EXAMENSARBETE INOM TEKNIK OCH LÄRANDE,
AVANCERAD NIVÅ, 30 HP
STOCKHOLM, SVERIGE 2020

Enhancing the degradation rate of microplastics and organizing a study visit about sustainability

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SKOLAN FÖR INDUSTRIELL TEKNIK OCH MANAGEMENT

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EXAMENSARBETE INOM TEKNIK OCH LÄRANDE PÅ PROGRAMMET CIVILINGENJÖR OCH LÄRARE

Titel på svenska: Förbättring av nedbrytningshastigheten av mikroplaster och organisering av ett studiebesök om hållbarhet.
Titel på engelska: Enhancing the degradation rate of microplastics and organizing a study visit about sustainability.
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Sammanfattning

Mikroplaster tar hundratals till tusentals år att bryta ner i naturen och utgör ett hot mot miljön. En fotokatalytisk nedbrytningsprocess har utvecklats där solljus utnyttjas för att bryta ner mikroplaster, dock tar det flera månader att bryta ner mikroplaster med den processen. Syftet med denna studie är att förbättra nedbrytningshastigheten av mikroplaster genom att syntetisera ett material där fotokatalys kombineras med Fenton-reaktion. Ett material med zinkoxid nanorör belagda med tennoxid och dekorerade med järnpartiklar ($ZnO/SnO_2/Fe^0$) syntetiserades och användes för att bryta ner metylenblått, polystyren och polypropen. Resultatet visar att nedbrytningshastigheten med $ZnO/SnO_2/Fe^0$ – materialet är snabbare än med ett ZnO – material, och att $ZnO/SnO_2/Fe^0$ – materialet kan användas för att bryta ned polystyren och polypropen.

Elevers syn på forskning och forskare kan påverka utvecklingen av deras intresse och inställning till vetenskap. Studiebesök på laboratorier har använts för att öka elevernas intresse och ge dem nya erfarenheter. Syftet med denna studie är att undersöka vad och hur gymnasieelever lär sig under ett studiebesök i ett nanotekniklaboratorium och hur studiebesöket påverkar gymnasieelevernas intresse och motivation för forskning och lärande. Ett studiebesök med 5 stationer organiserades och eleverna fick ett frågeformulär om vad de lärde sig under studiebesöket. Tematisk analys användes för att analysera elevernas svar. Resultatet visar att studiebesöket ökade elevernas intresse för forskning och vikten av att utforma stationer så att de är kopplade till elevernas tidigare kunskaper och ligger inom deras proximala utvecklingszon.

Nyckelord: Ackommodation, assimilation, den proximala utvecklingszonen, Fenton reaktion, fotokatalys med synligt ljus, mikroplast, polypropalen, polystyren, studiebesök, zinkoxid nanorör.

Abstract

Microplastics take hundreds to thousands of years to degrade in nature, and pose a threat to the environment. A photocatalytical degradation method have been developed to take advantage of solar light to degrade microplastics, however it takes several months to degrade microplastics with the process. The purpose of this study is to enhance the degradation rate of microplastics by synthesizing a material where photocatalysis is combined with Fenton reaction. A material with zinc oxide nanorods coated with tin oxide and decorated with iron particles ($ZnO/SnO_2/Fe^0$) was synthesized and used to degrade methylene blue, polystyrene and polypropylene. The result show that the degradation rate with a $ZnO/SnO_2/Fe^0$ – sample is faster than with a ZnO – sample, and that it can be used to degrade polystyrene and polypropylene.

Students' view on researchers can affect the development of their interest and attitude towards science. Study visits to laboratories have been used to increase students' interest and give them new experiences. The purpose of this study is to investigate what and how high school students learn during a study visit to a nanotechnology laboratory, and how the study visit affects high school students' interest and motivation for research and learning. A study visit with 5 stations was organized, and students were given a questionnaire about what they learned during the study visit. Thematic analysis was used to analyze the students' answers. The result shows that the study visit increased students' interest in research, and the importance of designing stations so that they are connected to students' previous knowledge and are within their proximal development zone.

Keywords: Accommodation, assimilation, Fenton reaction, microplastics, polypropylene, polystyrene, proximal development zone, study visit, visible light photocatalysis, zinc oxide nanorods.

Acknowledgements

I want to thank my supportive family and friends, my supportive and helpful supervisors Abdusalam Uheida and Helena Lennholm, and Professor Joydeep Dutta, and my sweet and helpful colleagues at the laboratory, Regina Irunde, Johan Nordstrand, Santosh Kumar, Minchao An, Siddharth Sahu, Karthik Laxman Kunjali, Esteban A. Toledo Carrillo, and Maria I. Alvarado Avila. I also want to thank Lena Geijer and Jakob Gyllenpalm for their help with the pedagogical part of my thesis.

I learned a lot while doing this master thesis, and my colleagues made it a truly joyful experience.

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1 Introduction

1.1 Plastic waste and microplastics in water

It is well known that plastic waste have been accumulating in the oceans, shorelines and even in the deep sea, threatening marine life. The degradation of plastics in water is extremely slow, thus resulting in accumulation that is life threatening for a lot of marine organisms (Barnes, Galgani, Thompson, & Barlaz, 2009).

Many plastic packages have been replaced with biodegradable plastic packages as a solution to the environmental issue with the plastic pollution. Polylactide is commonly used as a biodegradable plastic alternative to conventional plastics however, it only degrades at temperatures above $55°C$. This means it can be degraded by biological composting processes but not in soil or in seas. The fact that it is called a biodegradable plastic might make the users think that it would degrade in nature, due to the lack of knowledge about the different types of biodegradability. (Salač et al., 2019). When plastic waste in oceans is exposed to UV light, it slowly breaks down to smaller fragments (microplastics), however marine organisms attach around plastic fragments which results in the fragments becoming shielded against UV light (Barnes et al., 2009).

Microplastics are plastic particles with a diameter less than 5 mm. Microplastics are persistent pollutants that take hundred to thousands years to degrade in nature, thus making them a global environmental concern (Barnes et al., 2009), (Tagg et al., 2017), (Tofa, Ye, Kunjali, & Dutta, 2019a). Wastewater treatment plants are unable to completely remove microplastics from drinking water (Ljung et al., 2018).

The production and usage of microplastics can be found in the everyday life. For instance, washing clothes produce microplastics and microplastics can also be found in hygiene products such as scrubs (Cole, Lindeque, Halsband, & Galloway, 2011). Microplastics have also been found in consumable products. A recent study have shown that plastic teabags release microplastics and nanoplastics in tea (Hernandez et al., 2019).

Sustainable ways to degrade microplastics in water have been developed. Photocatalysis, with zinc oxide (ZnO) nanorods as catalyst and solar/visible light have been used to degrade microplastics in water. The reason nanorods are used is because they have a high surface-to-volume ratio, which means that they have a large reaction surface while taking very little space. The photocatalytic process produce hydroxyl radicals ($^{\bullet}OH$) that degrade microplastics. Since zinc is a cheap and nontoxic material, and since the process takes advantage of solar/visible light, the degradation process is both economic and environmental friendly, however, it takes several months for the degradation to be completed (Tofa, Kunjali, Paul, & Dutta, 2019b). To increase the degradation rate of microplastics, Fenton reaction can be integrated to the photocatalytic process since Fenton reaction produces the same active chemical that breaks down microplastics ($^{\bullet}OH$), and is a process that is commonly used to purify wastewater (Tagg et al., 2017). In this study, a material where both of these processes are combined, is developed and used to degrade polystyrene and polypropylene microplastics. Polystyrene and polypropylene are plastics that are commonly used in different everyday products like packaging materials, toys and household devices (Naturskyddsföreningen, 2019).

Discussing sustainability is a part of the high school curriculum in chemistry (Skolverket, 2011). In this study, a study visit for high school students was organized, where the students were taught about environmental issues such as microplastics pollution, and sustainable solutions.

1.2 Study visits

1.2.1 Students' learning during study visits

Study visits to informal learning environments such as museums, laboratories and science centers are used as a more entertaining and practical alternative to formal education (Anderhag, 2015). The students rarely visit the same informal learning environments continuously, and therefore there is not so much opportunity to influence the students' learning and interest in the long term. Informal learning environments can be used to develop students' scientific way of reasoning and increase their interest and understanding of science. Teachers give detailed descriptions of how the study visits are connected to the curriculum, however the main reasons teachers take students on study visits is to give them a break from the formal learning environment, to give them an opportunity to experience something different, and to let them have fun (Anderhag, 2015).

Students often remembers the social aspects of study visits, such as who was there and what was discussed, stronger than they remember the content of the study visits (Falk & Dierking, 2017). The study visits have potential to affect students learning, interest and choice of studies. There is a correlation between study visits to science centers and students' increased knowledge, interest, and curiosity for science. The opportunity for active practical or verbal participation, and students' previous knowledge can affect students' learning during study visits. (Anderhag, 2015).

1.2.2 Students view on researchers

Students' view on researchers can affect the development of their interest and attitude towards science (Miller, Nolla, Eagly, & Uttal, 2018). The majority of young students from different countries describe researchers in a stereotypical way, white males wearing lab coats, glasses, and working with chemicals. Students' stereotypical view of researchers decreases with age, however, students who have visited science museums have a more stereotypical view than the ones who haven't. On the other hand, students who have visited science laboratories don't show a different view on researchers compared to the ones who haven't. (Thomson, Zakaria, & Radut-Taciu, 2019)

There is a huge gap between how research is conducted and the laboratory work high school students do during chemistry class. A lot of high school teachers do laboratory work where the question, method and result is given (zero degrees of freedom). This type of laboratory work is called "cookbook approach", and the Swedish national agency of education (Skolverket) is encouraging high school chemistry teachers to have laboratory work with higher degrees of freedom. (Angelin, Gyllenpalm, Wickman, Forslin Aronsson, & Bergmark, 2017). In this study, students will gain insight into how research is conducted where the researchers themselves present parts of their projects.

Previous research have shown that students learn during study visits, and that study visits increase the students' interest, (DeWitt & Hohenstein, 2010; Falk et.al., 2014), however there has been no focus on *how* high school students learn during study visits, and how study visits affects high school students' interest and motivation for research and learning. In this study, some light will be shed on those topics.

2 Aims and research questions

In this section the aims and research questions of the technical and pedagogical part of this study are given.

2.1 Technical aim and research question

Technical aim

The aim of this work is to investigate the enhancement of the degradation rate of microplastics using integrated processes including both: (1) photocatalysis and (2) Fenton reactions. These processes generate hydroxyl radicals ($^{\bullet}OH$) that can oxidize organic matter and thus degrade microplastics. The reason for using integrated processes (photocatalysis and Fenton reaction) is to increase the production of reactive radicals to enhance the photo-oxidation processes.

Technical research question

To what extent will the degradation rate of microplastics be enhanced by combining photocatalysis with Fenton reaction?

2.2 Pedagogical aim and research questions

Pedagogical aim

The aim of this work is to investigate what and how high school students learn during a study visit to a laboratory and how their motivation for research change after the study visit.

Pedagogical research questions

What and how does high school students learn during a study visit about nanotechnology at a laboratory and how does the study visit affect interest and motivation for research and learning?

3 Background

In this section the technical background and the pedagogical framework for this study are given.

3.1 Technical background

In the technical background an overview of photocatalysis, Fenton reaction, and the combination of these two processes is given.

3.1.1 The mechanism of photocatalysis

Photocatalysis is a redox process that uses catalysts and light (visible or UV light) to increase the rate of a chemical reaction (Tofa, Kunjali, et al., 2019b; Zhang, Tian, Wang, Xing, & Lei, 2018). The environmental benefit of using catalysts is that they increase the rate of a chemical reaction without being consumed, and thus can be reused many times. The catalysts that are used in a photocatalysis process are called photocatalysts as they are activated after absorbing light. When the light has energy that is equal to the bandgap of the photocatalyst (or larger), the electrons will be excited from the valence band to the conduction band. This results in the production of electrons (e^-) and holes (h^+). The electrons can react with oxygen (O_2) producing superoxides (O_2^-) and the holes react with the water to produce hydroxyl radicals ($^\bullet OH$). Hydroxyl radicals and superoxides are very reactive and used to degrade pollutants in water. When hydroxyl radicals and superoxides react with pollutants in water, for instance microplastics, carbon dioxide and water is produced. (Zhang et al., 2018; Sakka, 2013).

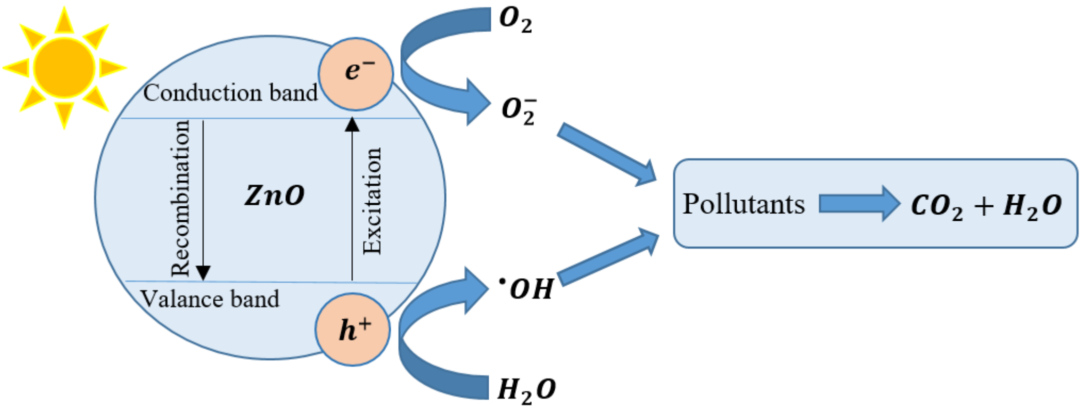

Fig. 1. An illustration of the photocatalysis process.

To be able to take advantage of solar/visible light when doing photocatalysis it's essential to have a bandgap that is in a suitable interval. Since visible light has the wavelength interval 380-740 nm, the suitable band gap interval will be 1.68-3.26 eV.

Metals have no band gap, the valence electrons of metals don't need to be excited to conduct electricity. Insulators have a large band gap and thus are non-conductive. Semiconductors on the other hand have a band gap that is larger than 0 but not too large like insulators, this allows the material to conduct electricity when the valence electrons are excited by visible/UV light. In other words, the bandgap of semiconductors make them suitable for photocatalysis.

Zinc oxide (ZnO) is a popular semiconductor photocatalysts because it is easy to synthesize, it is non-toxic, and has a band gap of 3,37 eV (Baruah & Dutta, 2009b; Baruah, K. Pal, & Dutta, 2012; Tofa, Kunjali, et al., 2019b). The hexagonal structure of ZnO nanorods have small defects, those defects result in the material having an optical band gap that is smaller than the band gap. ZnO nanorods have an optical band gap within the interval 1.68-3.26 eV thus making it a material that absorbs light in the visible region. (Baruah, Mahmood, Myint, Bora, & Dutta, 2010; Bora, Sathe, Laxman, Dobretsov, & Dutta, 2017; Mahmood, Baruah, & Dutta, 2011).

The ZnO nanorods can be prepared through a hydrothermal method (see section 4.1.1), (Tofa, Kunjali, et al., 2019b), and have a hexagonal shape. When the nanorods are grown hydrothermally in a chemical bath consisting of zinc nitrate and hexamine, the hexamine acts as support, so that the ZnO can form long straight nanorods. (Baruah & Dutta, 2009a; Sugunan, Warad, Boman, & Dutta, 2006).

3.1.2 Application of photocatalysis

Semiconductor photocatalysts have been used to degrade pollutants that are not easily degradable by other methods. The advantage of using semiconductor photocatalysts is that they are cheap, energy efficient, and disposable without causing environmental problems. Another advantage is that photocatalysis takes place in moderate temperature and pressure, which results in an overall cheap degradation process. (Bora & Dutta, 2014; Tofa, Kunjali, et al., 2019b; Zhang et al., 2018).

Zinc oxide nanorods have been used to degrade microplastics. The hydroxyl radicals and superoxides that are produced due to photocatalysis react with the microplastics and oxidizes them. This creates cracks on the surface of the microplastics because parts of the surface are turning into carbon dioxide and water. With time, the increased amount of cracks lead to the degradation of the microplastics. (Tofa, Kunjali, et al., 2019b; Tofa, Ye, et al., 2019a).

3.1.3 The mechanism of Fenton reaction

The Fenton reaction is a reaction that produces hydroxyl radicals by using iron as a catalyst and consuming hydrogen peroxide. The Fenton reaction can be briefly described by these two reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \qquad (2)$$

Iron acts as a catalyst and is not consumed during the Fenton reaction. The hydroxyl radicals ${}^{\bullet}OH$ which are generated by the reactions above are very reactive and have been used to degrade microplastics. Reaction (2) is much slower than reaction (1) and can therefore be seen as the rate-limiting reaction, however, the rate of reaction (2) can be increased by using solar/visible light. The Fenton reaction require pH to be between 2.5 and 4 to be effective. Below $pH = 2.5$ the iron catalysts will precipitate significantly, and above $pH = 4$ the Fenton reaction is slow. (Pignatello, Oliveros, & MacKay, 2006).

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \qquad (3)$$

The hydroxyl radicals are not only generated by the Fenton reaction. As reaction (3) shows, H_2O_2 can photolyse with light which will generate hydroxyl radicals (Pignatello et al., 2006).

3.1.4 Combining photocatalysis with Fenton reaction

ZnO nanorods dissolve at the pH interval where the Fenton reaction is optimal. In order to circumvent, a thin layer of tin oxide (SnO_2) can be coated on ZnO nanorods in order to reduce the dissociation of the ZnO nanorods. As SnO_2 is a wide bandgap material, and since it is very thin, visible light easily passes on to ZnO and when absorbed, would lead to photocatalysis processes. (Al-Hamdi, Sillanpää, Bora, & Dutta, 2016).

