum theory are mutually incompatible, and this gave problems in the attempts to unify these two theories into a unifying framework. The problem of time has become one of the most investigated topics in quantum gravity.
We can say that the two fundamental questions concerning the features of time are as follows:

- if time is a fundamental quantity of Nature;
- how the clock time emerges in the experimental description of dynamics.

To date, the fundamental idea is that the physical time cannot be considered as a primary physical reality; the idea is that, at a fundamental level, the background space of physics is timeless, i.e. that the duration of physical events measured with clocks is an emergent quantity.

According to a recent line of approach, physical processes do not take place in an idealized time and have no duration on their own. In physical space, time is an "emergent mathematical quantity"; with clocks we measure the speed and the numerical order of material changes. Changes of the state of universe and of the state of any physical system can be considered the primary phenomena generating the evolution of the universe. This evolution can be described with the introduction of a mathematical parameter, providing only the order of events.

Recent NASA measurements have confirmed that the universe is flat and infinite, with an infinite amount of energy. Bijective analysis confirms that the Big Bang model is a prediction without any experimental evidence. The universe would be a non-created system in a permanent dynamic equilibrium, falsifiable and based on a direct reading/interpretation of data (Šorli, 2019[b]; *wmap.gsfc.nasa.gov*; Di Sia, & Šorli, 2020[b]; Di Sia, & Šorli, 2020[c]).

Conclusion

Man has always placed his attention and tried to understand the meaning of time, from its presence in everyone's daily life and in a more rigorous and deep way through philosophy and science, mathematics and physics in particular.

Physics has dealt and deal with the problem of time and its technical language is mathematics. From classical physics, time has placed its stamp in modern physics, involving important key concepts such as decoherence, superposition, entanglement, information theory and chaos theory. It is an elusive concept and not yet fully defined and framed, even by a strictly scientific point of view.

Recent interdisciplinary insights show that in physics the concept of time is used in two different ways: as an outer attribute of motion or as an implicit variable that measures the inner evolution of a system. In the first case, time is a label attached to the system, in the second one it is a quantity informing about its intrinsic evolution.

In both cases, time measured with clocks cannot be considered as a primary physical reality, but it is an emergent quantity indicating the numerical order of material changes. Moreover, the duration of a given material change requires the measurement of an observer.

Therefore, in physics we can consider two kinds of times:

a) a "fundamental time", that is the numerical order of change that exists independently by an observer;
b) an "emergent time", that is a duration of material change and is originated by the measurement of an observer.

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PREPARATION OF TRANSDERMAL FILMS FOR CONTROLLED RELEASE OF DONEPEZIL HCL

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ABSTRACT
Transdermal drug delivery systems, also known as "patches" have been attracted a great deal of attention for the past few decades since it delivers the drug through the skin in a predetermined and controlled. Transdermal delivery is a viable alternative to conventional oral therapy and provides a controlled drug release by increasing patient compliance and avoiding first-pass metabolism. Donepezil Hydrochloride is an active pharmaceutical ingredient for Alzheimer's disease (AD) It has been widely used by oral route. But this type of treatment may have some disadvantages when a chronic neurological disorder is present because of the patient's unwillingness to swallow and forgeting to take or carry pills in the day. So, transdermal patches can be used as an alternative treatment for AD.
The aim of this study was to develop a transdermal drug delivery system for controlled release of Donepezil HCl. For this purpose, hydroxyethyl cellulose/sodium alginate/gelatin combined with polyvinylpyrrolidone (PVP) and PEG-400 in the formulation of transdermal patches. Transdermal patches were prepared by Franz diffusion cell method. Hydroxyethyl cellulose, sodium alginate and gelatine as matrix-forming agent and transcutol as plasticizer was in the transdermal films. Fourier transform infrared (FT-IR) spectroscopy) was used to characterize the films. In vitro drug release studies were performed for donepezil hydrochloride-loaded hydrogels at 7.4. To study the release kinetics, data obtained from in-vitro drug release studies were plotted in various kinetic models which include zero order, first order, Higuchi and Korsmeyer-Peppas. The results in the present investigation confirm the controlled release of Donepezil HCl and sodium alginate content of transdermal patch can extend the release of donepezil. The study demonstrates that the fabricated transdermal system of Donepezil HCl can be considered as a suitable alternative of the oral route. Also studies have shown promising results, further studies are needed for pharmacokinetic evaluation.
Keywords: Transdermal Films

Introduction

The permeation of drugs through the skin offers promising route for treatment of some illness due the fact that skin is the largest organ of the human body (Javadzadeh, 2017; Groeber, 2011). Transdermal drug delivery systems have several important advantages over traditional systems including avoidance of the first-pass metabolism, longer duration of action, reduction in dosing frequency and good patient compliance. Additionally this type treatment is an alternative for people who forget or unable to take pills (specially fornauseated or unconscious patients). For this reasons, delivering drugs through the skin for treatment of diseased states is gaining increasingly great importance. However, the skin's low permeability limits the number of drugs (Escobar-Chávez, 2012; Badilli, 2018). There is a clear need to develop transdermal drug delivery systems like asthma, hypertension, diabetes, epilepsy, Alzheimer etc (Madan, 2015).

