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Teaching learning sequence for the introduction of superhydrophobicity in secondary education

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Many biological surfaces are known for their micro- and nanoscale structures, which combined with their hierarchical properties lead to superhydrophobic surfaces. The lotus leaf is the most studied leaf surface that exhibits superhydrophobicity. The knowledge gained by examining its leaf properties helps scientists design superhydrophobic surfaces that benefit humanity on a daily basis. Therefore, there is a necessity to update school science curricula by integrating nanotechnology-related concepts that are both relevant and meaningful to students. This work suggests a proposal for the introduction of superhydrophobicity in secondary education through the development of a teaching learning sequence. Through the MER methodology, the scientific content is analyzed and transformed into a content structure for instruction, defining the learning objectives of each unit through the 5E Instructional Model and considering the difficulties and misconceptions that students may have. The implementation of the educational reconstruction will be presented considering all the parameters involved in the learning process.

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1. Introduction

In the 1990s, biologists and scientists began to study natural superhydrophobic surfaces. The surface structure affects wettability. For example, liquid droplets are in contact with the upper part of a rough surface and the lower part is filled with air when the surface of solid is superhydrophobic. Some examples of superhydrophobicity from nature, show that some leaves, such as those of lotus, cauliflower, acacia, etc, have the tendency to repel water 1. This water-repellent feature is due to the hierarchical structure of the leaves (micro- and nano-bumps) and the presence of a hydrophobic wax coating. Water droplets on such surfaces sit on top of the nanostructures, with air filling the "valleys" of the structure below the droplet [1]. Although this phenomenon is observed in other plant leaves besides the lotus, this property has been called the "lotus effect". Several commercial products are mimicking the lotus leaf surface. For instance, superhydrophobic textiles are available as well as coatings with exceptional water repellency [2].

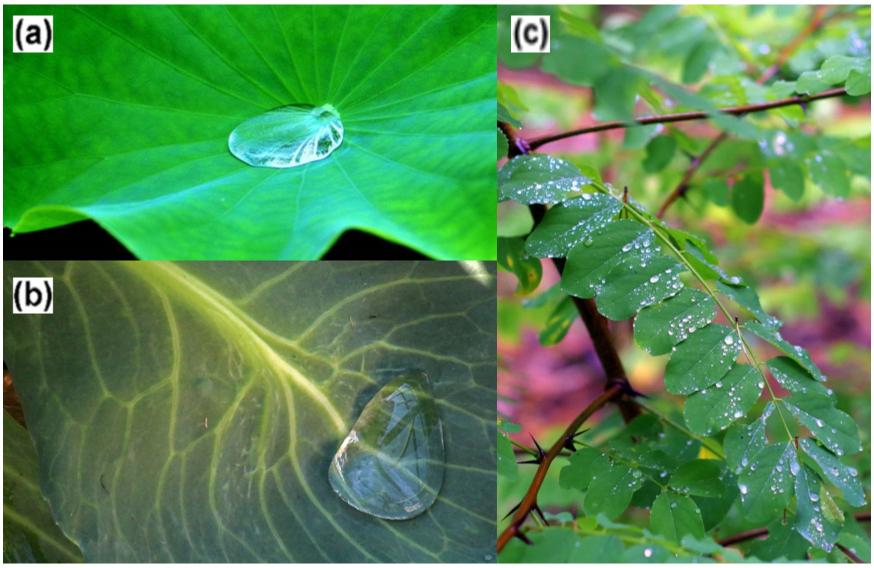

Figure 1: Water droplets on the superhydrophobic leaves of (a) lotus, (b) cauliflower and (c) acacia.

Often these surfaces are characterized by contact angle measurement, with water, to quantify the hydrophobicity of the surface. As a rule, a superhydrophobic surface shows a water contact angle higher than 150 degrees. Perfectly hydrophobic surfaces are found to exhibit advancing θ_A and receding θ_R contact angles of 180 degrees. However, recent studies showed that even though contact angle measurement is an accurate method for contact angles below 120 degrees, errors increase with the increase of measured contact angle. Thus, Gao and McCarthy [3] developed a method for testing extreme hydrophobicity to distinguish between surfaces exhibiting contact angles of 180 and 179 degrees.