Fenton reaction is active when pH is between 2.5 and 4. However, Fenton reaction still works reasonably well at $pH = 5$ (Altinbas, Aydin, Faik Sevimli, & Ozturk, 2003) and since H_2O_2 is stable at $pH = 5$, (Jung, Lim, Park, & Kim, 2009), it is possible to carry out the degradation of microplastics at $pH = 5$ instead of $2.5 \leq pH \leq 4$, to avoid significant dissociation of the ZnO/SnO_2 nanorods.

3.1.5 Degradation mechanism

Photocatalysis and Fenton reaction are processes that produce hydroxyl radicals ($^{\bullet}OH$). Microplastics that come in contact with $^{\bullet}OH$ will oxidize and degrade. A general degradation mechanism of microplastics is described below (Shang, Chai, & Zhu, 2003).

$$-(CH_2CHR)- + {}^{\bullet}OH \rightarrow -(CH_2\dot{C}R)- + H_2O \quad (4)$$

$$-(CH_2CHR)- + {}^{\bullet}OH \rightarrow -(\dot{C}HCHR)- + H_2O \quad (5)$$

When the microplastics react with $^{\bullet}OH$, the carbons will be radicalized and water will be produced as seen in reaction (4) and (5).

$$-(CH_2\dot{C}R)- + O_2 \rightarrow -(CH_2C(O\dot{O})R)- \quad (6)$$

$$-(\dot{C}HCHR)- + O_2 \rightarrow -(CH(O\dot{O})CHR)- \quad (7)$$

When the carbon radical comes in contact with an oxygen molecule, the carbon will bind to one of the oxygen atoms, which lead to a breakage of the double bond between the oxygen atoms, and the other oxygen atom becoming a radical, which is seen in reaction (6) and (7).

$$-(CH_2C(O\dot{O})R)- + -(CH_2CHR)- \rightarrow -(CH_2C(OOH)R)- + -(CH_2\dot{C}R)- \quad (8)$$

$$-(CH(O\dot{O})CHR)- + -(CH_2CHR)- \rightarrow -(CH(OOH)CHR)- + -(CH_2\dot{C}R)- \quad (9)$$

When the oxygen radical in the oxidized microplastics react with other microplastics, hydroxyl groups and carbon radicals are formed (see reaction 8 and 9).

$$-(CH_2C(OOH)R)- \rightarrow -(CH_2COR)- + {}^{\bullet}OH \quad (10)$$

$$-(CH(OOH)CHR)- \rightarrow -(CHOCHR)- + {}^{\bullet}OH \quad (11)$$

The hydroxyl groups can change and become carboxyl groups instead, resulting in the formation of hydroxyl radicals ($^{\bullet}OH$), which is seen in reaction (10) and (11). Fourier Transform Infrared Spectroscopy can be used to detect hydroxyl groups and carboxyl groups.

3.2 Pedagogical framework

In this section an overview of the cognitive and socio-cultural perspective on learning is given, together with theories about slow and fast learning, and the importance of motivation for learning.

3.2.1 The cognitive and socio-cultural perspectives on learning

Students learning can be analyzed through a cognitive perspective and a socio-cultural perspective. According the cognitive perspective, there are two dominant processes for the development of thinking, assimilation and accommodation (Piaget, 2008). Assimilation is a process where the brain finds a connection between new and old information. The existing structure is appropriate for the new information and no new thinking is required by the brain to accept it. Accommodation is a process that occurs when the information that is being taught requires reconstruction of the existing information. When the information is restructured, the brain can receive the new information that would otherwise not fit into the old way of thinking. The process of understanding the outside world, adaptation, requires and equilibrium between assimilation and accommodation. (Piaget, 2008).

From a socio-cultural perspective of learning, optimal learning occurs if the information lies within the proximal development zone (Vygotsky, 2001). When information is within the proximal development zone, a student needs guidance from a teacher (or anyone else who knows the subject) in order to be able to understand the given information themselves. The information is thus at a level that the student would not be able to understand on their own.

Information is conveyed via artifacts, i.e. tools such as language and pictures (Vygotsky, 2001). Artifacts can be used to facilitate the assimilation process. For example a picture that shows how electrons orbit around a nucleus (Bohr’s atomic model) is a concept that is easily accepted by students since it is an assimilation of how planets orbit around the sun. The use of artifacts in teaching can also promote the accommodation process. The teacher can use visual artifacts to show orbitals and their different energy levels, giving the students a new perspective on why chemical reactions occur. This can contribute to a deeper understanding of the subject. The use of artifacts in teaching can thus contribute to students' cognitive development. (Al-Ghorabi, 2014).

3.2.2 Motivation and learning

Motivation can be divided into two categories, extrinsic motivation and intrinsic motivation (Skaalvik & Skaalvik, 2016). Extrinsic motivation is when an activity is done to gain or avoid something, for instance to gain a good grade or to avoid the fear or shame of getting a bad grade. Extrinsic motivation can also be when an activity is done because the student see a value in it but doesn’t find the activity interesting or entertaining. Intrinsic motivation is when a topic feels interesting, and learning about the topic or doing an activity related to it feels entertaining. The entertainment lies within the activity and not within the good grade or the praise received because of it. (Skaalvik & Skaalvik, 2016). Studies have shown that intrinsic motivation promote a higher quality in the learning outcome (Deci & Ryan, 1994).

Motivation for studying and learning has become a major topic over time as several research results on learning have shown that motivation is an important component of learning (Illeris, 2007). The teacher's character and behavior can affect the students' motivation for the subject and their presence at lectures, which in turn can affect the students' study results. Motivating students to learn has not been easy. According to Illeris, motivation problems are already seen in primary school students (Illeris, 2007; Al-Ghorabi, 2014).

Motivation for studying and learning is connected to several different aspects of a student’s mind. The students’ belief in their own capacity, the self-evaluation of their knowledge in the school topics, the goals they want to achieve, the values they see in the school subjects, and their social relationships play a role in their motivation. (Skaalvik & Skaalvik, 2016).

An increased experience of utility value for a school subject increases the motivation for it. The utility value of a school subject is how useful the school subject is for the students’ future plans. For example, studying chemistry courses to fullfill the requirements for becoming a chemical engineer. (Wigfield & Cambria, 2010). According to a study, when students make connections between their lives and science course material, their interest and grades increases (Hulleman & Harackiewicz, 2009).

It is worth mentioning that assessment situations can be counterproductive during study visits, since the social and emotional dimensions of the visit can be adversely affected (DeWitt & Hohenstein, 2010). Assessment situations can create stress for students and negatively affect their motivation (Klapp, 2015). The fact that the students perceived that the study visit had no assessment role may have contributed to a more comfortable learning situation for them. However, this also means that there will be no extrinsic motivation since the students won’t get graded during the study visit (Klapp, 2015).

4 Method

In this section the technical method and the pedagogical method are described.

4.1 Technical method

The idea is to synthesize a material that can function as photocatalysts and allow Fenton reaction to take place. The photocatalytic degradation was designed using ZnO/SnO_2 nanorods catalysts coated onto glass fibers. The glass fibers were used as a substrate to facilitate the entrapment of the microplastics when used in a continuous water flow system. For the Fenton reaction zero-valent iron nanoparticles (Fe^0) in combination with hydrogen peroxide (H_2O_2) is used.

The ZnO nanorods were grown on glass fibers using a hydrothermal method (Tofa, Kunjali, et al., 2019b). Due to the fact that Fenton reaction is only effective at low pH ($2.5 \leq pH \leq 4$) and that ZnO dissolves at low pH, the ZnO nanorods had to be coated with SnO_2 to be protected from dissolving (Al-Hamdi, Sillanpää, & Dutta, 2015; Baruah & Dutta, 2011). The ZnO/SnO_2 nanorods were decorated with Fe^0 by using iron sulfate ($FeSO_4$) as the iron source, and sodium borohydride ($NaBH_4$) as the reducing agent to reduce the iron ions (Fe^{2+}) to Fe^0 (Rabé et al., 2019). The reason the ZnO/SnO_2 nanorods were *decorated* with Fe^0 particles and not coated is because the light has to reach the ZnO/SnO_2 nanorods for the photocatalysis to take place.

4.1.1 Synthesis of zinc oxide (ZnO) nanorods on glass fibers

A method similar to the one described in the article by Tofa (Tofa, Kunjali, et al., 2019b) was used to synthesize ZnO nanorods on glass fibers. A 10 mM seed solution of zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was prepared. A thin layer of glass fibers (0.8, 10cm x 10cm) was placed on a hot plate (450 ℃) and 10 ml of the seed solution was sprayed evenly on both sides of the layer of glass fibers. This process was repeated to make several seeded substrates. A 20 mM solution of zinc nitrate ($Zn(NO_3)_2$) and a 20 mM solution of hexamine ($(CH_2)_6N_4$) were prepared separately and mixed together to make a chemical bath. An empty beaker was filled with the seeded substrates and the chemical bath was carefully poured into the beaker to ensure the soaking of all seeded substrates. Aluminum foil was placed over the beaker (to prevent evaporation of the chemical bath) and put in the oven at 90 ℃ for 5 h and 30 min. Afterwards the beaker was placed in a furnace for 1 h at 350 ℃. When the annealing was finished, the glass fibers with ZnO nanorods were washed and left to air-dry. The sample was analyzed with Scanning Electron Microscopy to see the growth of the ZnO nanorods.

4.1.2 Synthesis of ZnO/SnO_2

A 55 ml solution of 0.1 mM $SnCl_2$ was prepared with ethanol. 2.49 g of urea was added to the solution and mixed under 50 °C heating. The flask was sealed to avoid evaporation of ethanol. To increase the pH of the solution from 5 to 6, 0.05 mM $NaOH$ solution was dropped. A piece of glass fibers loaded with ZnO nanorods (0.8g, 10cm x 10cm) was placed inside an autoclave of 100 ml capacity and the solution was poured in the recipient of the autoclave. The autoclave was then placed in a furnace at 180 °C for 15 minutes. Following this, the piece of glass fibers with ZnO/SnO_2 nanorods was rinsed thoroughly and left to air-dry. The sample was analyzed with Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy to see the distribution of the SnO_2 coating on the ZnO nanorods.

4.1.3 Synthesis of $ZnO/SnO_2/Fe^0$

A 0.6 mM solution of iron sulfate ($FeSO_4 \cdot 7H_2O$) was prepared. The piece of glass fibers with ZnO/SnO_2 nanorods (0.8g, 10cm x 10cm) was added to the solution and sonicated for 15 minutes. Since the iron sulfate solution is acidic, the exposure of the ZnO/SnO_2 nanorods to the iron sulfate solution was kept short to avoid dissociating the nanorods. Afterwards, the piece of glass fibers was taken out from the solution and dipped into a 1.2 mM solution of sodium borohydride ($NaBH_4$) and sonicated for 15 minutes. The piece of glass fibers with $ZnO/SnO_2/Fe^0$ nanorods was rinsed thoroughly and left to air-dry. The sample was analyzed with Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy to see the distribution of the iron particles on the ZnO/SnO_2 nanorods.

4.1.4 Testing the photocatalytic efficiency with methylene blue dye

Methylene blue is an organic chemical substance that is blue, when it is oxidized (degraded) it becomes transparent. This process takes a few hours, making methylene blue a quick way to test whether a material can oxidize water pollutants or not. The $ZnO/SnO_2/Fe^0$ – sample was therefore used to degrade methylene blue. The initial concentration of the methylene blue was 2 ppm. Samples of the methylene blue were taken every 15 minute, except the two first samples that were taken every 30 minute. The samples became lighter in color with time, and were analyzed with Ultraviolet-Visible spectroscopy to determine the degradation rate of the methylene blue. The same was done to the ZnO – sample to compare the degradation rate. An absorbance calibration curve was made with Ultraviolet-Visible spectroscopy to determine the absorbance of methylene blue at different concentration (0.5 $ppm,$ 1 $ppm,$ 1.5 $ppm,$ and 3 ppm). This was done to be able to determine the absorbance of the degraded samples with unknown concentration of methylene blue.

Degradation of methylene blue with $ZnO/SnO_2/Fe^0$ – sample

A solution of methylene blue (6.25 μM) was prepared with $pH = 3.5$ by adding HNO_3 acid. The reason HNO_3 is chosen is because nitrate ions don't form complexes with Fe^{+2} or Fe^{+3}, and don't react with OH^- (Pignatello et al., 2006). A $ZnO/SnO_2/Fe^0$ – sample (0.92 g, 10 cm x 10 cm) was placed in a beaker. 120 mM of H_2O_2 was added to the sample. Afterwards the methylene blue solution was added to the sample. The beaker was placed on a shaker and a light source was placed above it with light intensity 1 Sun to mimic the sunlight's light intensity. Samples were taken and analyzed with Ultraviolet-Visible spectroscopy.

Degradation of methylene blue with ZnO – sample

A solution of methylene blue (6.25 μM) was prepared. A ZnO – sample (0.62 g, 10 cm x 10 cm) was placed in a beaker. The methylene blue solution was added to the sample. The beaker was placed on a shaker in an inert atmosphere and a light source was placed above it with light intensity 1 Sun to mimic the sunlight's light intensity. Samples were taken and analyzed with Ultraviolet-Visible spectroscopy.

Table 1. The samples and the time they were taken.

ZnO/SnO_2 $/Fe^0$- Sample	ZnO - Sample	Time (minutes)
Initial	Initial	0
1	1	30
2	2	60
3	3	75
4	4	90
5	5	105
6	6	120
7	7	135

Inductively Coupled Plasma spectroscopy measurements

After Degradation of methylene blue with $ZnO/SnO_2/Fe^0$– sample and with ZnO – sample, the amount of dissolved ZnO in the degraded methylene blue was determined by using Inductively Coupled Plasma spectroscopy to see how much the ZnO/SnO_2 nanorods were affected by the low pH in the Fenton reaction.

4.1.5 Degradation of polystyrene

A $ZnO/SnO_2/Fe^0$ – sample (0.61 g) was prepared. The sample was carefully inserted in a glass cylinder with a diameter of 2 cm. 12 mg of polystyrene microplastics was added on the fibers inside the cylinder. The cylinder was then connected to a pump and a beaker and placed 15 cm from a light source with the light intensity 1 Sun to mimic the sunlight's light intensity. A solution of H_2O_2 (120 mM, $pH = 5$) was prepared, where $NaOH$ was added to increase the pH. The pump was used to make the H_2O_2 solution run through the $ZnO/SnO_2/Fe^0$ – sample. Photoirradiation under continuous water flow was carried out for 10 days. See appendix 9.4 to see the setup.

4.1.6 Degradation of polypropylene

A $ZnO/SnO_2/Fe^0$ – sample (1.12 g) was prepared. The sample was carefully inserted in a glass cylinder with a diameter of 2 cm. 70 mg of polypropylene microplastics was added on the fibers inside the cylinder. The cylinder was then connected to a pump and a beaker and placed 15 cm from a light source with the light intensity 1 Sun to mimic the sunlight's light intensity. A solution of H_2O_2 (120 mM, $pH = 5$) was prepared, where $NaOH$ was added to increase the pH. The pump was used to make the H_2O_2 solution run through the $ZnO/SnO_2/Fe^0$ – sample. Photoirradiation under continuous water flow was carried out for 60 h. See appendix 9.4 to see the setup.

4.2 Pedagogical method

In this section, the study visit is described and the method that was used to analyze the students' answers on what they learned at each station and what they knew before, what questions and thoughts they had after each station, and about their view on research.

4.2.1 A visit to the high school

The high school was visited one week before the study visit. The students were informed about the schedule of the study visit and told briefly about the different topics that they will learn about during the visit. The students were also told that they will answer a questionnaire at the end of the study visit, and that the questions will be about what they have learned, what they knew before the visit, and if they have any thoughts or questions after each station in the study visit.

4.2.2 The visit to the laboratory

The laboratory is located in Electrum Laboratory (Isafjordsgatan 22, 164 40 Kista) and the study visit took place 14 November 2019.

4.2.2.1 Participants

The participants in this study were 57 high school students at the second year of the natural sciences program from a high school in Stockholm. The participants consisted of 36 girls, 18 boys and 3 others. The students were accompanied by 3 teachers. The participants were between 16 and 19 years old.

4.2.2.2 The design of the study visit

The study visit consisted of 3 parts; introduction, 5 different stations (4 of them were made and held by different researchers and a master student), and a questionnaire. See appendix 9.2 for an overview.

A chemistry teacher from the high school was contacted and a meeting with two other chemistry teachers was set to discuss about the study visit to the laboratory. The teachers wanted the focus of the study visit to be on how research is conducted, to prepare the students for their diploma work.

Since the amount of students was large, the study visit was designed to have 5 stations so that it’s maximum 12 students in one station. One of the stations was a snack-break station so that the students got some time to rest and reflect on what they have learned. The 4 other stations were led by researchers and a master student so that the students would come in contact with different researchers, see their passion for their work, and see that researchers work in a multicultural environment.

The topic of the gold nanoparticle station was picked to catch the students’ attention and increase their interest by having a laboratory demonstration.

The topic of the desalination station was picked to give the students a perspective on the importance of sustainability, and show them that research in nanotechnology and chemistry is not only about working with chemicals, but also about making simulations that can be used to predict for instance water desalination.

The topic of the microplastics station was picked to give the students an overview of the stages of research (Kracker, 2002), how there is a lot of trial and error involved, and to show how research can be used to achieve sustainability by finding solutions to environmental issues.

The topic of the Scanning Electron Microscopy station was picked to show the students an important analytical instrument that researchers use, and how the instrument works so that the students understand how the image of the ZnO nanorods in the microplastics station was made.

A discussion question was added to the desalination station and the microplastics station be able to analyze the students learning through a socio-cultural perspective.

Introduction of the study visit

The students were gathered in a conference room and told about the basics of nanotechnology, including the size of nanomaterials, the huge surface area of them, and examples of nanotechnology in nature. The students were also told that they are welcome to do their diploma work at the laboratory. Following this, the students were separated into 5 groups (each group consisted of approximately 12 students), with each groups exposed to each station. The whole study visit lasted 2,5h.