Skin can be accepted as a multilayered biomembrane and the transport of drug through the skin is a complex process. This process can be divided into three steps: penetration, permeation, and resorption. with particular absorption Among the various skin layers, the stratum corneum is the upper most layer of the skin and provides barrier to against drug absorption. To overcome this passive barrier system, chemical penetration enhancers are used (Encyclopedia of Toxicology, 2014; Bartosova, 2012; Pham, 2016). The physicochemical properties of the drugs are very important for absorption of drug into the skin (Albash, 2019).

Before the in vivo evaluation, in vitro drug release experiment can give reliable information about drug release from a transdermal patch. Although there is a number of methods can be used to evaluate drug release from the transdermal formulation, the Franz-diffusion cell widely used to investigate the efficiency of transdermal drug delivery systems in vitro (Al Hanbali, 2019; Salamanca, 2018). It determines important relationships between skin, active pharmaceutical ingredients and formulation (Franz, 1975; Senol, 2018). The image of the Franz difussion cell is given in Figure 1.

The aim of the present study was to develop a transdermal drug delivery system for controlled release of Donepezil HCl which is mainly used in the treatment of Alzheimer's disease. Alzheimer's disease is a type of dementia and

irreversible brain disorder that affects 6%-8% of people over the age of 65 years (Senol, 2018; Sozio, 2012). For this aim polyvinylpyrrolidone (PVP), hydroxyethyl cellulose (HEC), sodium alginate, gelatine and PEG-400 were used in the formulation of transdermal patches. Prepared films characterized by using FT-IR spectroscopy. The in vitro drug release studies were carried out using Franz diffusion cell for Donepezil hydrochloride loaded films at pH 7.4.

Figure 1. The image of Franz Diffusion Cell

The Study

Films were synthesized using PVP, HEC, Na alginate and gelatine polymers. The total film weight prepared is 10 grams. For this, all the components were added to the beaker and mixed in a magnetic stirrer. The films were then transferred to a glass petri dish and kept at room temperature for 24 hours and then kept in the oven at 40°C for 48 hours. Three formulations were developed by varying the polymer and keeping the drug load constant. Drug release started using the films taken out of the oven, Franz Diffusion Cell. Cellulose acetate membrane filter was used as a section taken from the film according to the mouth of the Franz Diffusion Cell and as a skin. pH 7.4 was used to represent blood and placed at the receptor site of the diffusion cell. The temperature was kept constant at 37°C. Drug release was achieved in the diffusion cell for 72 hours. The hourly samples were read in the UV Spectrophotometer and the percentage amount of drug release was measured. Synthesized polymers were prepared as shown in Table 1.

Table 1. Formulation design of PVP transdermal patches

Films	PVP	HEC	Na Alginate	Gelatine	PEG 400	pH 7.4	Transcutol	Distilled Water	Donepezil HCl
1	0.3	10			6.4	19.3	4.3	59.6	0.1
2	0.3		10		6.4	19.3	4.3	59.6	0.1
3	0.3			5	6.4	19.3	4.3	64.6	0.1

Findings

Characterization of PVP Films

Fourier transform infrared (FT-IR) spectroscopy was used to characterize the PVP transdermal patch. Figure 2 shows the photograph of film 1. The photograph also illustrates the relatively smooth surfaces of the PVP film.

Figure 2. Photograph of PVP Film 1

The FT-IR spectra of PVP are presented in Figure 3. The FT-IR spectrum of PVP had a peak at ~3420 cm^{-1} which indicates O-H stretching. The peaks at ~2950 and ~1650 cm^{-1} proved the existence of asymmetric stretching of CH_2 and stretching of C-O, respectively. The peaks at ~1020 and ~570 cm-1 were attributed to the CH2 rock and N-C=O bending, respectively (Figure 3, Film 1). The bands at ~1590 cm^{-1} and ~1410 cm^{-1} corresponded to asymmetric and symmetric carboxyl group stretching vibration, respectively for sodium alginate (Figure 3, Film 2). Film 3 in Figure 3 shows FTIR spectrum of the gelatin showed that the peaks at ~1640 cm^{-1} was due to C=O stretching. C–H stretching at ~920 and 2850 cm^{-1}.