For the observation of the phenomenon of superhydrophobicity, that is, for the measurement of the contact angle up to the observation of the hierarchical structures at the level of the micro- and nanoscale, the optical microscope and the SEM (Scanning Electron Microscope) are used respectively. Optical microscopes use a beam of light, ranging from 400*nm* to 650*nm* in wavelength,

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allowing the observer to analyze the effect of light as it is applied to a specimen. On the other hand, SEMs scan a focused beam of electrons across the surface of a sample, where electromagnets are used to focus the negatively charged electrons. The electrons coming out of the sample are used to create a detailed image and reveal information including the morphology, chemical composition, crystalline structure, and material orientation. Because of the geometry of the imaging system, SEMs have a much greater depth of field than optical microscopes, where the whole specimen can be in focus. This is because, for the optical microscope, the depth of focus is the distance above and below the image plane over which the image appears in focus. As the magnification increases in the optical microscope, the depth of focus decreases. In contrast, SEMs can create a three-dimensional appearance of the specimen image. This is because of the method in which the data is obtained, where a fine electron beam is scanned over the surface and the detected secondary electrons form an image with a high depth of focus.

From the cognitive perspective, the explanation of the lotus effect seems to be an emergent process [4]. This claim is reinforced by the idea that the explanation of the lotus effect has neither an identifiable causal agent or agents nor an identifiable sequence of stages. It is a result of the collective interaction of all of the agents, namely the micro- and nanostructures of a leaf's surface, the distance between them and the trapped air in the intestinal spaces that increases the surface tension of the water droplets [4]. Although science education research on cutting-edge research topics is well advanced [5, 6], current scientific research topics such as lotus effect have not yet been broadly incorporated in science lessons [7]. Superhydrophobicity is an emerging Nanoscience and Nanotechnology (NST) topic that combines features from physics, chemistry, biology and engineering due to its unique nanoscale properties. Integrating NST topics in science classes familiarizes students with the processes of scientific research and attracts students' interest by exploring fascinating scientific applications [8].

The purpose of this work is the synthesis of a TLS for introducing senior high school students to the concepts and the applications of super-hydrophobicity. More specifically, the aims of this work are:

1. to analyse the scientific content so that the elementary ideas will be determined,
2. to reconstruct the scientific content into content which is suitable for instruction, through the the Model of Educational Reconstruction methodology,
3. to determine the working example (surface characterisation of leaves) and
4. to design the learning sequence through the 5E Instructional Model taking into account the students' difficulties and prerequisite knowledge.

This proposal is considered suitable for activities outside the school science curricula (e.g., science club) lasting 4-5 meetings.

2. Theoretical Background

2.1 Nanoscience and Nanotechnology in education

Science education research highlights the fact that science is usually presented as a robust, undisputed structure concealing its uncertain nature [9]. Cutting-edge research topics in science teaching can augment students' interest and promote scientific literacy, as they make them realize the necessity of acquiring some basic scientific knowledge in order to express informed opinions about its use in everyday life [10]. These topics also provide students with the experience of science as a procedure instead of the "ready", rigid science they are usually taught, as they can explore fascinating, real examples of scientific applications, making the lesson more attractive [11].

Nanoscience and Nanotechnology (NST) have been recognized as an emerging and promising technology of the 21st century. This is primarily due to the fact that NST unify many scientific subjects, such as physics, chemistry, biology and engineering and concurrently due to the unique properties that matter presents at the nanoscale [12]. NST constitutes a new interdisciplinary research field that focuses on the manipulation of matter as well as on the exploitation of materials' properties, in a size range approximately 1-100nm, widely recognized as nanoscale [6]. On this scale, materials appear to have unique properties that enable novel applications [6, 13]. As NST continues to develop, educators face the challenge of incorporating the new field in all of the levels of education [14–16]. In the Science Education field, there is an increasing interest in introducing NST concepts starting from primary school [12, 14, 17–19]. However, traditional school curricula do not include NST content [14]. The interdisciplinary nature and remarkable applications of NST have prompted science education researchers to particularly recognize the potential of NST in science teaching [20, 21].