Five different stations

There were five stations, gold nanoparticle station, Scanning Electron Microscopy station, water desalination station, microplastics station and a snack-break station. In all of the stations the students were free to interrupt the station leader to ask questions, and several students took the chance and asked about what they didn't understand or were curious to know.

4.2.2.3 Gold nanoparticle station

This station was made by a master student together with a senior researcher, and held by the senior researcher. The station took place inside the laboratory next to a fume hood. In this station the students were told about how to make gold nanoparticles by using gold chloride solution ($HAuCl_4$) as the source of gold, trisodium citrate ($Na_3C_6H_5O_7$) as capping agent, and sodium borohydride ($NaBH_4$) as reducing agent. With the station leader's instructions, two of the students did an experiment where they made a red gold nanoparticle solution in front of the rest of the group. Two other students did another experiment with slightly different concentration of the reducing agent, to make a blue gold nanoparticle solution. The station leader explained the chemistry behind the difference in the color of the gold particle solutions, and spoke about the usage of gold nanoparticles in medicine, the usage of nanomaterial-based catalysts in car exhaust systems, and the usage of surface functionalized nanomaterials to purify water from arsenic.

4.2.2.4 Scanning Electron Microscopy station

This station was made and held by a senior researcher. The station took place inside a small conference room with TV, next to the Scanning Electron Microscopy. In this station it was explained to the students how Scanning Electron Microscopy works by focusing an electron beam on the surface of a sample that is being analyzed, how the electrons scatter when they hit the sample surface, that a detector registers the scattered electrons and makes an image out of it, and how this technique can give an image with a resolution on the nanoscale. The students were also presented Scanning Electron Microscopy images that shows how the surface of different materials look on nanoscale.

4.2.2.5 Water desalination station

This station was made and held by a PhD student. The station took place inside a conference room with Power Point. During the presentation, a water desalination prototype and carbon fiber was shown to the students. The students were told about how much less the drinking water is compared to salt water, and the importance of being able to turn salt/brackish water to drinkable water in a cheap, environmental friendly and sustainable way. The students were asked to discuss which water desalination methods they knew of. The students were then informed about the main desalination methods that are currently being used, distillation, and reverse osmosis, and how distillation requires a lot of energy, and how the membranes used for the osmosis are not environmentally friendly and can’t be discarded without pretreatment. The station leader spoke about a desalination method that have been developed in the laboratory, which deionizes water by applying an electrical potential difference over two electrodes made by carbon fibers that attracts and captures the ions in the water. This type of water treatment technology is called capacitive deionization (CDI). The mathematics behind the concentration of charges and the net salt removal which are described by the dynamic Langmuir model was explained to the students. See appendix 9.5 for further information about the station.

4.2.2.6 Microplastics station

This station was made and held by a master student. The station took place in the laboratory. During the presentation, the students were shown a ZnO-sample, $ZnO/SnO_2/Fe^0$-sample, Scanning Electron Microscopy images of the samples, and a precipitated $FeSO_4$ solution. The students were also shown an ongoing experiment of microplastic degradation (see appendix 9.4), and different tools that were used to make or analyze the samples, like Inductively Coupled Plasma spectroscopy machine, Ultraviolet-Visible spectroscopy machine etc.

The students were asked to discuss what they think produces a lot of microplastics in the everyday life of a person. The students were then informed that washing fleece clothes lead to the production of microplastics, and that wastewater treatment plants are not fully capable of degrading the microplastics in water and how microplastics pose a danger to the health of humans and animals. It was explained to the students how microplastics can be degraded by a photocatalytic process using ZnO nanorods as catalysts to produce $^{\bullet}OH$ that degrades the microplastics. The photocatalytic process is too slow, and therefore it was combined with Fenton reaction that also produces $^{\bullet}OH$ using iron as catalyst. The students were shown the results of several experiments that were done to create and test the material that combines these two degradation processes. The station leader explained the process of developing such a material and how reading research articles is a critical part of it. See appendix 9.6 for further information about the station.

4.2.2.7 Snack-break station

In this station the students had a break and were given snacks and drinks.

4.2.2.8 Questionnaire

After the activities in the different stations the students were gathered to answer the questionnaire (see appendix 9.1). The questions were open to allow the students to write their opinions without being guided to answer with the same choice of words as the researcher (Bryman, 2018).

4.2.2.9 Pilot survey

A pilot survey of the questionnaire was done to avoid overlooking any possible misunderstandings or difficulties with the questionnaire (Bryman, 2018). The pilot survey was done on one high school student at the third year of the economics program at a high school in Stockholm. The high school student understood all the questions in the questionnaire, therefore the questions in the questionnaire were left unchanged.

4.2.3 Analytical method

The students' answers were analyzed with thematic analysis to observe if there was a pattern in the students' answers (Bryman, 2018). The students' answers were read and marked with different colors depending on what the students mentioned in their answers. Each color presented a theme. For example, if a student mentioned they had learned about something related to the color of gold nanoparticles they would receive a color different from the students who mentioned they learned about gold nanoparticles being used to cure cancer. Every answer with a specific theme was counted and plotted with a diagram. When one answer contained several themes, each part of the answer was counted to each theme. In other words, the number of answers in the diagrams does not correspond to the number of students. See appendix 9.3, fig. 1 to fig. 11 for further information about the themes that were found in the students' answers. The students' answers are originally written in Swedish but are translated to English in this study.

Whether the students underwent assimilation or not was determined by analyzing the students' answers on the question about what they knew about the topics presented in the stations before the study visit. If the students had some previous knowledge it would indicate they underwent assimilation during the station, if not then it would indicate they underwent accommodation. If the students' answers showed that they had some basic knowledge about a topic presented in a station then the topic is within their proximal development zone.

4.2.3.1 Ethical aspect

This study fulfills the ethical principles of research. None of the participants were exposed to harm or discomfort, they were all informed that they are free to participate in the study and that they are completely anonymous and that their answers will only be used in the study. (Bryman, 2018).

5 Results

In this section the technical and pedagogical results are given.

5.1 Technical results

5.1.1 Zinc oxide (ZnO) nanorods coated onto glass fibers

The results from the synthesis of ZnO nanorods can be seen below in fig. 2 and fig. 3.

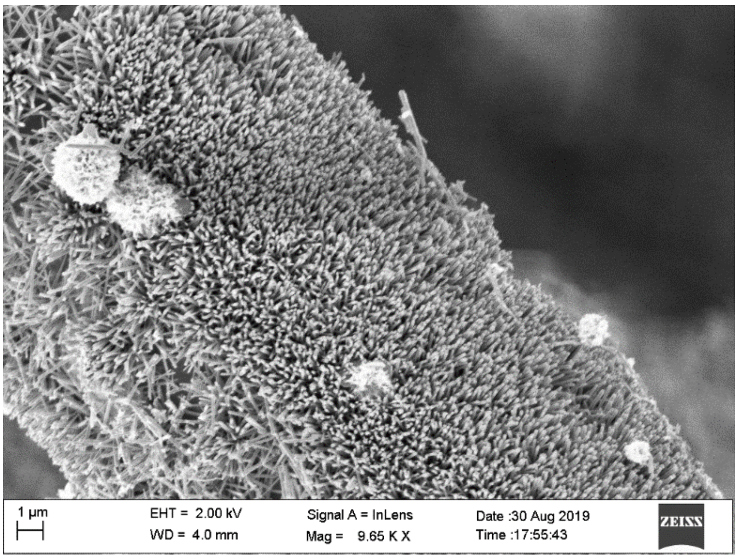

Fig. 2. A Scanning Electron Microscopy image of the synthetized ZnO nanorods on glass fibers.

From fig. 2 the homogenous growth of ZnO nanorods can be observed on an individual glass fiber with some clustering of nanoparticles as seen in the white spots in the Scanning Electron Microscopy image. This occur due to heterogeneous agglomeration in the reaction mixture. Upon closer inspection nanorods of approximately 2 μm length with roughly 50 nm thickness can be observed, which is clear from the crossectional micrograpth as shown in fig. 3.

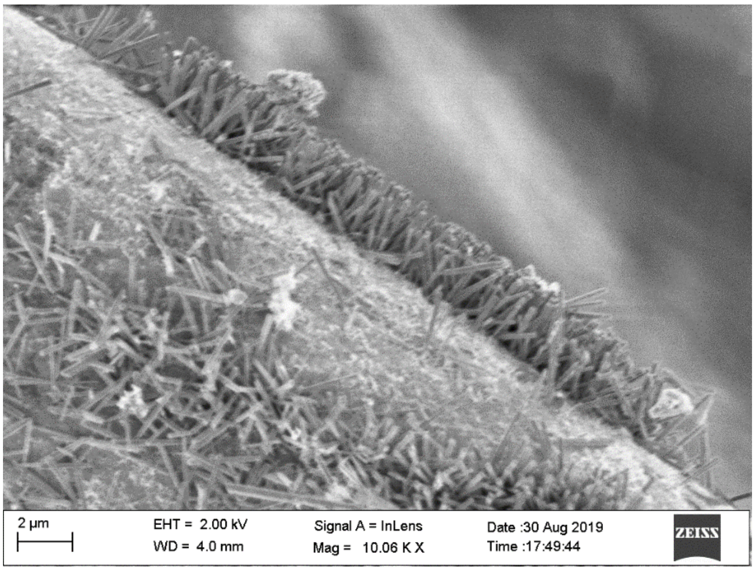

Fig. 3. Scanning Electron Microscopy image of ZnO nanorods on glass fibers showing the length of the ZnO nanorods.

5.1.2 Synthesis of zinc oxide nanorods coated with tin oxide

The results from the synthesis of zinc oxide nanorods coated with tin oxide (ZnO/SnO_2) can be seen below in fig. 4.

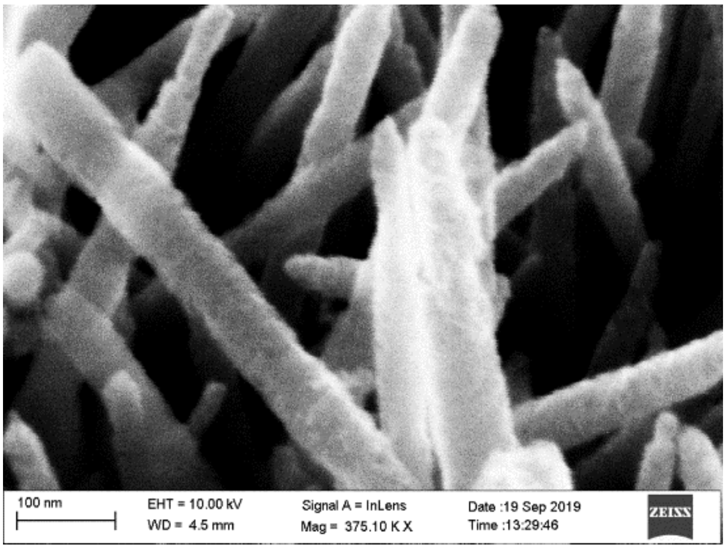

Fig. 4. A Scanning Electron Microscopy image of ZnO nanorods coated with SnO_2.

The hexagonal shape of the ZnO is not visible anymore due to the SnO_2 coating. This is most likely due to the edges getting etched during the synthesis. The ZnO nanorods being in contact with the tin oxide solution ($pH = 6$) causes the etching. When the nucleation and growth of SnO_2 coating occur, the SnO_2 coating prevents the ZnO nanorods from further etching.

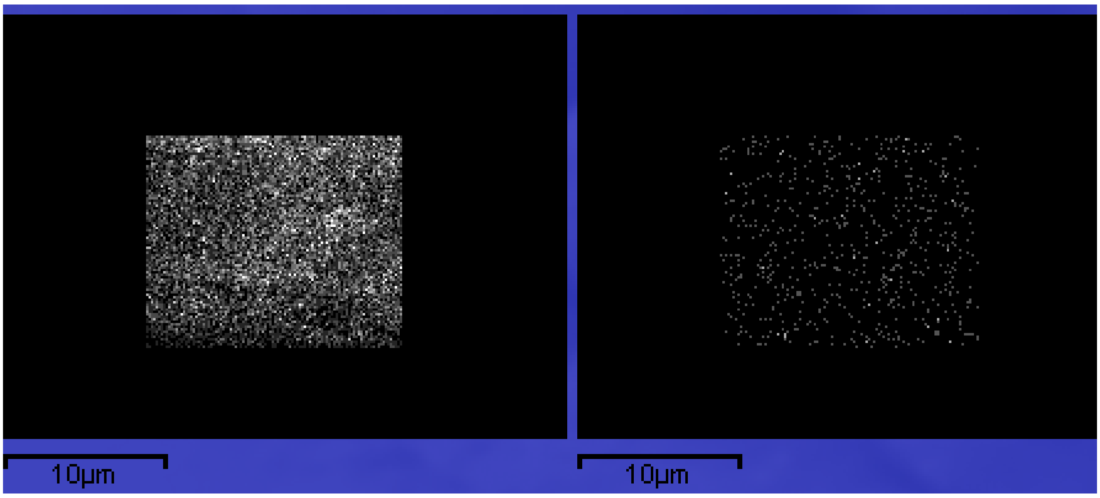

Fig. 5. Energy-dispersive X-ray spectroscopy image showing the homogeneous distribution of ZnO (left) and SnO_2 (right).

The Energy-dispersive X-ray spectroscopy image (fig. 5) shows a white dot for each detected Zn atom (left image) and Sn atom (right image) on a 15 x 15 μm surface of the ZnO/SnO_2 glass fiber sample. The homogeneous spread of the white dots indicate a homogenous distribution of the SnO_2 coating on the ZnO nanorods.

5.1.3 Synthesis of $ZnO/SnO_2/Fe^0$

The results from the synthesis of zinc oxide nanorods coated with tin oxide and decorated with iron particles ($ZnO/SnO_2/Fe^0$) can be seen below in fig. 6.

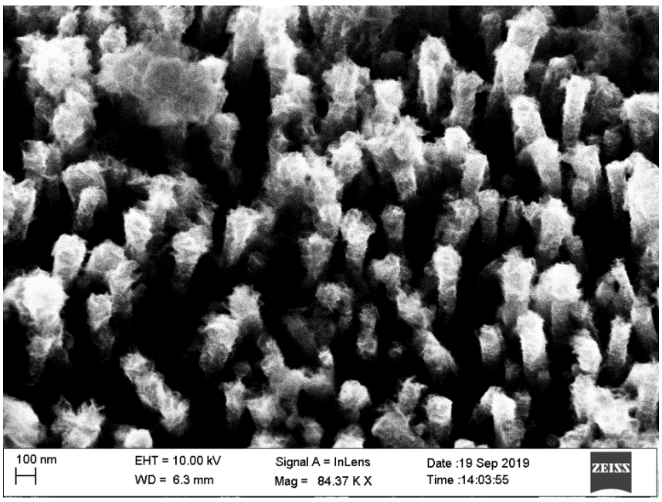

Fig. 6. Scanning Electron Microscopy image of the $ZnO/SnO_2/Fe^0$ – sample.

From the Scanning Electron Microscopy image (fig. 6) it can be observed that the iron particles form a network between the ZnO nanorods. An agglomeration of iron particles can be seen in the upper left corner of fig. 6.

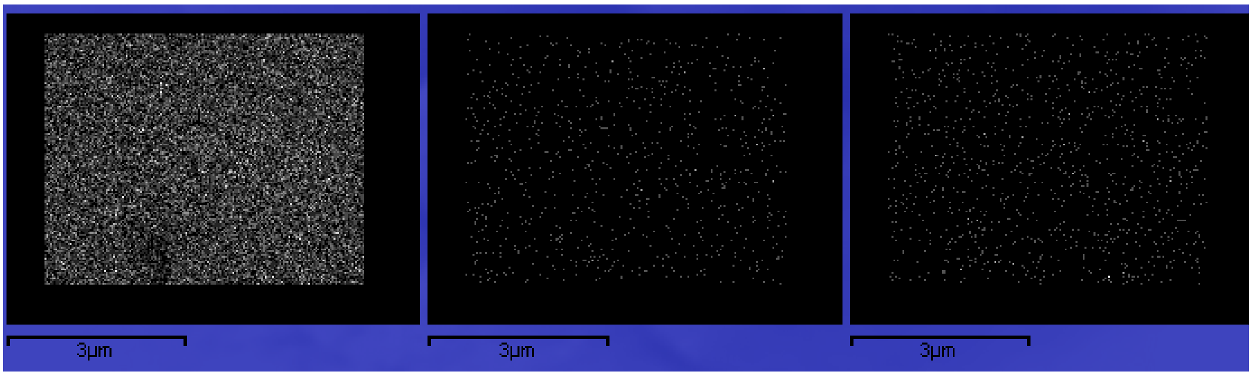

Fig. 7. The homogeneous distribution of ZnO (left), Fe^0(middle), and SnO_2 (right).

The Energy-dispersive X-ray spectroscopy image (fig. 7) shows a white dot for each detected Fe atom (middle image) on a 6 x 6 μm surface of the $ZnO/SnO_2/Fe^0$ glass fiber sample. The homogeneous spread of the white dots indicate a homogenous distribution of the iron particles on the ZnO/SnO_2 nanorods.

5.1.4 Results of the test with Methylene blue dye

The results of the calibration curve and the degradation of methylene blue can be seen below in fig. 8, 9 and 10.