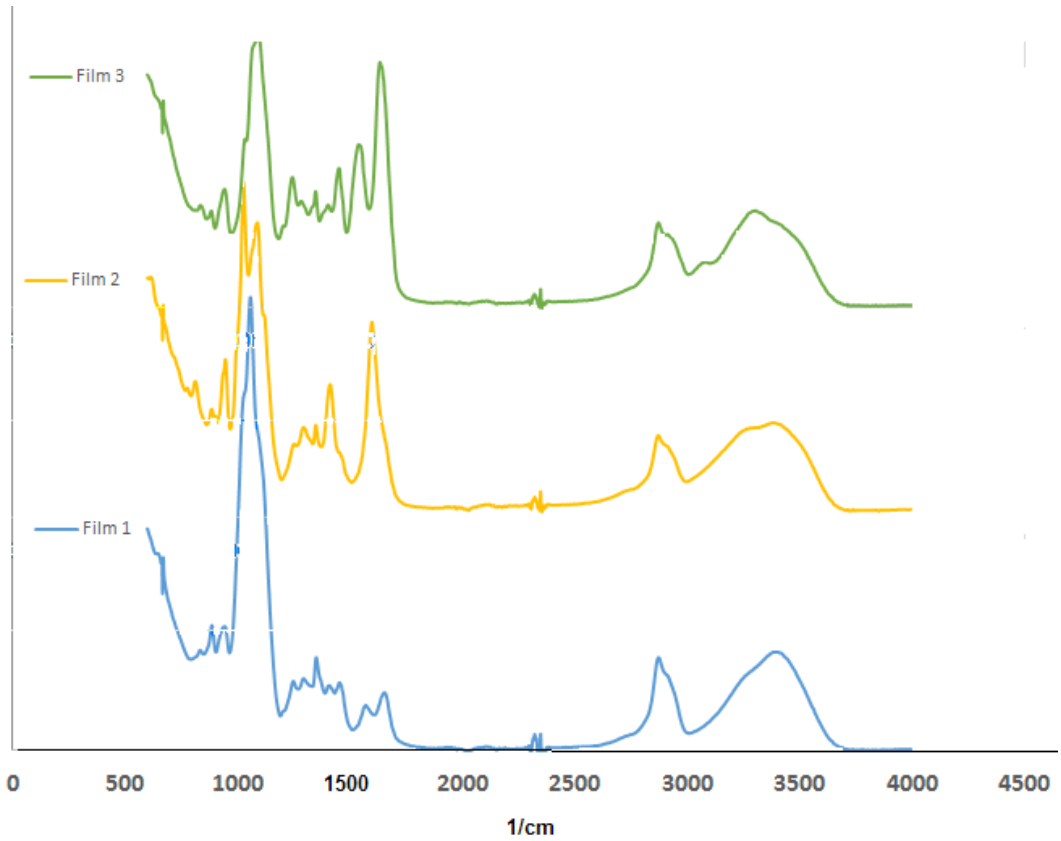

Figure 3. FT-IR analyses of PVP-based films.

In vitro drug release studies

The interaction of the films with donepezil hydrochloride at pH 7.4 and 37 ºC was seen in Figure 4. Donepezil HCl release studies were performed UV–Vis spectrophotometer at 270 nm. It has been found that film of sodium alginate show the highest release ratio with ~48%.