It is stated that students need to develop their nanoliteracy in order to come up with everyday issues arising from NST applications, taking informed decisions and estimating the potential risks and benefits [18, 22]. Students' understanding about microscale, and dimensionality was improved as a result of using the Atomic Force Microscope (AFM) with a haptic interface [6]. The results of this study suggested that the use of hands-on activities for learning about morphology of very small objects may be beneficial. Despite the fact that research on educational approaches is increasing, as far as educational practice is concerned, they are still considered as novelties [23].

2.2 The size and scale cognition in the context of NST

Big Ideas (BI) are concepts that are interdisciplinary in nature and can explain a wide range of phenomena both within and across disciplines. They are important because they provide a framework for the long-term development of conceptual understanding by students and teachers. Through the interdisciplinary nature of NST, an opportunity is presented to reorganize the scientific content and the way it is taught according to the curriculum. In this way the ideas could be addressed in an interdisciplinary manner, within a coherent curriculum.

Size and scale are fundamental for understanding other NST concepts, such as the BI size-dependent properties [13, 15]. In order for students to understand the size and scale, scholars adopted both qualitative and quantitative approaches. The qualitative approach is associated with the size and the quantitative with the scale cognition [24]. Concerning the size cognition in NST context, students should be able to classify objects into macro, micro, nano and atomic world and order objects according to their relative size [25]. According to the literature review of Peikos et al. [4], the understanding of size and scale seems to be difficult for students. Most students identify three vague objects categories (large, medium, small), facing difficulties in grouping non-visible objects. Tretter et al. [26] emphasized that difficulties regarding the conception of the size of non-visible objects for primary school students derived from their lack of experience with these objects, being in accordance with Magana et al. [25]. Last but not least, as the participants' age increased, they were able to identify more distinct conceptual categories of objects of different size [26].

Although most of the research literature on instructional approaches have been implemented to primary school students related to the NST content, the information they give us about the lotus effect and the phenomenon of superhydrophobicity is also quite useful for their application in secondary education. According to the literature review of Peikos et al. [4], a quasi-experiment conducted by Chen et al. [27], in order to examine the effectiveness of the expositive-teaching and the experiential-teaching approaches to students' learning, showed that the experiential-teaching was approved more effectively. The teaching approach included definitions of the nanometre and concepts related to size, the lotus effect, nanoparticles, and nanotubes. These hands-on activities helped students understand the lotus effect, recognising relevant commercial products. The research of Lin et al. [16] has examined if a half-day camp programme for nanotechnology could enhance students' knowledge concerning NST concepts. Students were informed of several NST aspects during lectures, such as the properties and applications of NST and the nanophenomena in nature, such as the lotus effect. The researchers have found out that the students' achievement was significantly improved after the intervention. Additionally, the effectiveness of an NST educational programme in gifted primary school students' learning was studied by Yu and Jen [19]. The basic phenomenon that was introduced was the lotus effect. The students did experimental activities with superhydrophobic materials and observed the nanostructures of a leaf using images from electron microscopes, and they watched relevant videos. The researchers have concluded that there was a significant improvement in students' learning. Finally, Mandrikas et al. [12] implemented a TLS aiming to identify if the students were able to understand NST concepts. Concerning Size and Scale, students were familiarised with the nanometres as well as the grouping and ordering of macro, micro, and nano world objects based on their size. Based on students' worksheets and group interviews after implementing the TLS, the researchers argued that students' understanding of the NST concepts was improved.

2.3 Theoretical framework of the TLS development

The Model of Educational Reconstruction (MER) [28] has been developed as a theoretical framework for studies investigating whether it is worthwhile and possible to teach particular science concepts, principles and views of the nature of science [23]. The major aim is to bring science content structure and educational concerns into a balance when developing teaching and learning sequences [29]. According to MER, the scientific content structure of a subject should be transformed into an educational one, which is suitable for students. This is achieved by studying and reconstructing the scientific content, after considering students' difficulties/ideas.