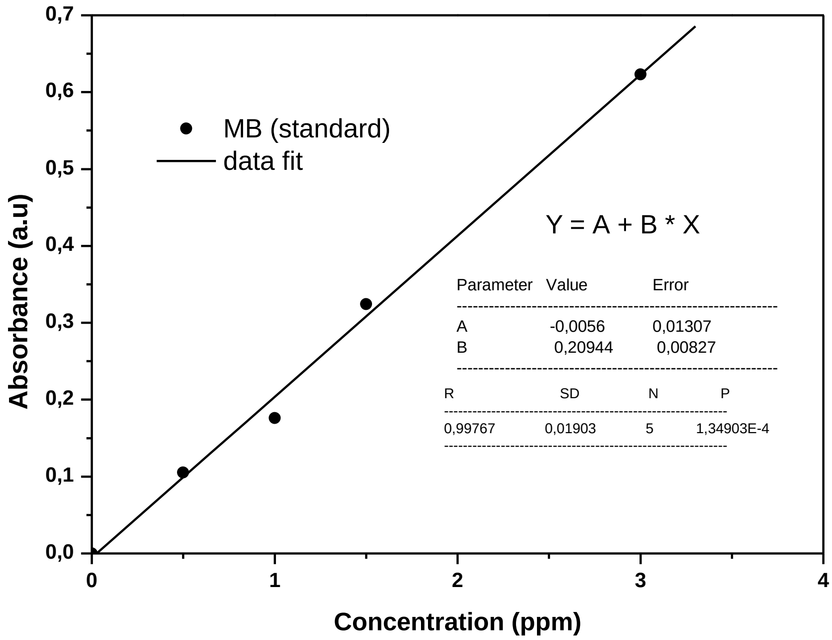

Fig. 8. Calibration curve of methylene blue.

The calibration curve of methylene blue solutions (0.5 ppm, 1 ppm, 1.5 ppm, and 3 ppm) is shown in fig. 8. The correlation coefficient (R) value is almost 1 (0.99767) indicating a minimal error in the calibration curve.

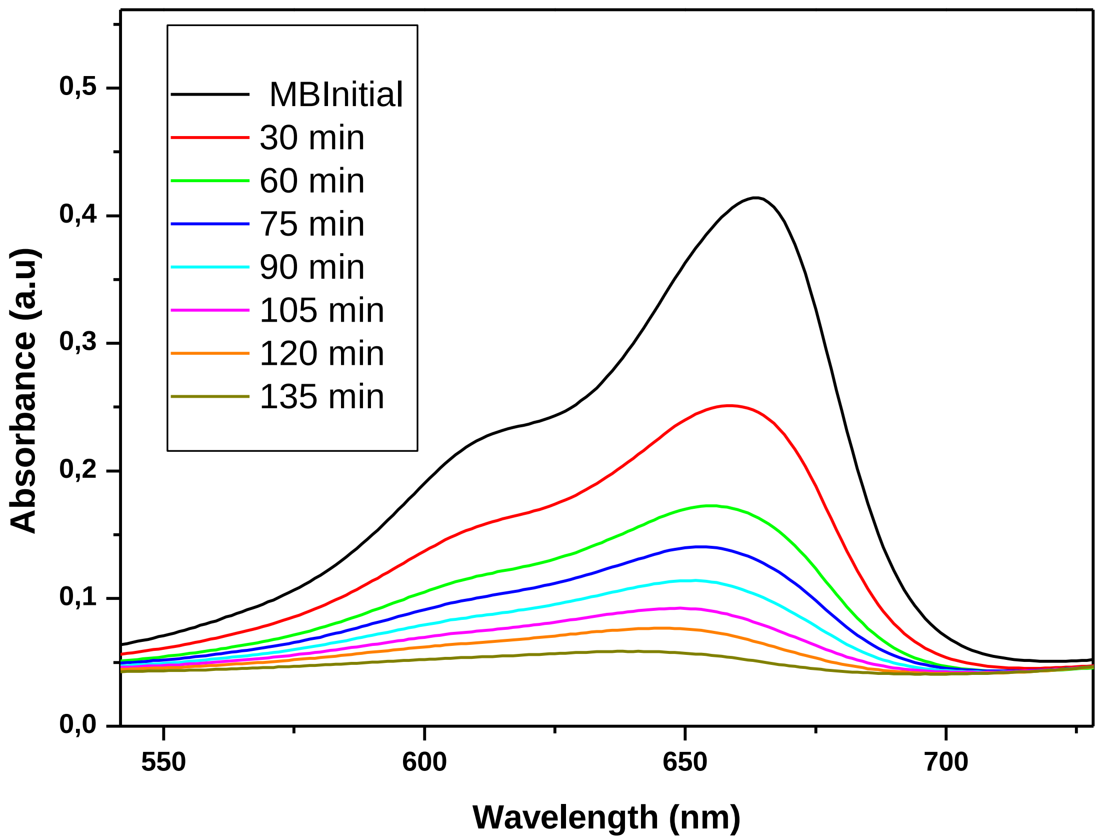

Fig. 9. Absorbance of methylene blue (MB) at wavelength $\lambda = 664nm$ at different time during the degradation of methylene blue with the $ZnO/SnO_2/Fe^0$ – sample.

From fig. 9 the degradation of methylene blue with the $ZnO/SnO_2/Fe^0$ – sample can be seen. The upper black curve show the absorbance of the initial concentration of methylene blue (2 ppm), and the lower (brown) curve that is almost flat is the absorbance value of the degraded methylene blue after 135 minutes.

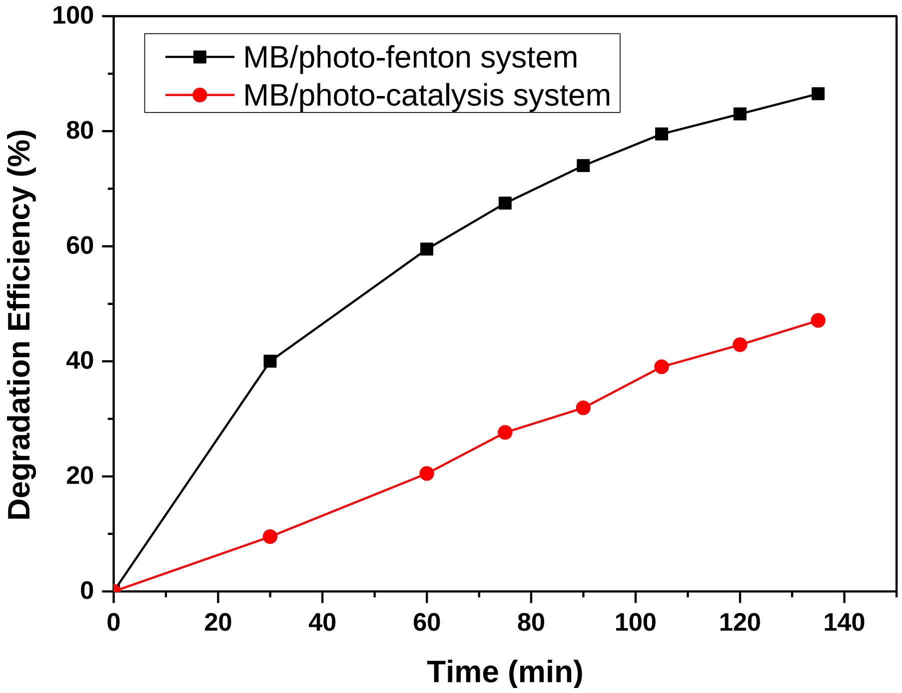

Fig 10. Degradation efficiency of $ZnO/SnO_2/Fe^0$ – sample (black) compared to ZnO – sample (red).

The degradation efficiency of the $ZnO/SnO_2/Fe^0$ – sample (black) is higher than the degradation efficiency of ZnO – sample (red). After 30 minutes, 10 % of the methylene blue was degraded in the photocatalysis system (ZnO – sample, red curve) while 40 % of the methylene blue was degraded in the system with the $ZnO/SnO_2/Fe^0$ – sample (black curve). It took 135 minutes for the photocatalysis system to degrade approximately 40 % of the methylene blue, however at that time, the $ZnO/SnO_2/Fe^0$ – sample had degraded approximately 85 % of the methylene blue.

5.1.5 Inductively Coupled Plasma spectroscopy measurements

After the degradation of methylene blue with the $ZnO/SnO_2/Fe^0$ – sample and the ZnO – sample, the amount of dissolved Zn in the degraded methylene blue was determined by using Inductively Coupled Plasma spectroscopy to see how much the ZnO/SnO_2 nanorods are affected by the low pH in the system with the $ZnO/SnO_2/Fe^0$ – sample. The amount of Fe was also measured to determine how much of the iron dissolved during the methylene blue degradation process.

Table 2. The amount of Zn on the $ZnO/SnO_2/Fe^0$ – sample and the dissolved amount of Zn in methylene blue (MB) at $pH = 3.5$.

Amount of Zn on $ZnO/SnO_2/Fe^0$ – sample	72 ppm
Amount of Zn dissolved in the MB solution	38.3 ppm

From table 2, it is observed that 35 % of the Zn on the $ZnO/SnO_2/Fe^0$ – sample was dissolved at $pH = 3.5$.

Table 3. The amount of Zn on the ZnO – sample and the dissolved amount of Zn in methylene blue (MB) at $pH = 6$.

Amount of Zn on ZnO – sample	57.9 ppm
Amount of Zn dissolved in the MB solution	6.3 ppm

From table 3, it is observed that 9.8 % of the Zn on the ZnO – sample was dissolved at $pH = 6$.

The amount of iron on the $ZnO/SnO_2/Fe^0$ – sample and the amount of dissolved iron in the degraded methylene blue was measured.

Table 4. The amount of Fe on the $ZnO/SnO_2/Fe^0$ – sample and the dissolved amount of Fe in methylene blue (MB) at $pH = 3.5$.

Amount of Fe on $ZnO/SnO_2/Fe^0$ – sample	20 ppm
Amount of Fe dissolved in the MB solution	0.035 ppm

From table 4, it is observed that 0.17 % of the Fe on the $ZnO/SnO_2/Fe^0$ – sample was dissolved at $pH = 3.5$.

5.1.6 Results of the degradation of polystyrene and polypropylene

To be able to investigate the degradation of polystyrene and polypropylene, the hydroxyl ($-OH$) absorbance peaks and the carbonyl ($C = O$) absorbance peaks were determined by using Fourier Transform Infrared Spectroscopy (see section 3.1.5). An increase in those peaks indicate that polystyrene and polypropylene have underwent degradation (Mylläri, Ruoko, & Syrjälä, 2015). The hydroxyl ($-OH$) and carbonyl ($C = O$) peaks are variable absorbance peaks that will change after degradation. Polystyrene has a non-variable absorbance peak (reference peak), which is an aromatic $C - H$ bond stretching vibration, and polypropylene has a non-variable absorbance peak (reference peak) that is a CH_2 bond. To quantify the extent to which the polystyrene and polypropylene degrade the ratios of the variable absorbance peaks and the non-variable reference peaks will be taken (Galgali, Agashe, & Varma, 2007), (Mathias, Hankins, Bertolucci, Grubb, & Muthiah, 1992). In other words, to determine the change in the $-OH$ peaks and the $C = O$ peaks after degradation, the absorbance ratios are calculated. This is done by using the ratio of absorbance of the $C = O$ peak at $1740\ cm^{-1}$ and the $-OH$ peak at $3425\ cm^{-1}$ to the aromatic $C - H$

bond stretching vibration peak at $1493\ cm^{-1}$ (reference peak) for polystryrene (Galgali et al., 2007), (Ashraf, 2014). For polypropylene the $C = O$ peak at $1752\ cm^{-1}$ and the $-OH$ peak at $3425\ cm^{-1}$ to the CH_2 bond peak at $2720\ cm^{-1}$ (reference peak) (Aslanzadeh & Haghighat Kish, 2010).

$$CO_{PS} = \frac{C = O_{PS}}{C - H} = \frac{1740\ cm^{-1}}{1493\ cm^{-1}} \qquad OH_{PS} = \frac{-OH_{PS}}{C - H} = \frac{3425\ cm^{-1}}{1493\ cm^{-1}} \tag{4}$$

$$CO_{PP} = \frac{C = O_{PP}}{CH_2} = \frac{1752\ cm^{-1}}{2720\ cm^{-1}} \qquad OH_{PP} = \frac{-OH_{PP}}{CH_2} = \frac{3425\ cm^{-1}}{2720\ cm^{-1}} \tag{5}$$

To calculate the absorbance ratios of the $C = O$ and the $-OH$ peaks to the reference peak, the area under the peaks are measured and a ratio between the areas are calculated. To calculate the area under a peak, the absorbance curve is integrated from the beginning of the peak to the end of it by using the software OriginPro 9.0 (see appendix 9.8 for chosen peak intervals and integration results).

Table 5. Absorbance ratio of the $C = O$ and the $-OH$ peaks to the reference peak ($C - H$), of polystyrene before degradation.

Polystyrene before degradation	$\boldsymbol{OH_{PS}}$	$\boldsymbol{CO_{PS}}$
Absorbance ratio	1.91	0.76

Table 6. Absorbance ratio of the $C = O$ and the $-OH$ peaks to the reference peak ($C - H$), of polystryrene after degradation.

Polystyrene after degradation	$\boldsymbol{OH_{PS}}$	$\boldsymbol{CO_{PS}}$
Absorbance ratio	15.88	1.10

After the degradation of polystyrene for 10 days, a 731 % increase in the $-OH$ absorbance ratio and 44.7 % increase in the $C = O$ absorbance ratio was observed.

Table 7. Absorbance ratio of the $C = O$ and the $-OH$ peaks to the reference peak (CH_2), of polypropylene before degradation.

Polypropylene before degradation	$\boldsymbol{OH_{PP}}$	$\boldsymbol{CO_{PP}}$
Absorbance ratio	7.13	3.35

Table 8. Absorbance ratio of the $C = O$ and the $-OH$ peaks to the reference peak (CH_2), of polypropylene after degradation.

Polypropylene after degradation	$\boldsymbol{OH_{PP}}$	$\boldsymbol{CO_{PP}}$
Absorbance ratio	17.83	2.20

After the degradation of polypropylene for 60 hours, a 150 % increase in the $-OH$ absorbance ratio and 34.3 % decrease in the $C = O$ absorbance ratio is observed.

The Fourier Transform Infrared Spectroscopy absorbance spectrum of polystyrene and polypropylene before and after degradation is shown below.

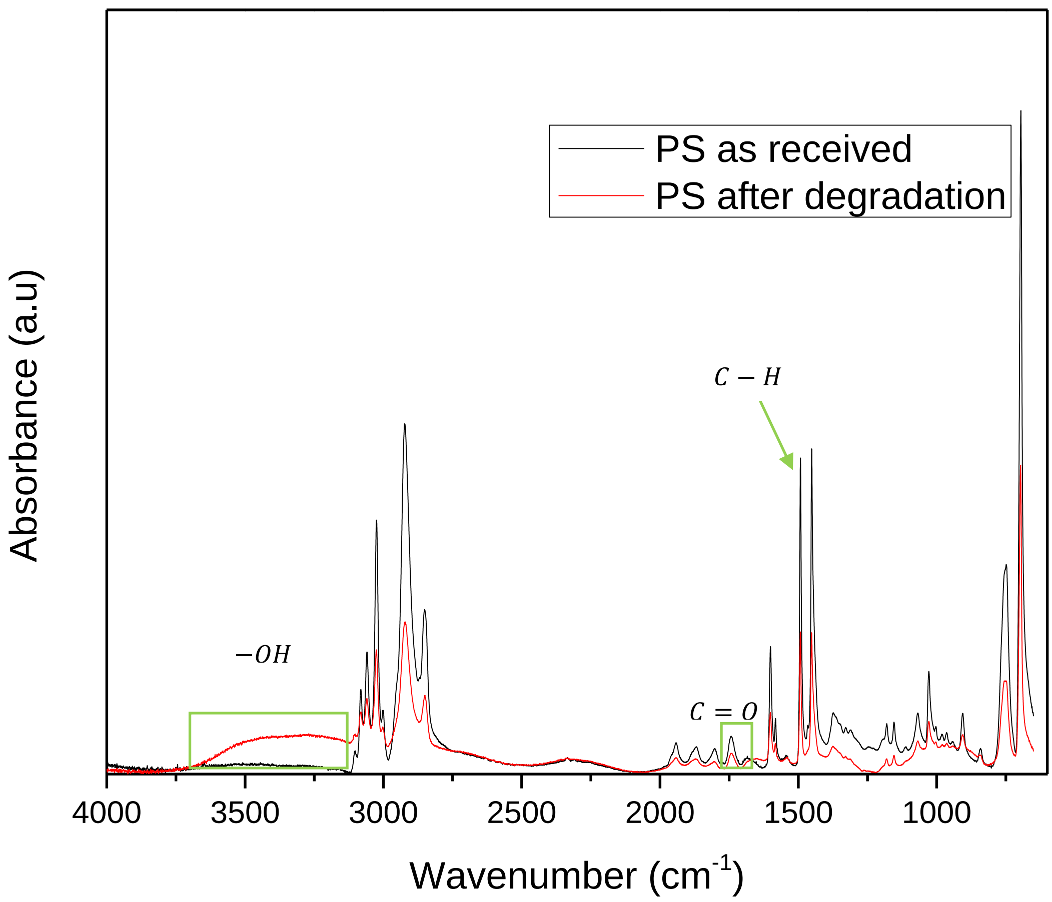

Fig. 11. Fourier Transform Infrared Spectroscopy spectrum showing the absorbance of polystyrene before (black curve) and after (red curve) 10 days degradation.

The absorbance spectrum of polystyrene before (black curve) and after degradation (red curve) is shown in fig. 11. The $-OH$ peak is in the interval $3131 - 3747\ cm^{-1}$, the $C = O$ peak is in the interval $1660 - 1760\ cm^{-1}$, and the reference peak ($C - H$) is in the interval $1484 - 1498\ cm^{-1}$ (see appendix 9.8).