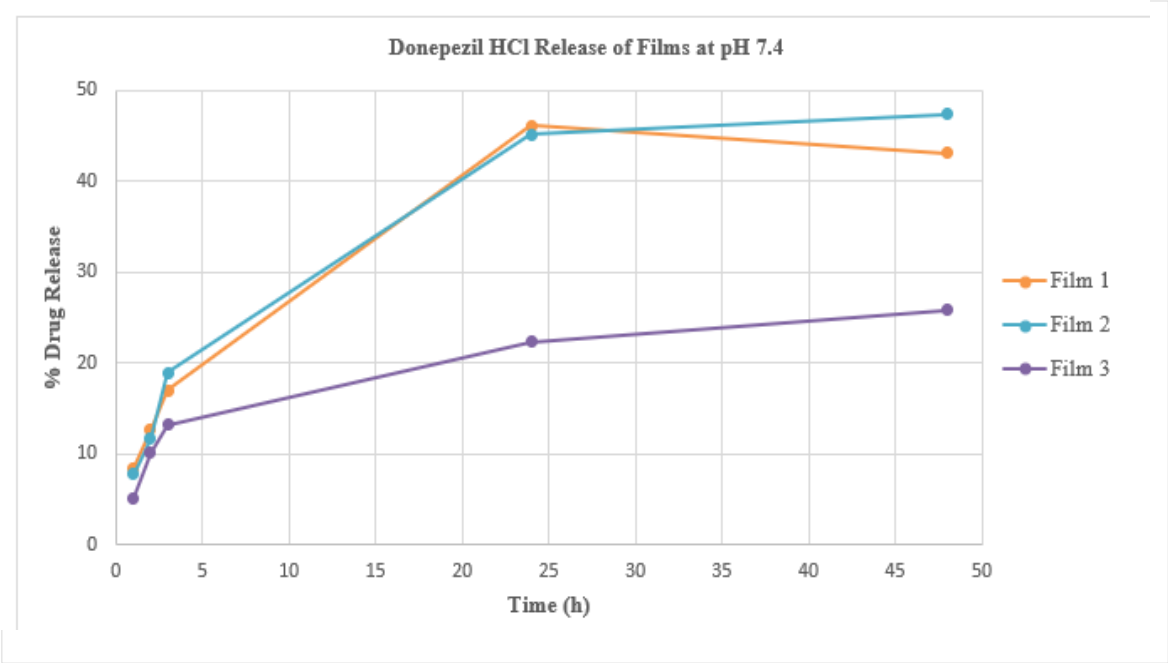

Figure 4. Donepezil HCl Release of Films

Drug Release Kinetic

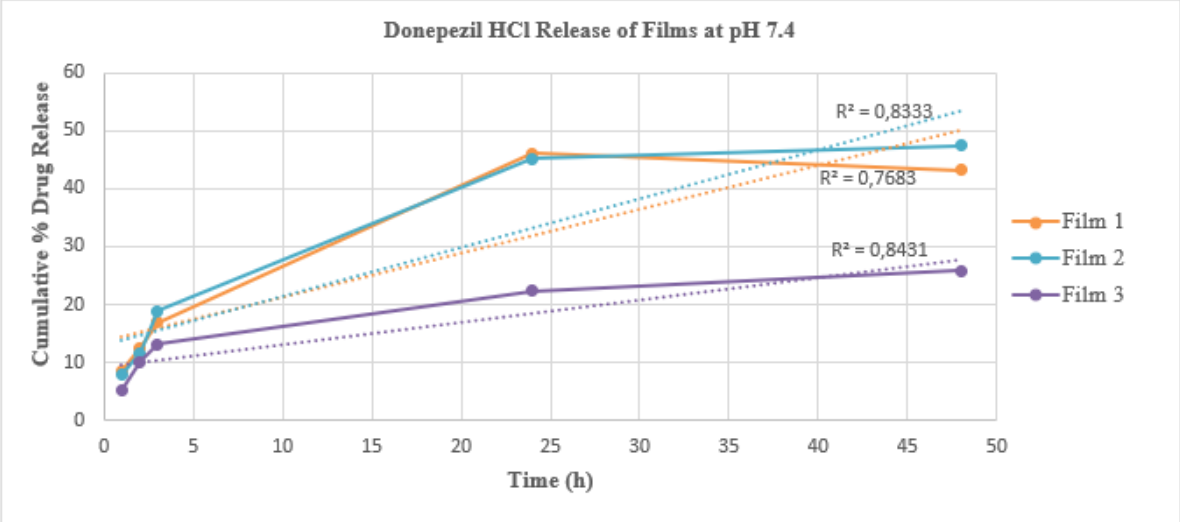

Figure 5. Zero Order Kinetic Model

The in vitro dissolution data of various formulation was analyzed by fitting the obtained data into various kinetic model to explain the release kinetics. Mathematical models that describe the kinetics of drug release from a transdermal patch include Higuchi, first order, zero order, and Peppas and Korsmeyer models. After data are collected and introduced into these models, the model that fits the data best is used to determine the mechanism of kinetic drug release (Dash, 2010). The kinetic profiles of PVP films are shown in Figure 5-8. According to the kinetic data, Higuchi kinetic Model were fitted suitable for all 3 films. Drug-release kinetics for films best corresponded to the Higuchi Kinetic model with good correlation with data with R^2 values varying between 0.89-0.93.