The model is based on a constructivist epistemological position of teaching and learning [30] and consists of three closely interrelated components: (a) Clarification and analysis of the science content, including analytical research on subject matter clarification and analysis of the educational significance of a particular science content. (b) Research on teaching and learning, comprising investigations of students' perspectives and their development towards the scientific view as well as studies on teachers' views and beliefs of the science concepts, students' learning and their role in initiating and supporting learning processes. (c) Design and evaluation of teaching and learning environments, comprising the design of instructional materials, learning activities, and teaching and learning sequences. The MER has been designed primarily as a frame for science education research and development. However, it also provides significant guidance for planning science instruction in school practice [23].

One of the methods that science education researchers have employed in order to inform such teaching practices in science classrooms is the development and dissemination of suitable Teaching Learning Sequences (TLS) [31, 32]. TLSs constitute "both an interventional research activity and a product" that highlight the close interconnection between the proposed teaching approach and the expected learning process to be followed by students as a result of TLS implementation [31]. Therefore, an attempt to develop a TLS on NST topics incorporating all these issues and the sequential larger-scale implementation of that TLS should be understood as a part of the effort for the development and dissemination of educational innovations [23].

The 5E Instructional Model [33] can be used to design a science lesson, and is based upon cognitive psychology, constructivist-learning theory, and best practices in science teaching [34]. While the model has been in existence since 1987, it recently gained renewed traction. According to Duran and Duran [34], the model consists of cognitive stages of learning that comprise engage, explore, explain, elaborate, and evaluate. Bybee [35] declares that using this approach, students redefine and change their initial concepts through interaction with their peers and their environment, as learners interpret objects and phenomena in terms of their current conceptual understanding.

3. Methodology

The scientific content for leaf surface characterization was identified through the corresponding section from Bhushan [1]. The educational reconstruction was based on the MER model. For the implementation of the educational reconstruction, it was deemed necessary to study the learning process from the student's point of view according to the Big Idea "Size-Dependent Properties" of NST from Stevens et al. [13]. The learning sequence was designed and organized according to the five stages of 5E Instructional Model. In several cases, students use original images from research papers. These images are used in an attempt to familiarize students with actual scientific research findings. All images used in the paper are properly cited.

Figure 2 shows the methodology followed for the development of the learning sequence for the introduction of superhydrophobicity in secondary education. This methodology combines the first two steps of the MER methodology with the 5E Instructional Model. The first step is about the clarification and analysis of the scientific content. The second step is the research on empirical studies conducted around the topic of superhydrophobicity in education, considering contemporary research on students' prior knowledge, difficulties and the instructional approaches regarding the specific topic. The last step is the design and the development of the TLS according to the five stages of the 5E Instructional Model. The implementation process, the evaluation and the TLS finalization

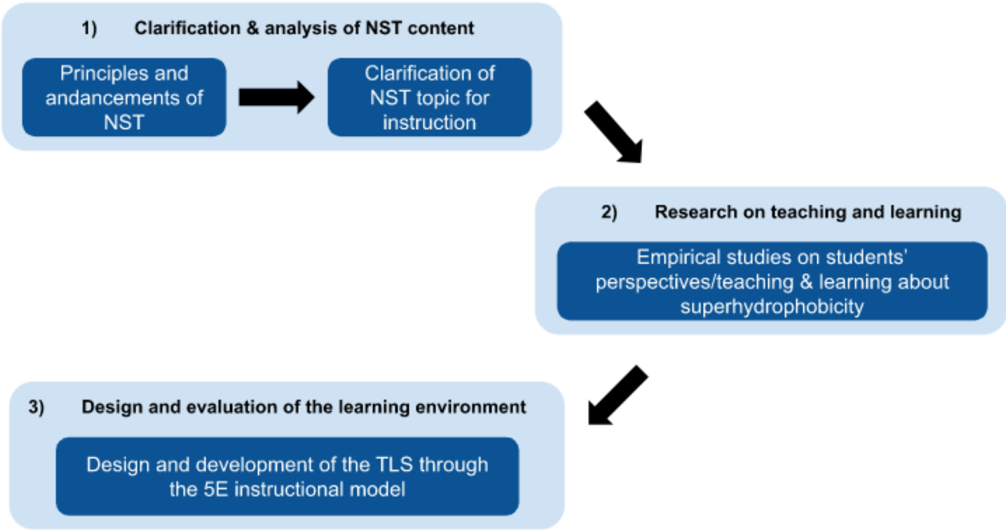

Figure 2: The methodology followed for the development of the learning sequence.

along with the development of teaching material for teachers and students, are not implemented in this work.