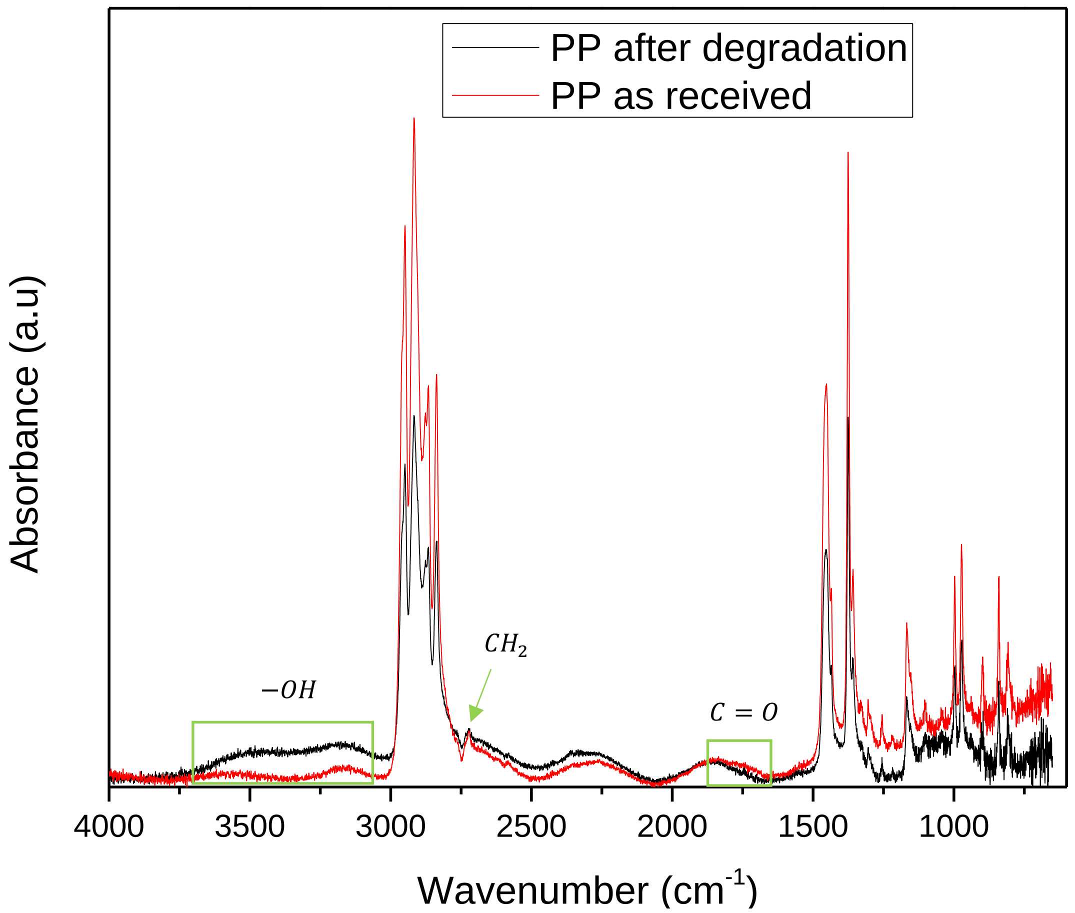

Fig. 12. Fourier Transform Infrared Spectroscopy spectrum showing the absorbance of polypropylene before and after 60h degradation.

The absorbance spectrum of polypropylene before (red curve) and after degradation (black curve) is shown in fig. 12. The $-OH$ peak is in the interval $3009 - 3718\ cm^{-1}$, the $C = O$ peak is in the interval $1654 - 1850\ cm^{-1}$, and the reference peak (CH_2) is in the interval $2711 - 2736\ cm^{-1}$ (see appendix 9.8). From fig. 12 it can be observed that the noise in the background (zig-zag pattern of the curve) is high.

5.2 Pedagogical results

In this section, the thematic analysis of the students' answers (see Analytical method 3.2.1) about the gold nanoparticle stations, microplastics station, and the water desalination station will be presented. The results of the Scanning Electron Microscopy station is not presented nor analyzed in this study because it is mainly about a machine and an analysis method. The stations that are going to be presented are about how nanotechnology can be used to solve issues in society, and are therefore more connected to the content in the curriculum for chemistry in high school which is to increase students' “knowledge of the importance of chemistry for individuals and society.”, and address societal issues such as sustainability (Skolverket, 2011).

Due to lack of time, each student were able to visit 4 out of 5 stations. The students were asked 3 questions for each station, what they learned at the station, what they knew before about the topic of the station, and if they have any questions or thoughts about what they learned at the station. The students were also asked about their view on research and if it had changed after the study visit. Plots of the students’ answers on what they learned is presented the section below, and the rest of the answers are shown in appendix 9.3.

Some of the students’ answers were hard to understand such as “I have learned that how” and “A”. Some of the answers seemed to answer another question in the questionnaire but it wasn’t very clear weather that was the case or not. Therefore these types of answers were categorized as “Incomprehensible answers”.

5.2.1 Students’ answers on what they learned from the visit

In this section, the students’ answers on what they learned during the different stations in the study visit are presented.

5.2.1.1 Gold nanoparticle station

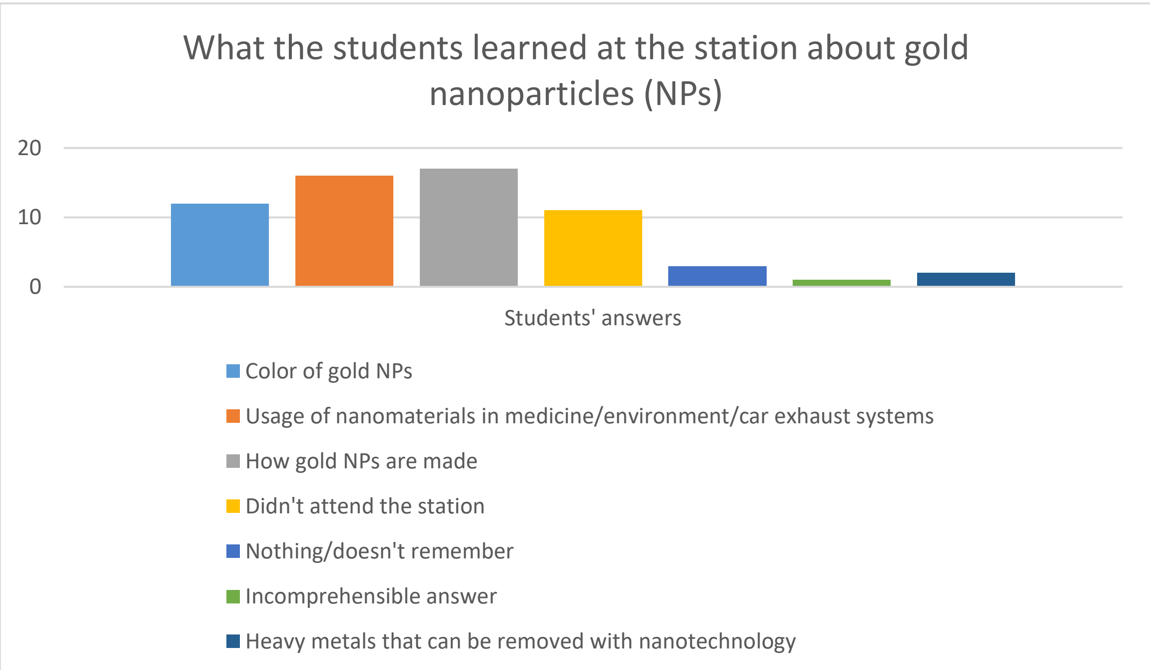

Fig. 13. Students’ answers on the question “What have you learned at the station about gold nanoparticles?”.

The majority of the student had no previous knowledge about gold nanoparticles (see appendix 9.3). The students learned about the color of gold nanoparticles, the usage of gold nanoparticles and how they are made. Generally the student didn't give very detailed answers about the chemistry behind making gold nanoparticles, however some students did. For instance, one student answered that they learned about "how to reduce gold by redox reaction with the help of TSC and 'sodiumbarohydrogen' ". Approximately half of the students asked questions about the usage of gold nanoparticles or asking for more details about gold nanoparticles (see appendix 9.3), for instance, one student asked "How does one work with it [gold nanoparticles] and how does one develop research around it?".

5.2.1.2 Microplastics station

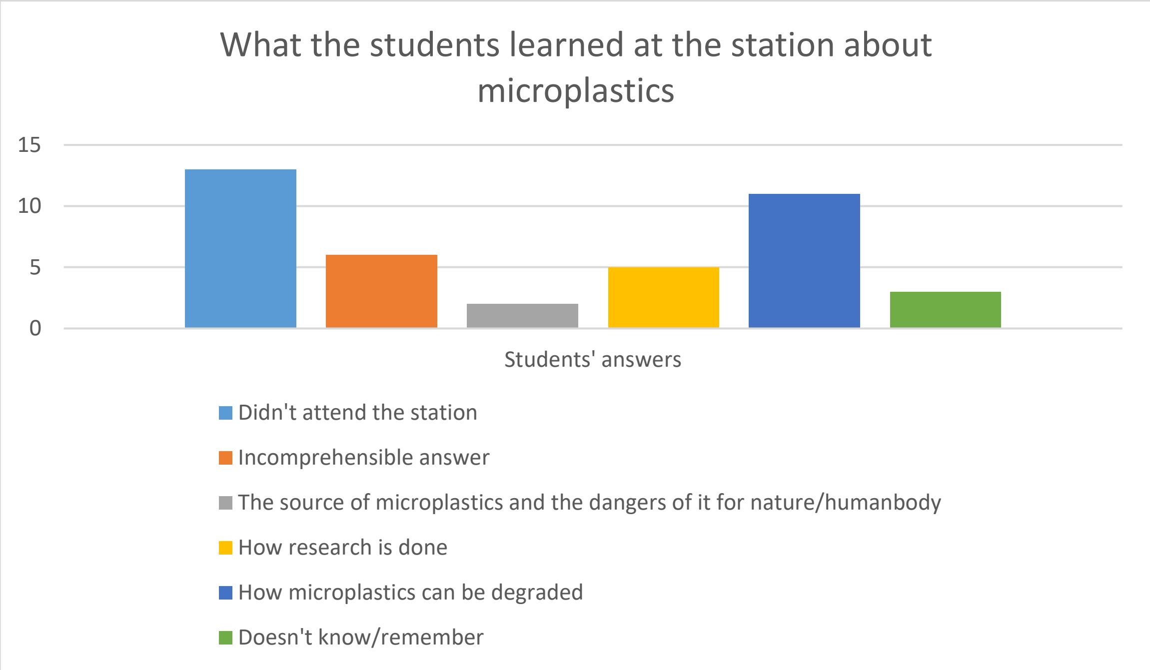

Fig. 14. Students' answer on the question "What have you learned in the station about microplastics and their degradation?".

The majority of the students had no previous knowledge about microplastics besides that it is dangerous for the environment (see appendix 9.3). The students mainly learned about how microplastics can be degraded, and how research is done. Some of the students answered with the chemical terms that were used during the station. For instance a student said they learned that "degrading microplastics is possible with iron and zinc oxide, however zinc oxide needs a photocatalyst which is light" and another student said they learned that "when we wash clothes we release microplastics, what photocatalysis is and what her experiment is. Glass fibers with spikes made of ZnO and how she got iron on the glass fibers so that it can produce more hydroxyl radicals and degrade microplastics".

Approximately half of the students asked questions about the future, globality, and effectivity of the microplastic degradation method (see appendix 9.3). One student asked "how cheap is the method and in what extent can it be used, in other words, is it effective to clean large amounts of water from microplastics?" and another asked "will we see this technology in our everyday life?"

5.2.1.3 Water desalination station

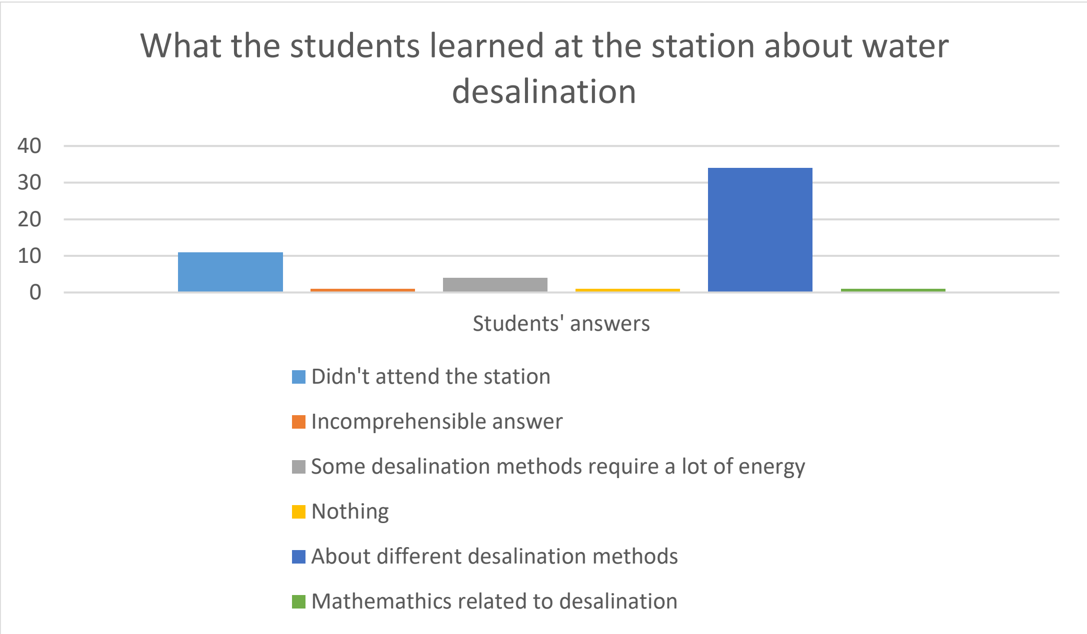

Fig. 15. Students' answer on the question "What did you learn at the station about converting salt water into drinking water?".

The majority of the students had some previous knowledge about distillation and filtration (see appendix 9.3). The majority of the students learned about different desalination methods. For instance one student said that they learned "that by taking advantage of ions' charges one can separate salt from sea water with a new process that mainly works for brackish water". Some answers were very detailed and shows that the students thought of water desalination through an energy consumption-, economical-, and environmental view. One student said they learned "that one normally tries to get clean [desalinate] water by using 'osmos' [reverse osmosis], but that one have discovered a new way to clean [desalinate] water that doesn't negatively impact the environment, and doesn't require much energy: instead of taking away water from salt, one takes the salt from water. The filter that is used consist of carbon, and the salt gets stuck there, and out from the pipe one gets clean water".

Almost half of the students asked questions about future usage or development of the desalination method that have been developed at the laboratory (see appendix 9.3).

One student asked “How will this product be used, in other words, will it be something that everyone has at home or something at a water treatment plant?”.

5.2.2 Students’ view on research after the visit

The result of students’ answer about if and how their view on research changed can be seen below in fig. 16.

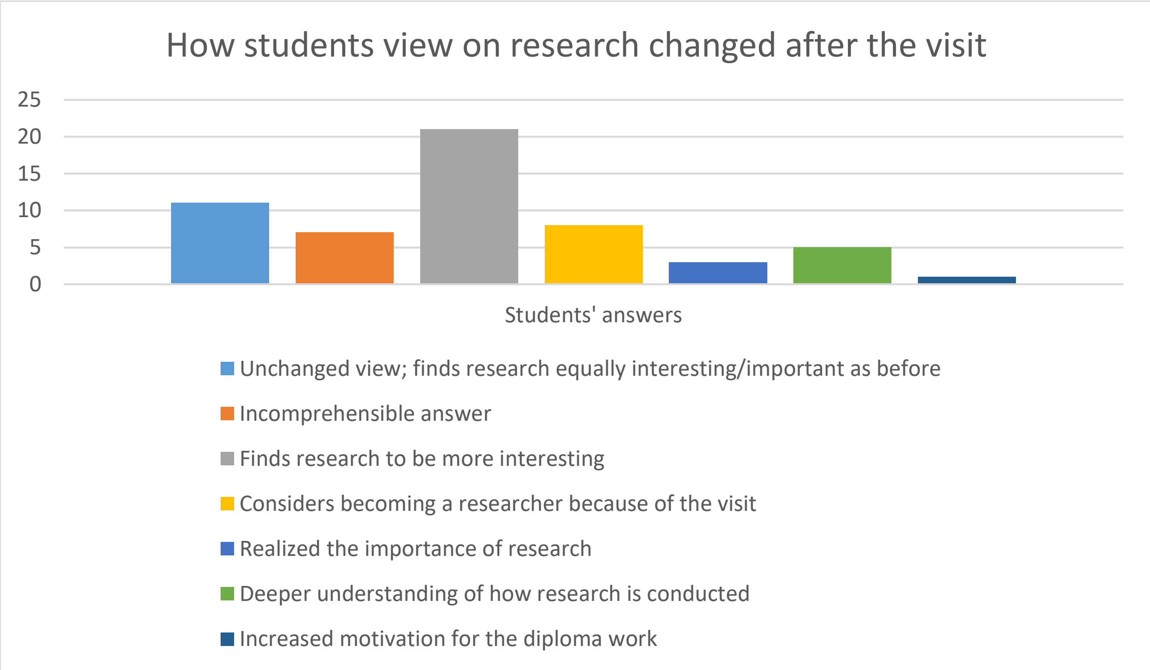

Fig. 16. Students’ answer on the question “Has it [your view on research] changed after this visit? If so, how?”.

The majority of the students found research to be more interesting, and some students even consider becoming researchers after the study visit. One of the students said that research “seems really interesting. I wanted to be a researcher and had given up on it, but now I am more interested again.” Another student said “After this visit I find research to be very interesting. I used to find it very boring, now I’m thinking that I’ll maybe become a researcher”.

6 Discussion

In this section the technical and pedagogical results are discussed.

6.1 Discussion of technical results

During the test degradation of methylene blue the system with the $ZnO/SnO_2/Fe^0$ – sample show significant improvement of degradation rate compared to the system with the ZnO – sample (see fig. 10). In the beginning of the degradation (30 minutes) the $ZnO/SnO_2/Fe^0$ – sample's degradation rate was 4 times faster than the ZnO – sample's degradation rate. However, the degradation rate of the $ZnO/SnO_2/Fe^0$ – sample starts to plane out after 135 minutes and the difference in degradation rate becomes smaller. After 135 minutes the $ZnO/SnO_2/Fe^0$ – sample's degradation rate becomes approximately twice as fast as the ZnO – sample's degradation rate.