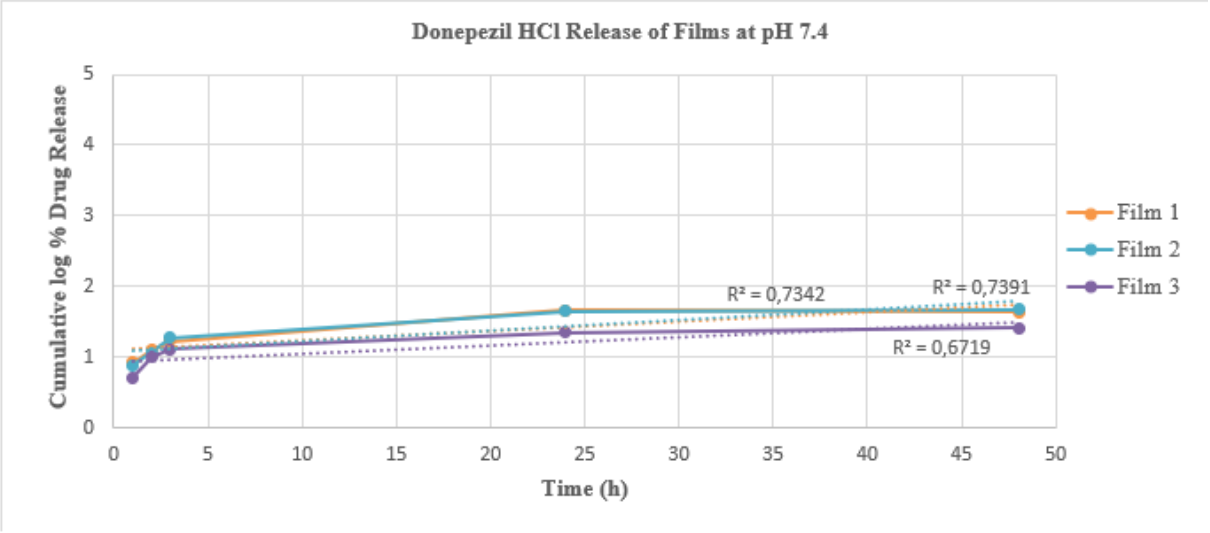

Figure 6. First Order Kinetic Model

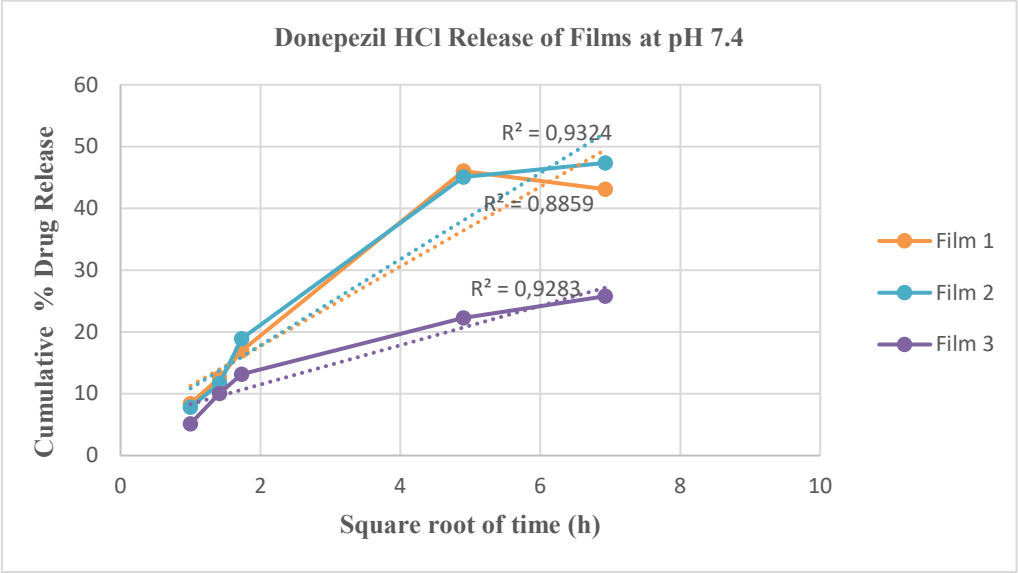

Figure 7. Higuchi Kinetic Model

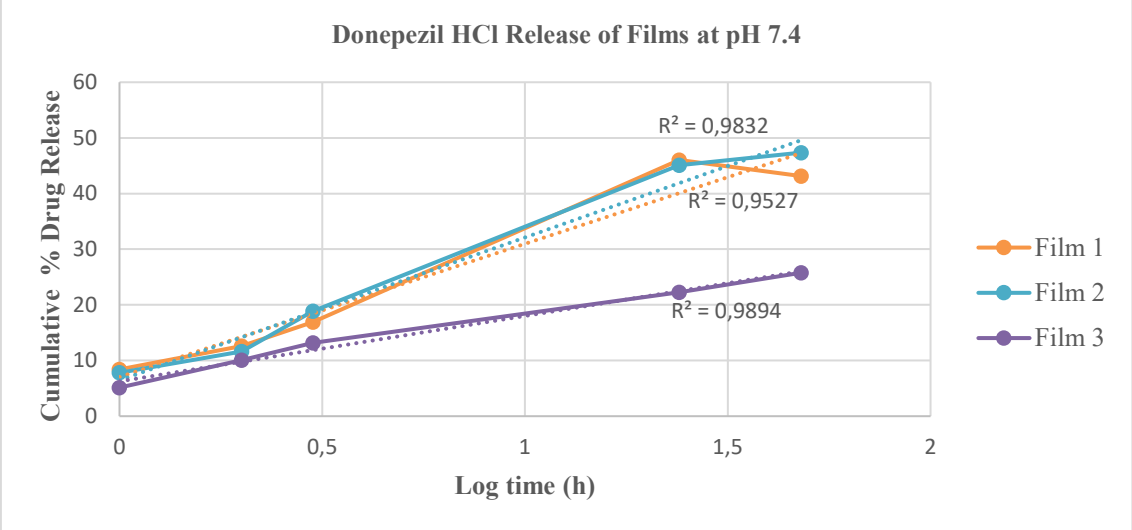

Figure 8. Korsmeyer-Peppas Kinetic Model

Conclusions

In this study, PVP based films were prepared successfully with Na-alginate and gelatine. It has been found that PVP film with Na-alginate has the highest drug release rate with 47.36 %. These results suggest that this type of films may be appropriate for use in the controlled release of drugs. The best fitted model showing the highest determination coefficient (R^2) was Higuchi Kinetic Model which is diffusion controlled transport mechanism of drug permeation.

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THE ACCURACY AND REPEATABILITY OF UV-DAD-HPLC METHOD FOR DETERMINATION OF CHOLESTEROL CONTENT IN MILK

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ABSTRACT
This paper is a report on the determination of the accuracy and repeatability of the proposed UV-DAD-HPLC method for the analysis of cholesterol content in milk sample. The accuracy and repeatability of the method are important values in the validation process and refer to the suitability of the method for given purpose. The sample preparation consisted of the saponification and extraction process. The conditions of saponification were as follows: time of saponification 15 min, the concentration of methanolic KOH solution 1 mol/L with a volume of 12 mL. The extraction of unsaponified residue was done two times with the mixture of n-hexane:chloroform (1:1, v:v). The samples were analyzed by HPLC chromatography with UV-DAD detector, C_{18} stationary phase, and with mobile phase consisted of an isocratic mixture of acetonitrile:methanol (60:40, v:v). In these conditions, the accuracy of method varied from 97.3 to 105.8%. The repeatability referred to the precision was evaluated from the relative standard deviation with the values ranging from 1.34 to 2.37%. From the results, it can be concluded that proposed HPLC method showed great accuracy and repeatability, and thus it could be suitable for the appropriate determination of cholesterol content in milk samples.
Keywords: cholesterol, HPLC, accuracy, repeatability, milk