4. Results

The results of this work are divided into three parts. In the first part the scientific content is developed, in the second part the educational reconstruction of the content structure for instruction is carried out through the MER methodology, while in the third part a TLS suitable for senior high school students is proposed considering the BI of NSE "Size-Dependent Properties" and the students' ideas and difficulties.

4.1 Scientific Content

The scientific content for this educational reconstruction concerning superhydrophobicity has as its central axis the surface characterization of leaves and is divided into two central categories: a) The surface structure and b) the properties of superhydrophobic surfaces (Fig. 3).

According to the mind map, the surface structure is divided in three categories depending on the leaves' surface roughness which Fourth activity from the flat (hydrophilic) to the roughest surface (superhydrophobic) and depends on the density and size scale of the bumps distributed on the leaf surface. As far as the properties of the superhydrophobic surfaces concerned, the three factors one needs to characterize a leaf surface are the surface structures, the hierarchical levels and the contact angle between the water droplet and the leaf surface. Along with measuring and characterizing surface roughness and contact angle, adhesion and friction properties of these leaves are also considered. Adhesion force is an attractive pulling force between different molecules. The property of adhesion in water molecules generates surface tension. Molecules on the surface are pulled inward by cohesive forces, reducing the surface area.

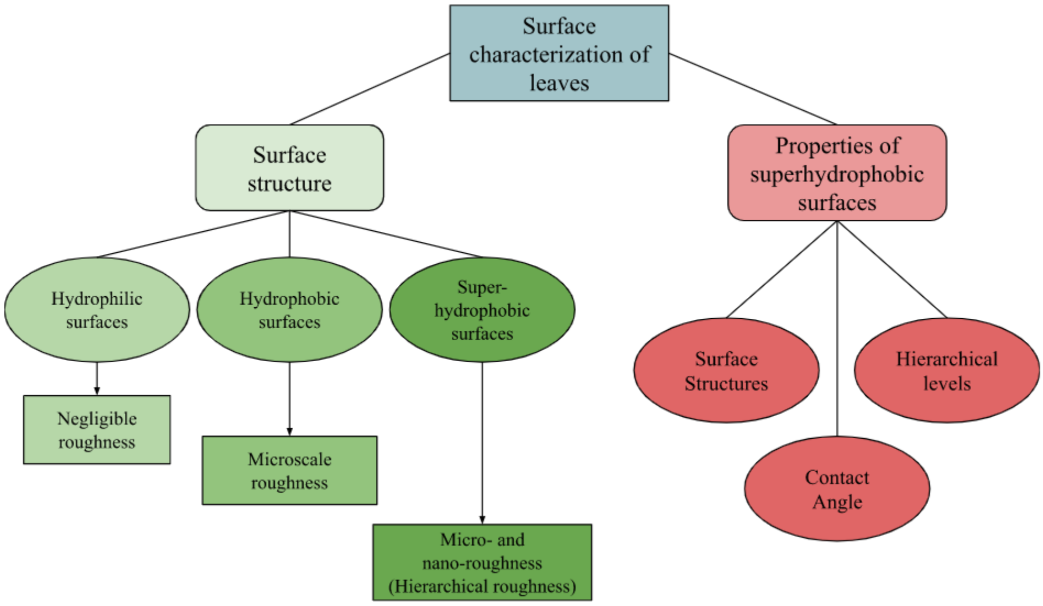

Figure 3: Scientific content of the surface characterization of leaves.