When the synthesized $ZnO/SnO_2/Fe^0$ material was used to degrade polystyrene for 10 days, the $-OH$ absorbance ratio was large (731 % increase), and the $C = O$ absorbance ratio was increased with 44.7 %. This indicates that the synthesized $ZnO/SnO_2/Fe^0$– sample can be used for degrading microplastics. The degradation results of polypropylene for 60 hours, revealed 150 % increase in the $-OH$ absorbance ratio and 34.3 % decrease in the $C = O$ absorbance ratio. The decrease is expected since the degradation time was only 60h, to see an increase in the $C = O$ peak the degradation have to be over 10 days. (Mylläri et al., 2015).

6.1.1 Future research

Due to lack of time, the degradation of polypropylene was for only 60 hours. The degradation of polypropylene can be investigated for a longer time interval. The optimization of the pH and the prevention of the disassociation of ZnO nanorods can be researched further.

6.1.2 Error source in technical method

The $ZnO/SnO_2/Fe^0$ – sample and the ZnO – sample had different weight when used for degrading methylene blue, (0.92g and 0.62g respectively). This could have affected the results in fig. 8.

The Fourier Transform Infrared Spectroscopy machine produced a lot of noise in the background in fig. 12, this could affect the measurement of the $-OH$ and $C = O$ peaks.

6.2 Discussion of pedagogical results

6.2.1 What the students learned during the study visit

Generally, the students didn't give detailed answers on what they learned, however, the answers of the ones who described what they learned indicate that the students learned something new about gold nanoparticles, microplastics and water desalination.

During the gold nanoparticle station the students were told about the usage of nanomaterials, and shown how gold nanoparticles are made and the color change of gold nanoparticle solutions (see section 4.2.2.3). From fig. 13 it is clear that the majority of the students learned about something related to these things. Most of the students didn't write so much about the chemistry behind the color change of gold nanoparticle solutions (see section 5.2.1.1) which indicate that the students didn't understand or remember it so well. In other words, the chemistry aspect of gold nanoparticles was too difficult for them to understand within such a short time.

During the microplastics station the students mainly learned about how microplastics can be degraded, and how research is done (see section 5.2.1.2), which is what the station leader put emphasis on during the presentation (see section 4.2.2.6). Some of the students used chemical terms in their answers. This is most likely because chemical terms such as ZnO, $^{\bullet}OH$ photocatalysis and Fenton reaction was repeated several times during the station and therefore were easier to remember.

During the water desalination station the majority of the students learned about different desalination methods (see section 5.2.1.3), which was the main topic of the water desalination station (see section 4.2.2.6). Mathematics related to water desalination was also presented during the water desalination station, however it was only one student who said they learned something related to mathematics (see fig. 14), which indicates that the mathematical aspect of the topic was too difficult for the students to comprehend.

The students' questions about the microplastics station and water desalination station had a similar theme. Many of the students asked about the future usage of the degradation method and the water desalination device. This indicates that they had an overall understanding of what was presented during the stations, and were more curious about the future usage of the method/device that were developed at the laboratory. However, the students' asked about the usage of gold nanoparticles and for more details about gold nanoparticles, which indicates that they found some things to be unclear to them during the gold nanoparticle station and wanted to know more about it. This shows the importance of being clear to the students about the purpose of the information that is being taught at the stations.

6.2.2 Cognitive perspective on learning during the study visit

The students had no previous knowledge at the gold nanoparticle station and the microplastics station, therefore they didn't undergo any assimilation, only accommodation (for cognitive perspective on learning see 3.2.2). In this section the focus will be on the water desalination station since the students had previous knowledge (see section 5.2.1.3) and therefore underwent both assimilation and accommodation, making their learning more analyzable.

Since the majority of the students who were at the water desalination station said they had some previous knowledge about how to desalinate water (many of the students said distillation and filtration), this indicates that they experienced some assimilation to the topic. For instance, the students who knew about distillation could assimilate to the new facts that was told to them about it. They knew that when heating water the water will evaporate, but the salt will not, and that water can be separated from salt that way. Therefore when they were told further information about how distillation can be done on a large scale, they can undergo assimilation. However, when the student learn about reverse osmosis while not having previous knowledge about it, they most likely undergo accommodation. This is because the students have to adjust and change their past knowledge that is somewhat related to the fundamentals of the topic osmosis, for example their knowledge about how concentrated juice becomes less concentrated when mixed with water because the molecules in the concentrated juice will move into the water to equalize the concentration. It's this type of knowledge that when adjusted and changed the students will undergo accommodation to comprehend reverse osmosis.

The students know the concept sustainability since it is part of the curriculum (Skolverket, 2011). When the students were told about the sustainability issues with some of the desalination methods, they underwent assimilation. This is observed in the students answers that shows how they thought of water desalination through an energy consumption-, economical-, and environmental view (see section 5.2.1.3).

6.2.3 Socio-cultural perspective on learning during the study visit

When the students discussed a topic that lied within their proximal development zone, they were able to learn about the topic by sharing their thoughts to each other and by being guided by the teacher (for socio-cultural perspective on learning see section 3.2.1).

When the students were asked to discuss what they think produces a lot of microplastics in the everyday life of a person, they were discussing something that lied within their proximal development zone since the students only knew that microplastics is bad for the nature and nothing about how they are produced. Some of the students' answered that they learned that washing fleece clothes produce microplastics (see fig. 13), which is strongly connected to the discussion questions the students had during the microplastics station. This also indicates that the students thought about microplastics through a sustainability aspect.

In the water desalination station the students were asked to discuss which water desalination methods they knew of and they were informed of the methods they didn't know of and how they work. Since the students had some previous knowledge about the topic, most of the presentation was within the students' proximal development zone, except the mathematical part that was way beyond their knowledge. It's observable from the students' answers that the station leader was able to guide the students to learn about different desalination methods, but not about the mathematics behind it since only one student mentioned something related to mathematics (see fig. 14).

Since some of the students' answers were connected to the discussion questions they had during the microplastics station and the water desalination station (see section 5.2.1.2 and 5.2.1.3), it seems that discussing topics within students' proximal development zone can help students to remember them better.

A lot of tools (artifacts) were used to convey information to the students during the study visit in terms of Power Point, Scanning Electron Microscopy images, and illustrations (see appendix 9.4, 9.5, 9.6, and 9.7). It is observable in the students' answers that using artifacts facilitated for the students to express their knowledge in the questionnaire, an example of this is when one of the students' said "Glass fibers with spikes made of ZnO" (see section 5.2.1.2 and fig. 1. in appendix 9.7).

6.2.4 Motivation

Students generally have no experience of how research is conducted and they often have a stereotypical view of researchers which can affect the development of their interest and attitude towards science. From the students' answers about how their view on research has changed after the study visit (see section 5.2.2) it is clear that the students who didn't have a positive view on research have become more interested in research after the study visit. The students' increased interest in research is something that indicates an increase in intrinsic motivation for research. It could also indicate an increase in their intrinsic motivation for the school subject chemistry, since most of what was spoken about during the stations is related to chemistry. An increased motivation would then result in better learning outcome (see section 3.2.2). However that is not necessarily what happens. The student might find the chemistry used in research to be interesting, but chemistry in a class room less interesting because of how it is presented.

The fact that some students said they wanted to become researchers because of what they heard and saw during the study visit (see fig. 16) might indicate that the students saw some utility value (usefulness) of chemistry in research that they didn't see before. This could make them view the school subject chemistry as a tool to attain a certain occupation, (researcher in this case), and in that way increase their motivation to study the school subject (see section 3.2.2).

6.2.5 Validity and reliability of the method and results

This study had only 57 participants from one high school, therefore the results of this study can't be generalized. However, the result of this study could be transferable when it comes to similar student groups with same education and age. Since the students were aware of that they were going to answer on a questionnaire about what they have learned during the study visit, there is a risk of a Hawthorne effect, in other words, that the students behave differently due to knowing that they are part of a study.

7 Conclusions

7.1 Conclusions of the technical results and discussion

The degradation rate of methylene blue with the $ZnO/SnO_2/Fe^0$ – sample is faster than the degradation rate with the ZnO – sample. It is 4 faster in the beginning of the degradation, but the difference in degradation rate decreases with time and becomes around 2 times faster.

The $ZnO/SnO_2/Fe^0$ – sample can be used to degrade polystyrene and polypropylene, however the degradation of polypropylene needs to be investigated for a longer time interval.

7.2 Conclusion of the pedagogical results and discussion

What and how high school students learn during a study visit about nanotechnology at a laboratory

The majority of the students learned about the color of gold nanoparticles, the usage of them, and how they are made. They also learned about how microplastics can be degraded, how research is done, and about different desalination methods.

The students' answers about what they learned in the water desalination station and microplastics station indicate that the students became more aware of the sustainability issues with water desalination methods and the production of microplastics by washing fleece clothes (see section 6.2.1 and 6.2.2).

During the study visit the students underwent assimilation and/or accommodation depending on how the station was designed. When the station was designed in a way where the students had some previous knowledge the student underwent both assimilation and accommodation thus enabling adaptation to take place, which is a process that is required to understand the outside world (see section 3.2.1 and 6.2.1).

As observed at the water desalination station, it's important that the topic is within the students' proximal development zone, otherwise the students won't be able to grasp or learn about the topic. Artifacts like images can facilitate for student to express their new acquired knowledge (see section 3.2.1 and 6.2.2).

How the study visit affects students' interest and motivation for learning

Study visits to a nanotechnology laboratory can be very effective at increasing students' interest for research and therefore also their intrinsic motivation for research. It also makes students see the utility value of chemistry in research, and thus increase their motivation for studying chemistry (see section 5.2.2 and 6.2.4).

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9 Appendix

9.1 Questionnaire

1. What have you learned at the station about gold nanoparticles?

2. What did you know about gold nanoparticles before the study visit?

3. What questions/thoughts do you have about gold nanoparticles after the study visit?

4. What have you learned in the station about microplastics and their degradation?

5. What did you know about microplastics and their degradation before the study visit?

6. What questions/thoughts do you have about microplastics and their breakdown after the study visit?

7. What did you learn at the station about converting salt water into drinking water?

8. What did you know about the conversion of salt water to drinking water before the study visit?

9. What questions/thoughts do you have about the conversion of salt water to drinking water after the study visit?

10. What is your view on research?

11. Has it changed after this visit? If so, how?

12. Other questions or comments

9.2 Program of the study visit

Location: Electrum laboratory - Isafjordsgatan 22, 164 40 Kista

Date: 14/11/2019

Group: about 70 students from Kungsholmens Västra Gymnasium

Program for the study visit

Gathering in the conference room 13:40-14:00

Information about KTH (Mats Ahmadi Götelid)

Introduction to Nanotechnology (Professor Joydeep Dutta)

Stations 14: 00-16: 00

Gold Nanoparticles (Abdusalam Uheida)

Microplastics (Marianne Al-Ghorabi)

Conversion of salt water to drinking water (Johan Nordstrand)

Scanning Electron Microscopy (Fei Ye)

Snack-break station (Anette Al-Ghorabi)

Gathering in the conference room 16: 00-16: 30

Survey (Marianne Al-Ghorabi)

9.3 Students answers on the questionnaire

Gold nanoparticle-station

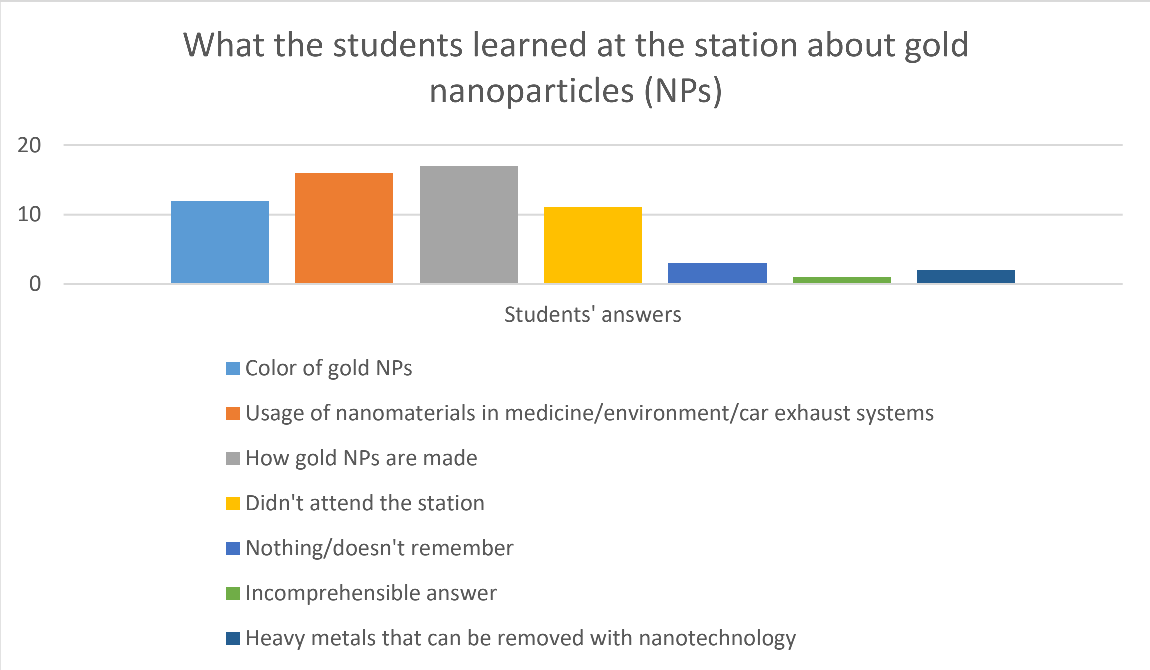


Fig. 1. Students' answers on the question "What have you learned at the station about gold nanoparticles?".

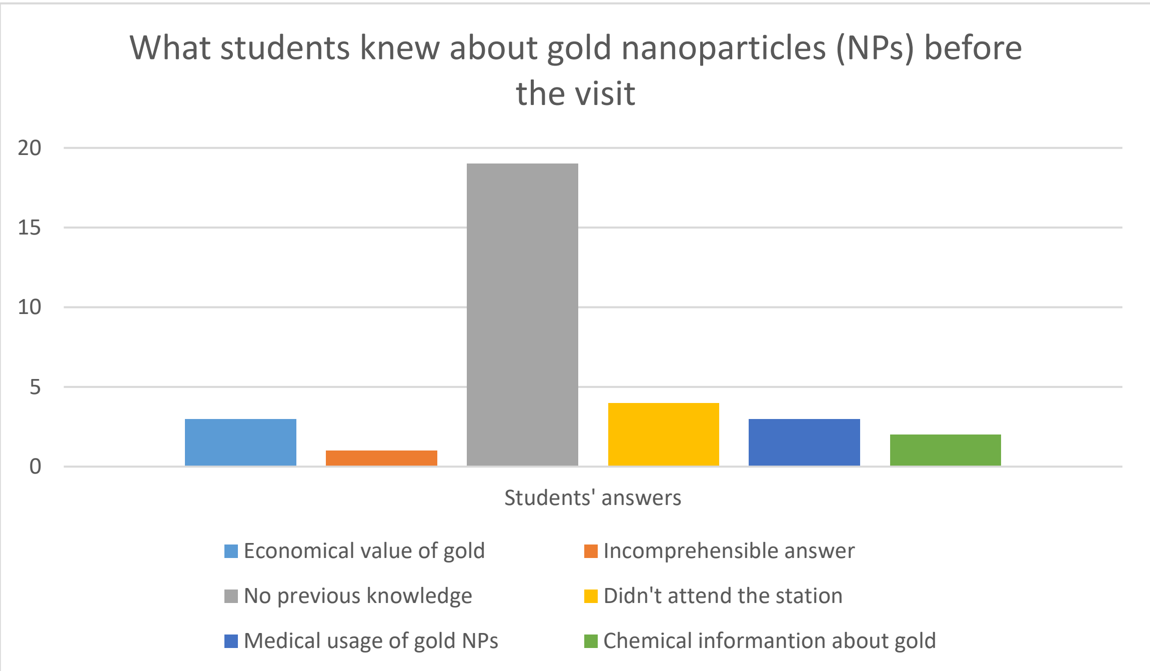


Fig. 2. Students' answers on the question "What did you know about gold nanoparticles before the study visit?".

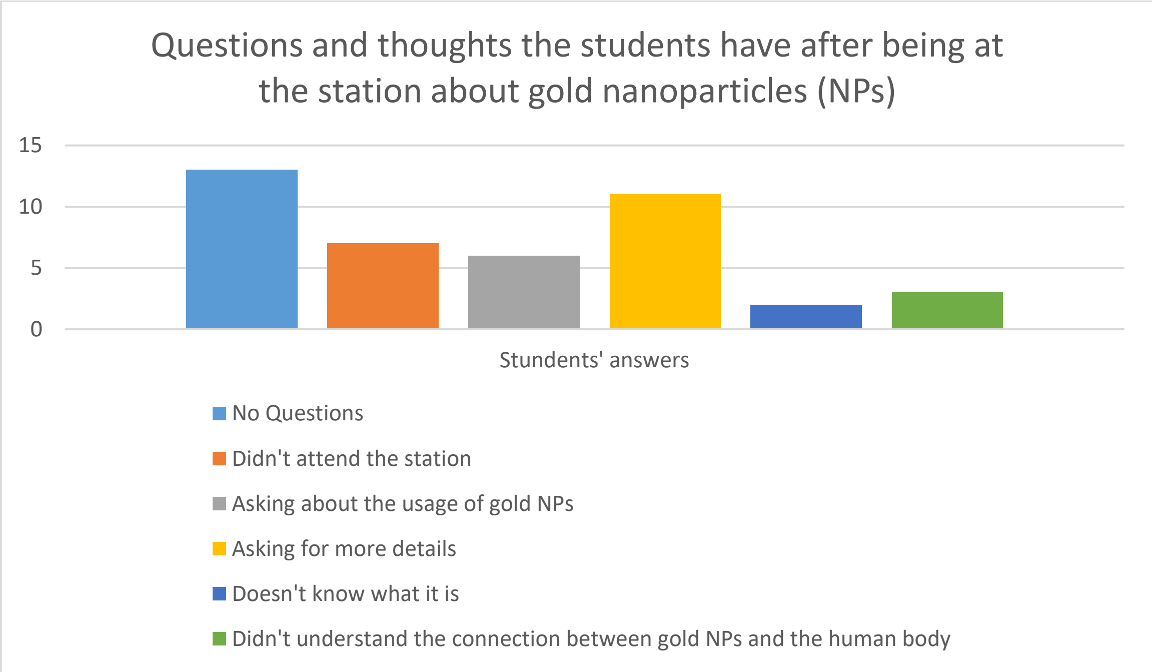


Fig. 3. Students' answer on the question "What questions/thoughts do you have about gold nanoparticles after the study visit?".