Introduction

Cholesterol (3β)-cholest-5-en-3-ol) is a sterol lipid produced by animal cells. Most cholesterol is produced in liver, adrenal glands, intestines, and in gonads, whereas 20-25% of cholesterol comes from the diet of animal origin (Li et al., 2019). The word cholesterol may quickly be associated with chronic heart disease and other heart problems. However, it has also essential functions in the body such as providing essential components of membrane and serving as a precursor of bile acids, steroid hormones, and vitamin D (Daksha et al., 2010). As elevated human plasma cholesterol concentration may increase the risk of cardiovascular disease and atherosclerosis, a maximum intake of 300 mg per day for adults is recommended (Bertolín et al., 2018). From a nutritional point of view, cholesterol is not found in significant amounts in plant sources, is mostly present in foods of animal origin such as milk products, eggs, meat, and fish. Regarding its relationship with cardiovascular disease, the analytical methods for cholesterol evaluation in foods are crucial (Albuquerque et al., 2016). Cholesterol determination in foods usually involves lipid extraction, separation of cholesterol from interfering components or liberation of cholesterol into the free form, and measurement of isolated cholesterol. Cholesterol can be measured using gravimetry, titration, colorimetry, refractometry, fluorometry, and chromatography (Dinh et al., 2011; Kolarič and Šimko, 2020). Classical chemical methods are relatively simple and inexpensive to perform but multi-step procedures are required. Enzymatic assays involve the use of costly enzymes, although limits of detection are usually low. Chromatographic and mass spectrometric methods are the most accurate and sensitive (Li et al., 2019). The HPLC system equipped with either a UV/VIS detector or a photodiode array detector has been the most common alternative to gas chromatography for the analysis of cholesterol and other sterols in foods. The UV wavelengths for cholesterol absorption range from 203 to 214 nm with maximum absorbance at 205 nm because of the unsaturated center and the hydroxyl group (Dinh et al., 2011). According to Albuquerque et al. (2016), the reversed-phase HPLC coupled with UV or DAD detector is the most common technique for the evaluation of cholesterol content in foods. In our previous study (Kolarič and Šimko, 2020), it has been shown that both spectrophotometric and HPLC methods could be suitable for the determination of cholesterol content in milk but HPLC exhibited higher sensitivity and lower limits of detection. According to Osman and Chin (2006), the HPLC method was found to be the most convenient and consistent in giving highest sensitivity and accuracy for the determination of cholesterol. The propose of this work was thus the evaluation of the accuracy and repeatability of the proposed UV-DAD-HPLC method for the determination of cholesterol content in milk as these parameters are required for the appropriate method validation.

Materials and Methods

All reagents and standards were of analytical grade. Cholesterol standard was from Sigma-Aldrich with a purity ≥99%. Chloroform, n-hexane, ethanol, and sodium sulphate anhydrous were purchased from Centralchem s.r.o. (Bratislava, Slovakia). Methanol and acetonitrile (HPLC grade) were purchased from Fisher Chemical (Loughborough, UK). The cow´s milk (3.5% fat, Rajo a.s., Bratislava, Slovakia) was bought in a local market.

The saponification process was performed according to our previous study with slight modifications (Kolarič and Šimko, 2020). The 5.0 g of milk sample was refluxed with the methanolic solution of KOH (1 mol/L) using the volume of 12 mL and reaction time 15 min. The extraction process was performed two times with a mixture of n-hexane and chloroform (1:1, v/v)). The volume of extraction solvent was 15 mL. The extraction system consisted also of 10 mL of deionised water and 1 mL of ethanol (96%). After the extraction, the solvent was filtrated through anhydrous sodium sulphate, and evaporated using a vacuum evaporator (Heidolph, Germany). The residue was dissolved in 3 mL of methanol. The solution was filtered using syringe filters with PTFE membrane and particle size 0.2 µm (PTFE, 13 mm, 0.2 µm, Agilent Technologies, USA). The prepared solution was directly analysed by HPLC chromatography.

HPLC analysis was performed using an Agilent Technologies 1260 infinity system (USA) equipped with a vacuum degasser, a quarterly pump, an autosampler, and the UV-DAD detector. Cholesterol was detected at UV wavelength of 205 nm. Isocratic elution was performed at a flow rate of 0.5 mL/min using the mobile phase consisted of acetonitrile/methanol 60:40 (v/v). The injection volume was 10 µL and the temperature was set at 30 °C. As a stationary phase, a Zorbax Eclipse Plus C_{18} column (2.1x100 mm, 3.5 µm particle size, Agilent, USA) was used with the guard column Zorbax SB-C_{18} (4.6x12.5 mm, 5 µm particle size, Agilent, USA). Total run time of analysis was 7 min with retention time of cholesterol in 5.6 min. The results were recorded using the OpenLab CDS software, ChemStation Edition for LC, and LC/MS systems (product version A.01.08.108).