4.2 Educational Reconstruction

According to the MER model for elucidating and analyzing the scientific content, the central idea of this work must first be defined: **"Many biological surfaces, such as that of the lotus leaf, exhibit micro- and nanoscale structures, which combined with their hierarchical properties lead to superhydrophobic surfaces"**. According to [36], lotus is a semi-aquatic plant and develops peltate leaves up to 30 cm in diameter with remarkable water repellency. The stomata are located in the upper epidermis. The lower epidermis consists of convex cells covered with wax tubules and contains only few stomata. The upper epidermis features the distinctive hierarchical structure consisting of papillae with a dense coating of agglomerated wax tubules, which is the basis for the famous superhydrophobicity (Fig. 6). Adhesion allows for the water to stick to the organic tissues of plants. Leaf water drop adhesion is the retention of water droplets by leaves and can be measured as the amount of surface water per unit leaf area at a point which additional water can no longer be retained and starts to drip off.

The necessary prerequisite knowledge based on the BI of NSE "Size-Dependent Properties" for the TLS is:

- Matter is not a continuous material but consists of structures that are too small to be seen with the naked eye (Fig. 6).
- Knowledge of orders of magnitude, concepts of subdivisions and multiples, and units of measurement.
- The properties of a material determine how it looks, how it behaves, how it interacts with the environment and for which applications it can be useful.

Every teaching intervention must also consider the students' misconceptions and difficulties and deal with them:

- The macroscopic properties of a material are erroneously attributed to the individual atoms or molecules rather than to the properties of its surface structures (Fig. 7).
- Students find it difficult to compare very small sizes not visible to the naked eye, which affect the visible part, such as micro- and nano-scale surface roughness in leaves (Fig. 6).

Based on the central idea, the difficulties that the students may face, as well as the prerequisite knowledge, the content for instruction is then reconstructed and integrated in the following TLS.

4.3 Teaching Learning Sequence

The six teaching units organized according to the five stages of the 5E Instructional Model are presented below with different teaching objectives each.

4.3.1 Engage

The goal of the engage stage is to pique student interest, uncover prior knowledge, generate curiosity, and build a community of learners eager to discover more about the contact angle as an important property for the surface characterization of the leaves.

1. *Orientation experiments with various leaves*: Each group tests using an optical microscope the shape of a water droplet on leaves of different plants and classifies the wetting behavior according to their contact angle (Fig. 4). When analyzing the patterns of water drop adhesion on different leaves, students can notice that the plants appear to have a broad spectrum of water retained on their leaf surfaces. An increase in surface roughness sometimes inhibits the spread of droplets on leaf surfaces [37].
2. *Introduction of Basic concepts - contact angle*: Students split into small groups (3-4 persons). The teacher gives a short introduction to the concept of the contact angle as a property of the superhydrophobic surfaces. The instructional goal for this activity is for students to:

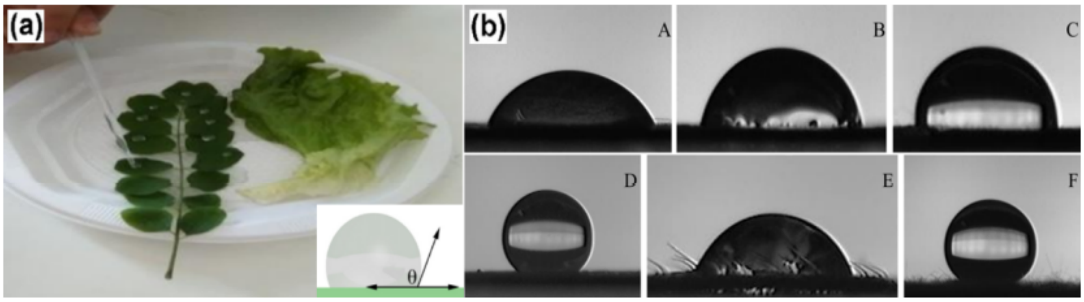

Figure 4: (a) Acacia and lettuce leaves, (b) Optical microscope side views of $6\mu l$ droplets of distilled water placed on some typical plant leaf surfaces [37].

- Describe the wetting behavior of various plant leaves according to the shape of the water droplet and the contact angle.

4.3.2 Explore

In this phase, data is collected by students, and evidence-based claims are made to connect their observations to the concept of the surface characterization of leaves.

3. *Exploration of Superhydrophobic surfaces – Lotus effect*: Students watch a video about the lotus effect and they discuss the surface structure of the leaves and their hydrophobic properties. They have the opportunity to observe the macroscopic properties of the lotus effect through the perspective offered by a digital camera (Fig. 5).