Microplastic-station

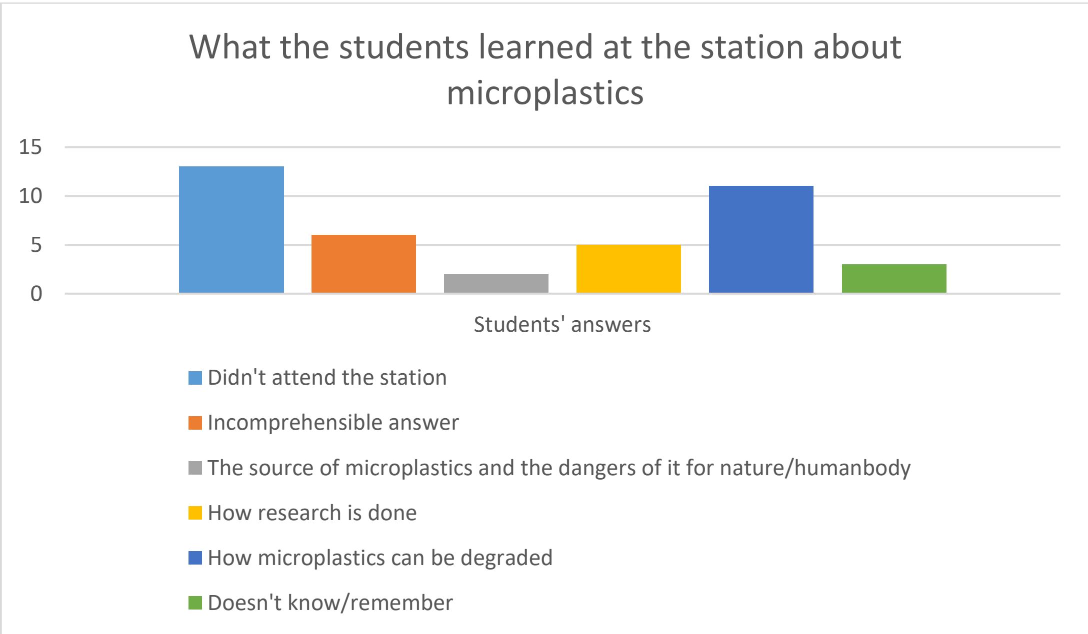


Fig. 4. Students' answer on the question "What have you learned in the station about microplastics and their degradation?".

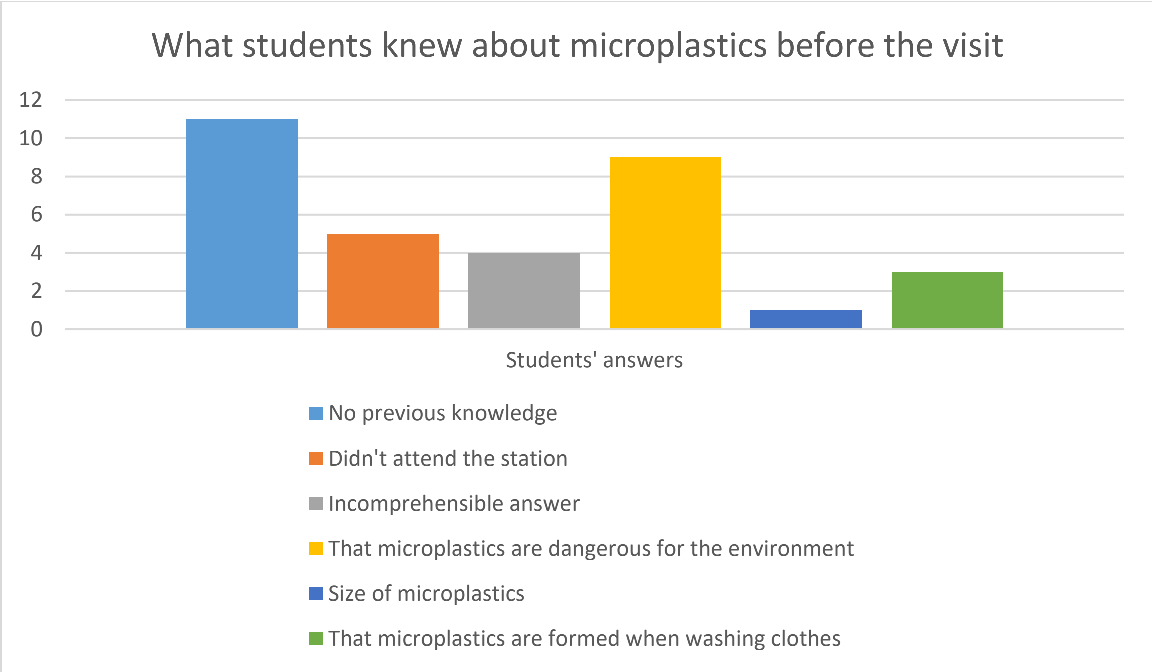


Fig. 5. Students' answer on the question "What did you know about microplastics and their degradation before the study visit?".

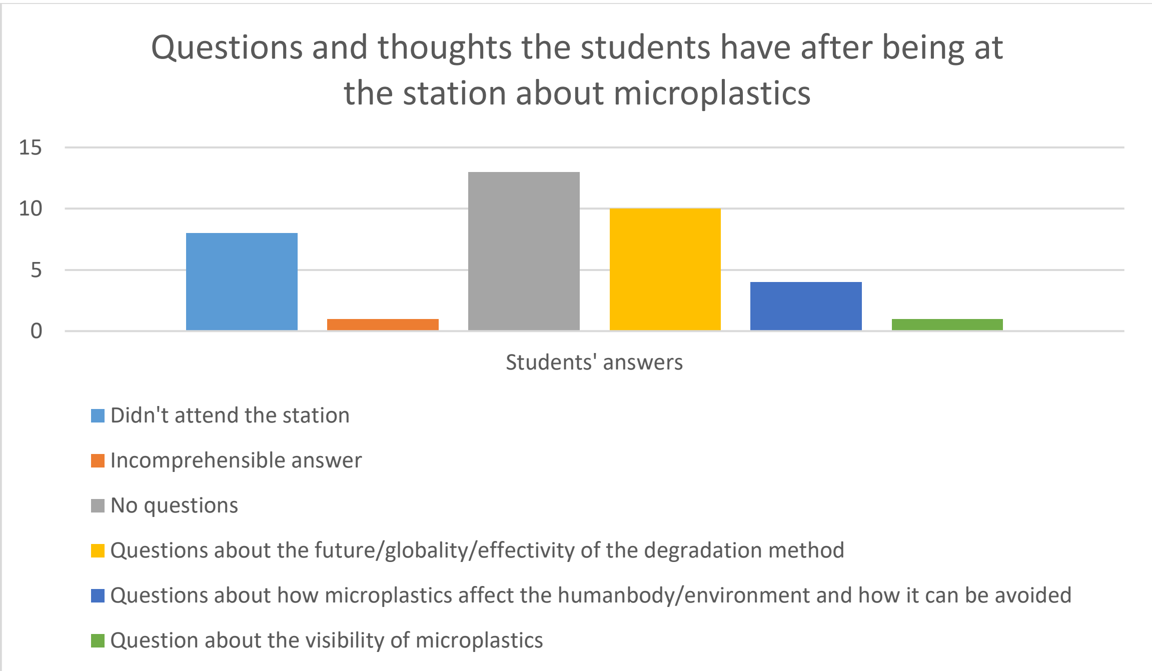


Fig. 6. Students' answer on the question "What questions/thoughts do you have about microplastics and their breakdown after the study visit?".

Water desalination-station

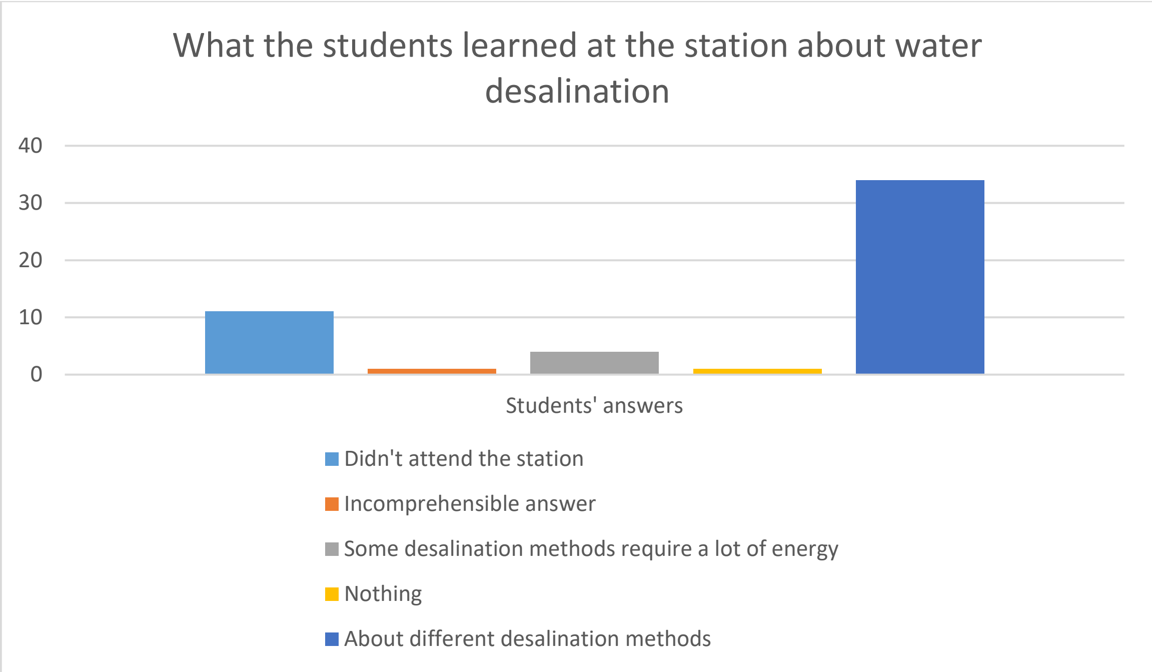


Fig. 7. Students' answer on the question "What did you learn at the station about converting salt water into drinking water?".

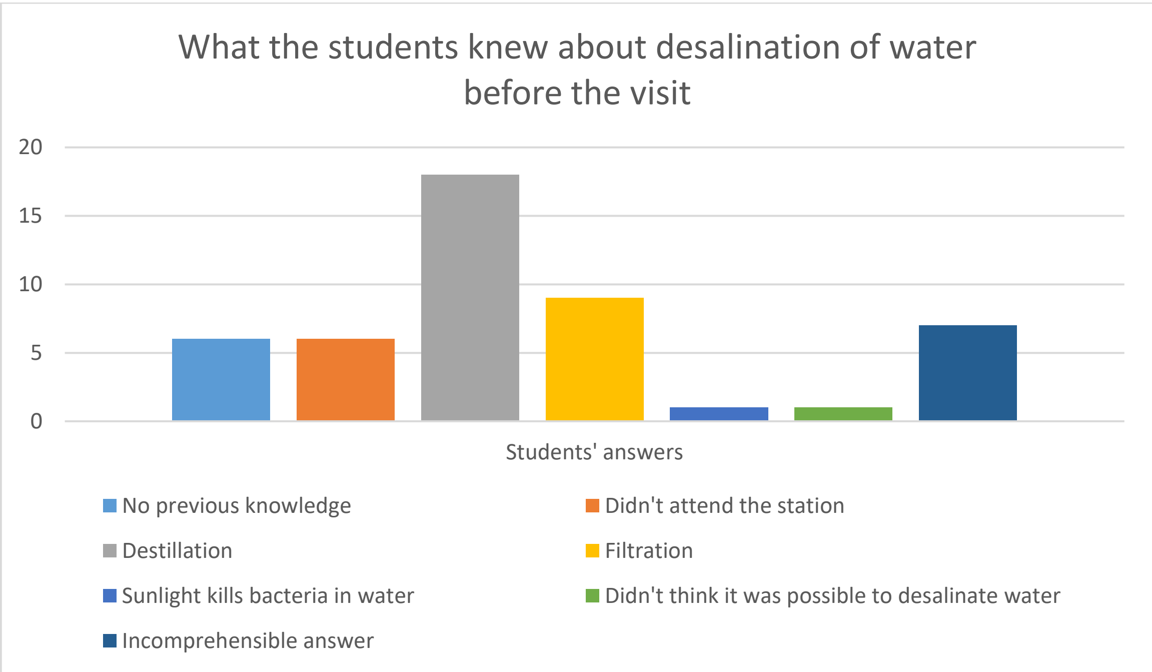


Fig. 8. Students' answer on the question "What did you know about the conversion of salt water to drinking water before the study visit?".

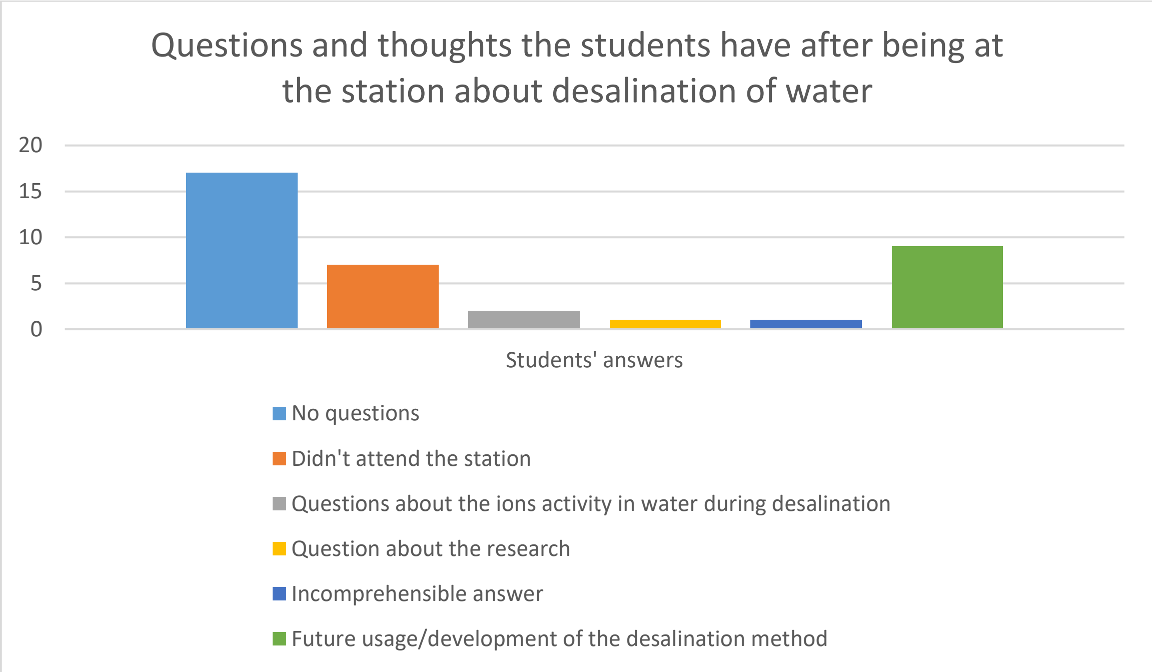


Fig. 9. Students’ answer on the question “What questions/thoughts do you have about the conversion of salt water to drinking water after the study visit?”.

Students view on research

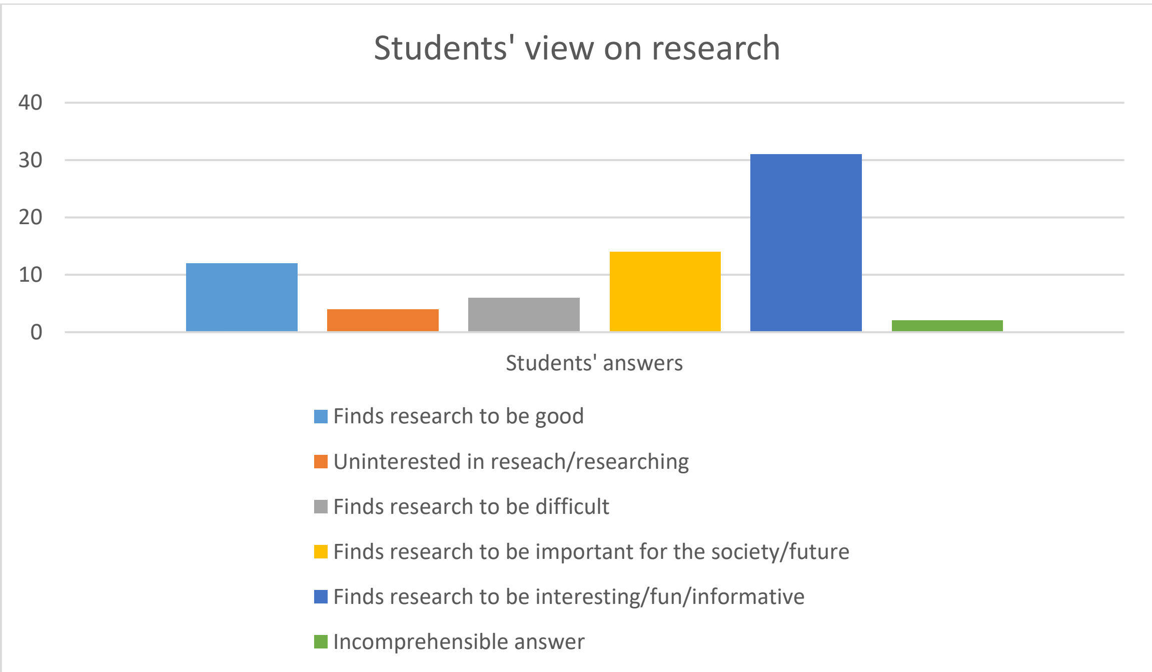


Fig. 10. Students’ answer on the question “What is your view on research?”.