The accuracy of the method was determined by recovery tests after spiking the milk samples with cholesterol standard using five different concentrations (0.1, 0.3, 0.5, 1.0, and 1.5 mg/mL). After the quantification of the analytes in the fortified samples and in the control, the recovery percentage (% REC) was calculated according to equation 1 (Kolarič and Šimko, 2020):

$$\%REC = \left(\frac{Obtained\ conc. - Control\ conc.}{Expected\ conc.}\right) x\ 100 \quad (1)$$

The repeatability was investigated by injecting four replicates of sample in quadruple on the same day. The intermediate precision was evaluated on three different days by preparing four replicates from the same sample on each day. The precision was then evaluated from the relative standard deviation (RSD).

Statistical analysis was performed using Microsoft Excel version 365 and the results are expressed as mean ±standard deviation or as percentage.

Results and Discussion

Method validation is the process of defining an analytical requirement and confirming that the method under consideration has capabilities consistent with what the application requires. The performance characteristics commonly evaluated during method validation are selectivity, limit of detection and quantification, working range, analytical sensitivity, trueness (bias, recovery), precision (repeatability, intermediate precision, and reproducibility), measurement uncertainty, and ruggedness (Eurachem Guide, 2014). The accuracy of the method is determined as recovery and precision. In the cholesterol analysis in food products, accuracy is an important parameter as the sample preparation could vary in different food matrices.

The recovery of our proposed HPLC method for the determination of cholesterol content in milk is summarized in Table 1. The chromatograms of the analysis of spiked milk samples with the cholesterol standard at different concentrations are shown in Figure 1. Three general approaches are applicable for the evaluation of method recovery: 1. analysis of reference materials, 2. recovery experiments using spiked samples, and 3. comparison with the results obtained with another method (Eurachem Guide, 2014). In our study, the recovery of the method was studied by spiking samples with the cholesterol standard using five different concentrations (0.1, 0.3, 0.5, 1.0, and 1.5 mg/mL). The method showed great recovery ranging from 97.3 to 105.8%. The obtained results thus prove the efficiency of the proposed method. According to Bauer et. al (2014), the analyte recoveries close to 100% are ideal, but smaller values are admitted if the precision is good. Based on their results, the recovery of the method of cholesterol determination in milk ranged from 100.63 to 103.90% using the three different cholesterol standard concentrations (75, 150, and 300 µg/mL, respectively). Almost the same results were described by Ramalho et al. (2011). Their HPLC-DAD method for determination of cholesterol content in milk samples showed recovery ranging from 97 to 101%. The greater recoveries are described by Albuquerque et al. (2016), which varied from 111 to 125%. The recovery of the HPLC method is mainly influenced by two critical steps in sample preparation, the saponification and extraction. In the extraction process, the choice of extraction solvent is crucial. Most of the previous studies showed great recovery with the n-hexane solution. In our previous study (Kolarič and Šimko, 2020), the recovery using the pure n-hexane was only 91.05%. In this study, it was shown that the extraction with a mixture of n-hexane and chloroform (1:1, v/v) achieved better recoveries. Oh et al. (2001) studied the cholesterol

recovery using the different extraction methods (method A – saponification and extraction with diethyl ether, method B – extracted sample from method A passed through silica Sep-pak, method C – saponification and extraction with hexane, and method D – solid phase extraction) by adding 1.0, 2.0, and 3.0 mg of cholesterol to milk samples. Based on their results, the mean recoveries of methods A, B, C, and D were 99.3-100.2, 98.8-99.3, 100.1-100.3, and 99.7-100.7%, respectively, thus the differences were not significant. The saponification of the sample can be direct or indirect. The indirect saponification involves fat extraction, however, cholesterol forms complexes with other phospholipids and proteins, and this changes their overall physical properties, resulting in inefficient extraction of cholesterol, which explains the poor recovery of cholesterol (Oh et al., 2001). The direct saponification is thus preferred. In our study, the direct saponification with the methanolic KOH solution was also applied. Ahn et al. (2012) used method, which required only a sample pretreatment time of 5 min per sample and involved no-heating saponification. In the recovery test, the values were also satisfying, ranged from 98.11 to 102.34%. The recovery of the method of cholesterol determination in food is also influenced by the proper analytical technique. In our previous study, better recoveries were achieved by HPLC chromatography (91.05%) than spectrophotometric determination (85.34%). According to Albuquerque et al. (2016), the UHPLC method recovery ranged from 80 to 106% in comparison to HPLC (111 to 125%). Osman and Chin (2006) described that the mean recoveries of methods using a spectrophotometer, HPLC, and gas chromatography were 86.67-126.67, 73.33-110.00, and 60.00-146.67%, respectively.

Table 1: The recovery of proposed HPLC-UV-DAD method for the determination of cholesterol content in milk.