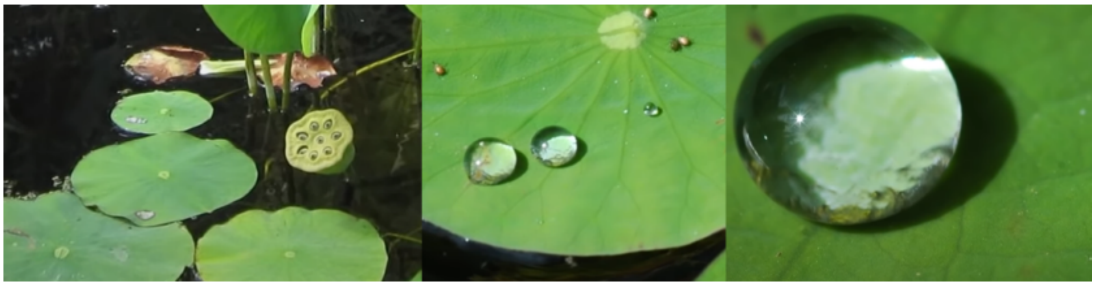

Figure 5: Digital camera lotus leaf surface images.

The instructional goal for this activity are for students to:

- Explain that natural water-repellent surfaces have hierarchical structure, which combined with the nanoscale roughness of the wax prevents the gaps between the bumps from filling with liquid.

4. *Exploration of Roughness & Hierarchical Structure of the Lotus Leaf*: Each group discusses the structure of lotus leaves and their superhydrophobic properties. Through the capabilities offered by a SEM microscope, students can observe the microscopic properties of a superhydrophobic surface such as lotus as they move through different size Fourth activity (Fig. 6).

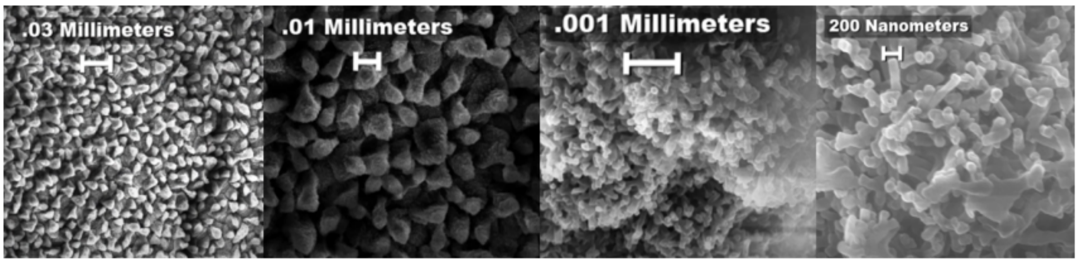

Figure 6: SEM images of the surface structure of the lotus leaf.

The instructional goal for this activity is for students to:

- Correlate the water repellent properties with the surface structure of the lotus leaves.

4.3.3 Explain

The Explain stage creates space for the student to share what they have learned, make deeper connections to the main concept, and for the teacher to introduce the new science content.

5. *Explanation of superhydrophobic surfaces*: Each group recreates the leaf surface in a way to explain the effect of lotus leaf micro- and nano-structure on the water droplet shape (Fig. 7). According to Frigione and Lettieri [38], several methods have been used to design and produce superhydrophobic surfaces, hierarchically structured and often bioinspired. The most common procedures include sol-gel processes and controlled nano-particle embedding into polymer matrices. The obtained hybrid polymer films, applied on the stone surface, are able to reduce the surface tension of the substrate, thus increasing the surface hydrophobic properties. Hydrophobicity can be further enhanced by increasing the surface roughness.

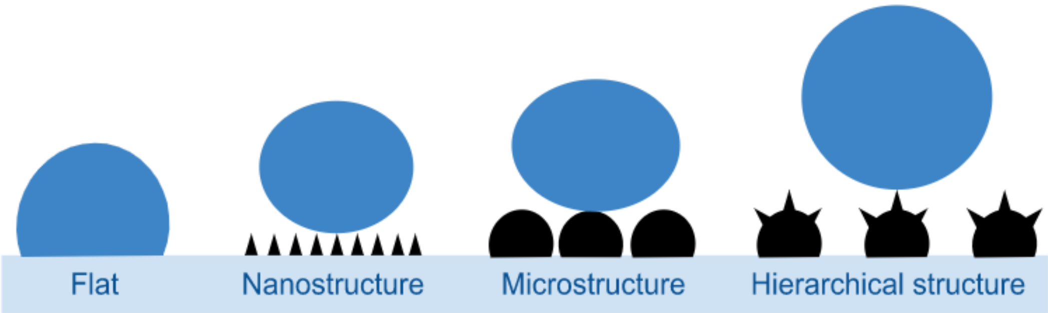

Figure 7: Wetting types of leaves according to their surface roughness.

The instructional goal for this activity is for students to:

- Use models of the lotus leaf micro- and nano-structure to predict its water-repellent properties.

4.3.4 Elaborate

In this phase, students are encouraged to apply the concepts and content learned to new or unfamiliar situations. This step can take the form of presentations, projects, engineering design challenges, and reflective writing.

6. *Superhydrophobic applications in everyday life*: Each group discusses the contribution of superhydrophobicity in relation to everyday technological applications and they present their findings. For example, a durable and eco-friendly superhydrophobic coating can be used as the potential coating to sustain the efficiency of a solar panel by inhibiting the dust deposition [39]. The instructional goal for this activity are for students to:

   - Describe situations in which a superhydrophobic surface would be useful in everyday applications.

4.3.5 Evaluate

It is crucial for students to evaluate their learning and for the teacher to use summative and formative assessments to determine student knowledge and skills. An assessment provides an opportunity to celebrate growth and student learning. It is also a time to assist and encourage the student struggling to understand new concepts.

In the framework of summative assessment, each group demonstrates their work through portfolios where they will record the entire process they followed to reach their conclusions regarding the phenomenon of superhydrophobicity. They will also carry out an overall assessment of their reasoning process in order to acquire the necessary meta-cognitive skills. Educators can evaluate student responses using a built-in rubric and provide feedback to students, who can then use that feedback to identify their weaknesses regarding the specific NST concept and the research process in general.

5. Conclusions

Following the process of designing and developing the TLS through the principles of MER for the scientific content of the surface characterization of leaves, the educational reconstruction is carried out considering all the parameters involved in the learning process. The present study illustrates that the teaching-learning sequence developed appears to provide students valuable insights on the phenomenon of superhydrophobicity through the basic ideas of NST. Through the development of this TLS by educationally reconstructing cutting-edge science topics following methodologically research-based approaches, i.e. MER, the students will be able to recognize the surface characteristics of a leaf, describe its properties, be able to justify the shape of the droplet based on the comparison of the sizes of the micro- and nanostructures that form on its surface, but also to give examples of technological applications in everyday life. Combined with MER, the 5E Instructional Model serves as a flexible learning cycle that assists curriculum developers and classroom teachers create science lessons that illustrate constructivist, reform-based, best teaching practices [34]. This proposal is also estimated to enhance students' understanding on nanotechnology taking into account the students' difficulties and prerequisite knowledge that have been detected in the research literature [25, 40]. Although this TLS was not implemented in any secondary class, due to the explorative character of the study, the results have to be understood as hypotheses that require evaluation and further processing.

There is not a lot of literature on superhydrophobicity in science lessons in compulsory education. This study intended to investigate the extent to which secondary students are able to approach NST topics through their interaction with a TLS on superhydrophobicity. The introduction of the lotus effect in science education has been attempted by other researchers with upper and lower secondary students [41–44]. As far as the TLS itself is concerned, taking into consideration the axes of specification and development as criteria of the usability of curriculum materials, even if the TLS on NST topics was both highly specified, the included alternatives that it provided to the teachers rendered it flexibly adaptive to many contexts without requiring significant changes [23].

It is clear that there is a need for fundamental research on superhydrophobicity including curriculum, instructional strategies, teacher professional development and assessment. The innovations and advancements in science are advancing rapidly. Therefore, it is crucial that research in science education research keep pace with these advancements so that educational practices can be shaped effectively.

Acknowledgments

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