Added cholesterol standard concentration [mg/mL]	The cholesterol content in milk sample [mg/kg] [a]	Recovery [%]	RSD [%]
0.0	105.78 ±1.35	-	-
0.1	104.51 ±2.20	98.8	2.11
0.3	111.89 ±0.32	105.8	0.29
0.5	111.17 ±0.96	105.1	0.87
1.0	102.93 ±1.25	97.3	1.22
1.5	104.16 ±3.36	98.5	3.23

[a] The values are expressed as mean ±standard deviation; RSD, relative standard deviation

The repeatability is a measure of the variability in results when a measurement is performed by a single analyst using the same equipment over a short timescale while intermediate precision gives an estimate of the variation in results when measurements are made under more variable conditions (Eurachem Guide, 2014). In this study, the repeatability and intermediate precision were determined comparing the standard deviation (SD) and relative standard deviation (RSD) of the results obtained in three days. The repeatability refers to precision, which is important for the final accuracy of the proposed method. The values obtained for the repeatability and intermediate precision of the proposed method for cholesterol determination in milk are found in Table 2. From the results, it can be noticed that our method showed great repeatability with the RSD varied from 1.3 to 2.8% and intermediate precision with the RSD 0.5% thus our method is precise. The RSD of 3% was described by Ramalho et al. (2011) for intermediate precision while Albuquerque et al. (2016) showed the RSD values ranging from 1.66 to 1.95%. The RSD values of up to 15% are acceptable, although a maximum variation of 5% for micro constituents is recommended (Bauer et al., 2014). In general, the HPLC or gas chromatography has the highest precision in the analysis of cholesterol content in food, where the HPLC-UV seems to be the most suitable. The comparison of different methods for the determination of cholesterol content in food samples described by Daneshfar et al. (2009) showed that the RSD values obtained by electrophoresis were up to 6.3%, reverse micelle up to 11%, solid phase extraction-gas chromatography-flame ionization up to 3.6%, and HPLC-fluorimetric up to 5.6% while HPLC-UV showed the RSD 3.1%. Higher interday precision using gas chromatography tandem mass spectroscopy in the analysis of cholesterol in milk powder was also noticed by Chen et al. (2015) with RSD 8%.

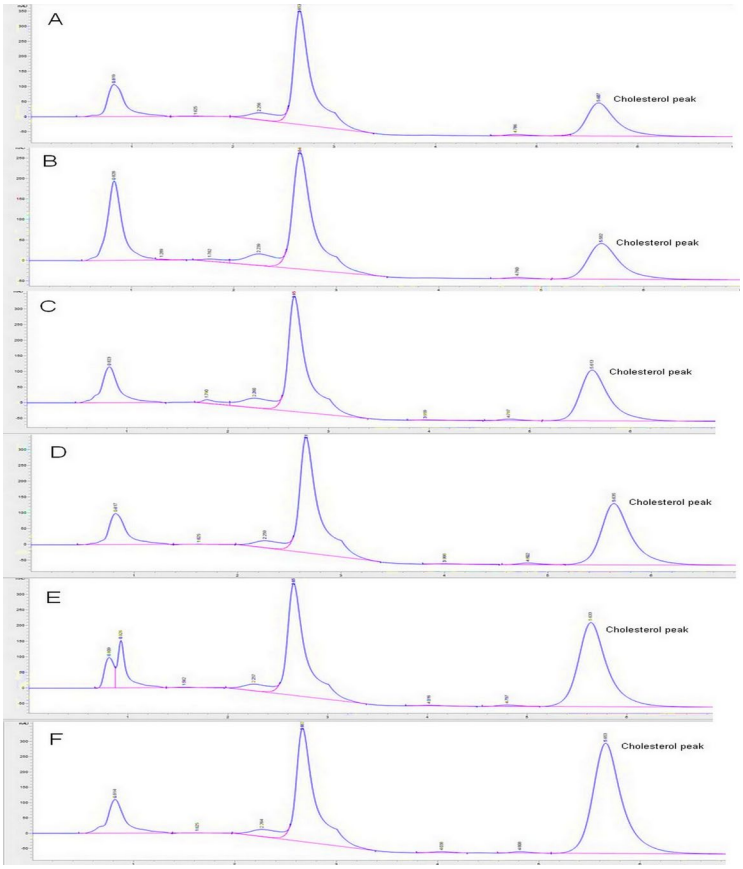

Figure 1. The chromatograms of the analysis of spiked milk samples with the cholesterol standard at different concentrations: A – control sample, B – 0.1 mg/mL, C – 0.3 mg/mL, D – 0.5 mg/mL, E – 1.0 mg/mL, and F – 1.5 mg/mL.

Table 2: The repeatability and intermediate precision of the proposed method for cholesterol determination in milk

Repeatability	The cholesterol content in milk sample [mg/kg] [a]	RSD [%]	Intermediate precision RSD [%]
Day 1	120.92 ±2.86	2.37	0.53
Day 2	120.47 ±1.61	1.34	
Day 3	119.41 ±2.37	1.98	

[a] The values are expressed as mean ±standard deviation; RSD, relative standard deviation

Conclusion

In this study, it was proven that proposed UV-DAD-HPLC method for the determination of cholesterol content in milk has great accuracy, precision, and repeatability. The sample preparation was optimized by using the extraction solvent consisted of the mixture of n-hexane:chloroform (1:1, v:v), and the saponification time in 15 min. In these conditions, the recovery of method varied from 97.3 to 105.8%, and the repeatability referred to the precision from 1.3 to 2.4%. These findings are important as the solvent consumption and time of sample preparation was optimized and simplified in comparison to the previously published HPLC methods. This method is thus accurate and can be used for appropriate evaluation of cholesterol content in milk.

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