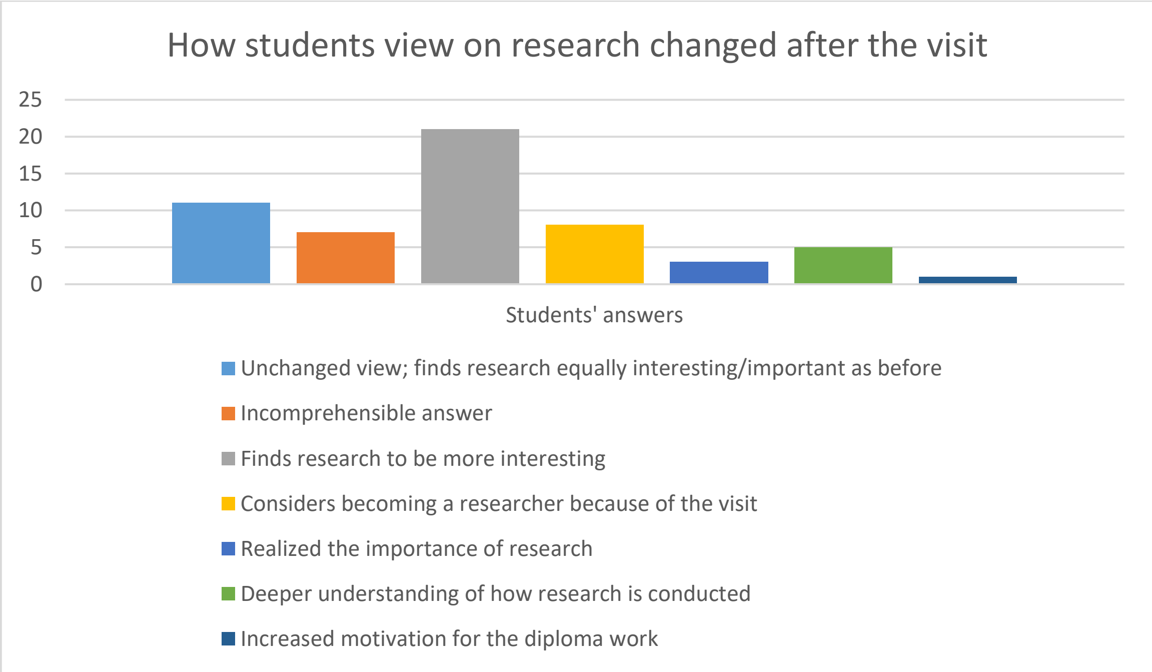


Fig. 11. Students’ answer on the question “Has it changed after this visit? If so, how?”.

9.4 Microplastic degradation setup

The microplastic degradation setup that was shown to the students during the microplastics station is shown below.

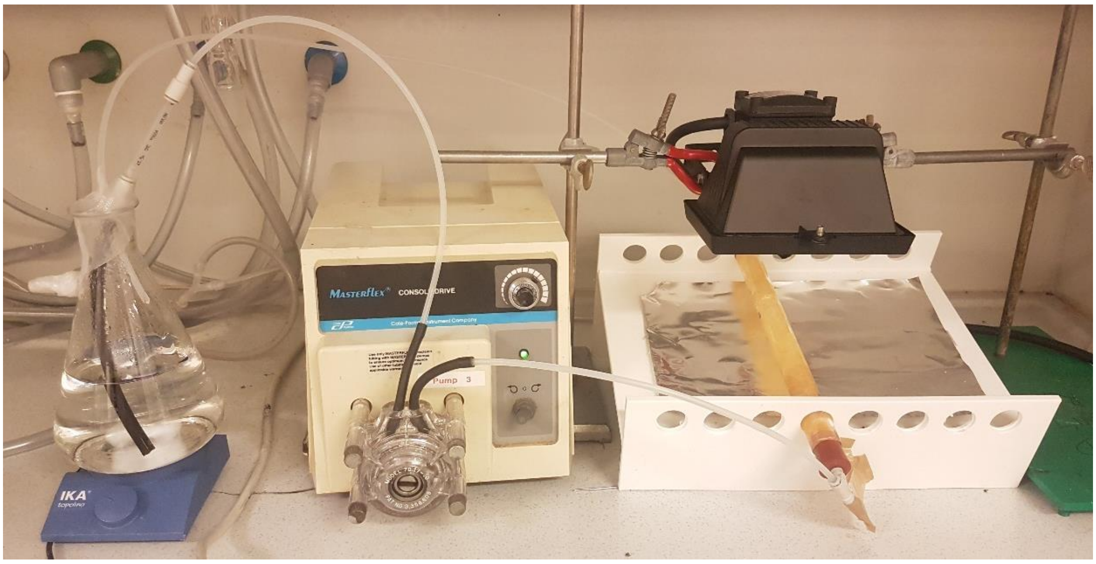


Fig. 1. The setup used to degrade polystyrene and polypropylene.

9.5 Water desalination station PowerPoint

The PowerPoint slides (made by Johan Nordstrand) that were shown to the students during the water desalination station are shown below.

The Dynamic Langmuir Model

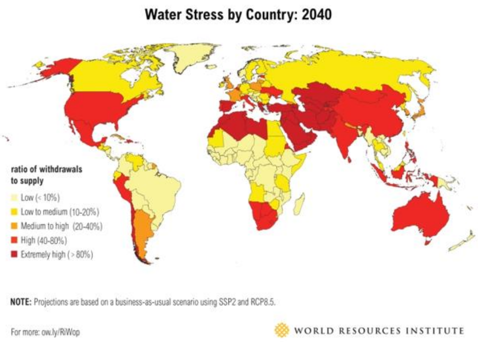
A Simpler Approach to Modeling Water Desalination by Capacitive Deionization

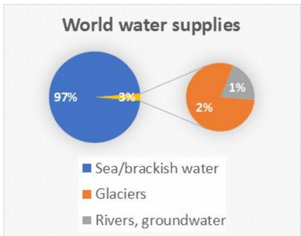
JOHAN NORDSTRAND

KTH ROYAL INSTITUTE OF TECHNOLOGY

SWEDEN

The Need for Fresh Water





Data from: J. Kocera, *Desalination - Water to water*. John Wiley & Sons, 2014.

Water shortage 'a global problem'

By Imogen Foulkes
BBC News, Geneva

Sverige

SMHI: Risk för vattenbrist i stora delar av Sverige

UPPDATERAD 2018-07-26 PUBLICERAD 2018-07-26

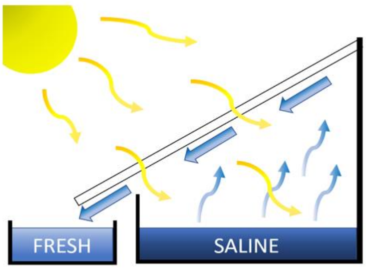
Question

Examples of desalination techniques?

Desalination Technologies

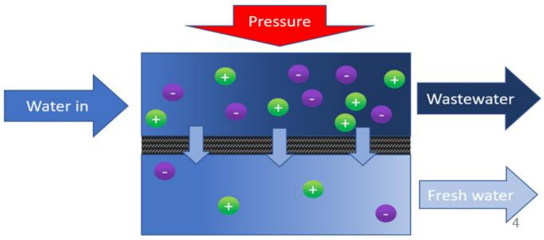
Thermal methods

- Intuitive
- Use solar evaporation



Reverse osmosis (RO)

- Most common
- Pushes water through membranes
- Uses high-pressure pumps



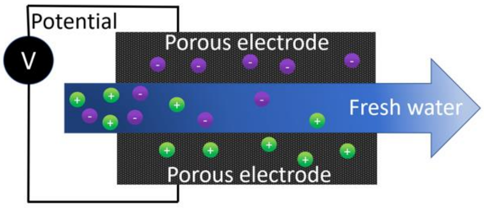
Capacitive Deionization (CDI)

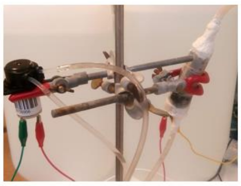
Cell with porous carbon electrodes

Ions removed when a voltage is applied

Desalination and regeneration

Competitive and environmentally friendly





5

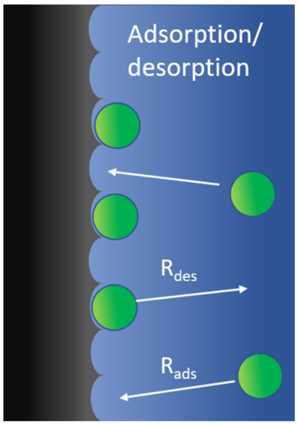
Dynamic Langmuir Model: Basic Idea

Fundamental question:

What are the key underlying principles of salt removal, and how can they be represented in a simple way?

Underlying principle:

Adsorption rate depends on water concentration and remaining storage capacity. Desorption rate depends on storage.



Two properties of interest:

Concentration of charges

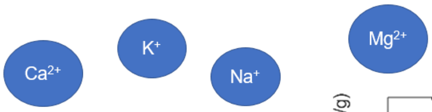
$$\frac{d\sigma_{ads}}{dt} = k_{ads}\sigma(S - \sigma_{ads}) - k_{des}\sigma_{ads}$$

Net salt removal

$$\frac{dc_{ads}}{dt} = k_{ads}c(S - \beta_0 - \beta_1 c_0 - c_{ads}z) - k_{des}c_{ads}$$

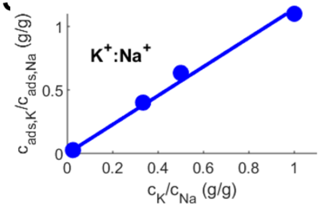
Application to Real-world Conditions: Multiple Ion Types

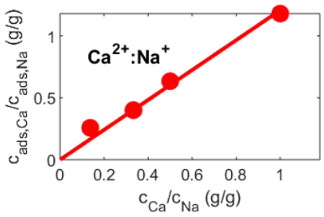
The DL model can simply predict desalination performance for water with multiple ion types, such as fluoride, calcium, and heavy metals.



At saturation, the total adsorption is proportional to the concentration of each ion.

$$\frac{c_{ads}^{(i)}}{c_{ads}^{(j)}} = \alpha \frac{c^{(i)}}{c^{(j)}}$$





Figures: Experimental data and model lines show relative adsorption between K^+ and Na^+, and between Ca^{2+} and Na^+.

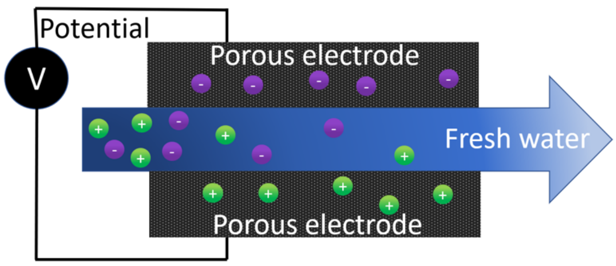
Data from: Hou, C.; Huang, Z.-Y. A Study of Electrosorption Selectivity of Anions by Activated Carbon Electrodes in Capacitive Deionization. *Desalination* **2015**, *369*, 46–50. https://doi.org/10.1016/j.desal.2015.04.022.

Conclusions

CDI is promising for environmentally friendly and cost-effective desalination

The dynamic Langmuir (DL) model was developed to make modeling and optimizing CDI processes more accessible

The DL model could extensively describe key operational parameters in CDI, including the effects of voltage, concentration, ion types etc.



Thank You!

Acknowledgements:

Thanks to my colleagues at the Functional & Nano Materials (FNM) group at KTH and special thanks to my supervisors.

References:

[1] J. Nordstrand and J. Dutta, “Dynamic Langmuir Model: A Simpler Approach to Modeling Capacitive Deionization,” *J. Phys. Chem. C*, p. acs.jpcc.9b04198, 2019.

[2] J. Nordstrand, K. Laxman, M. T. Z. Myint, and J. Dutta, “An Easy-to-Use Tool for Modeling the Dynamics of Capacitive Deionization,” *J. Phys. Chem. A*, 2019.

[3] J. Nordstrand, K. Laxman, M. T. Z. Myint, and J. Dutta, “An Easy-to-implement Optimization Method for Desalinating Water using Capacitive Deionization,” *Ready for submission.*

9.6 Gold nanoparticle station laboratory work

Teacher's Guide: Laboratory demonstration - Color change of gold nanoparticle solutions

---

Time required: 20 minutes

Group size: 10-12 students

Course: Chemistry 2

Topic: Nanotechnology

Assumed previous knowledge

- The students know what a reduction reaction is.
- The students know what ions and ion solutions are as well as repulsion between equal charges.

Purpose and goal

To increase students' "knowledge of the importance of chemistry for individuals and society."

To develop students' "ability to [...] interpret and report experiments and observations as well as the ability to handle chemicals and equipment. " (Skolverket 2011 Curriculum for high school).

Curriculum connection

Based on the central content, the following points will be addressed:

Analytical Chemistry

• Qualitative and quantitative methods for chemical analysis.

Based on the purpose of the subject, the following points will be considered:

• Contribute to students' development of the ability to work experimentally [...] and to communicate with the help of scientific language.

• [..] seek answers to questions and perform experiments as well as process, interpret and critically review results and information.

• Provide opportunities for the students to argue and present their analysis and conclusions.

Implementation plan:

Preparations for the laboratory demonstration.

1. Make sure you have at least 40 ml of gold chloride solution, $HAuCl_4$ (0,25mM)
2. Make sure you have at least 40 ml of trisodium citrate solution, $Na_3C_6H_5O_7$ (0,25mM)
3. Make sure you have at least 0.7ml of sodium borohydride solution, $NaBH_4$ (0,1M)
4. Make sure you have enough material, see the student manual in the appendix
5. Make sure that you read the see risk assessment of the chemicals.
6. Make sure that you know what to do if an accident with the chemicals happens (see risk management).
7. Tips for the laboratory demonstration: Prepare by putting the materials and chemicals that you (or two students) will use in the fume cover.

The laboratory demonstration

1. Make sure that all students wear lab coat, protective gloves and goggles.
2. Hand out the student laboratory work document (see student instructions) and ask them to read it carefully.
3. Inform about the chemicals and the risk management and show the shower and eye shower, inform about the rules in the laboratory.
4. Explain to the students the theory behind the laboratory demonstration.
5. Discuss results and students' thoughts during the course of the laboratory demonstration. Try to guide them, but don't give the answer right away.

Theory

The gold chloride solution ($HAuCl_4$) contains gold ions. The gold ions are positive and the oxidation number of it is $+5$. Since the gold ions have the same charge, they avoid being close to each other (repulsion between equal charges).

When the trisodium citrate solution ($Na_3C_6H_5O_7$) is added to the gold chloride solution, the citrate ion (negatively charged, see fig. 1) will surround the gold ion (positively charged). Fig. 2 shows that one of the negative oxygen ions of the citrate ion is close to the gold ion, while the other two negative oxygen ions have taken up hydrogen from the water. Since the gold ions are surrounded by citrate ions, the gold ions will be kept apart.

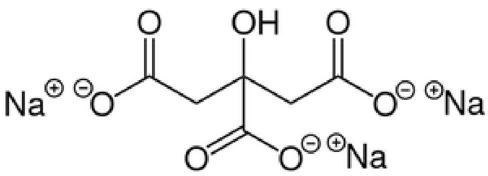


Fig. 1. Citrate ion together with three sodium ions.

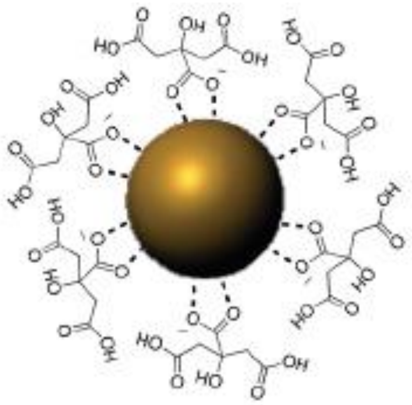


Fig. 2. A gold ion surrounded by 6 citrate ions.

Sodium borohydride is a reducing agent. It reduces the gold ions oxidation number from +5 to 0. Thus, it reduces the gold ions to gold atoms.

When gold atoms are formed, the nearby gold ions surrounded by citrate ions will want to be close to the gold atom. This happens because molecules strive to have as low energy as possible. The negative charges strive to be near positive charges to reduce the energy, so the neutral charges end up next to each other, in this case, the neutral exterior of the citrate ions and the neutral gold atom.

The result is that the gold ions gather around the gold atoms. For example, if we only have one gold atom in a solution, many gold ions will try to gather around it, then a large cluster of gold ions will form around a gold atom (Fig. 3). But if we have a lot of gold atoms, there will be fewer gold ions around a gold atom (fig.4).

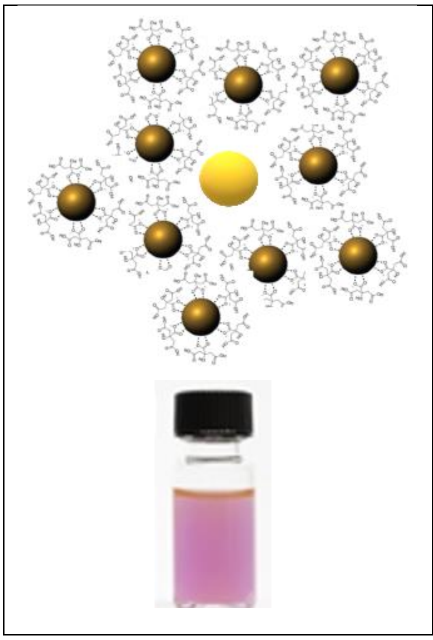


Fig. 3. Large cluster of gold nano-particles. Violet colored solution.

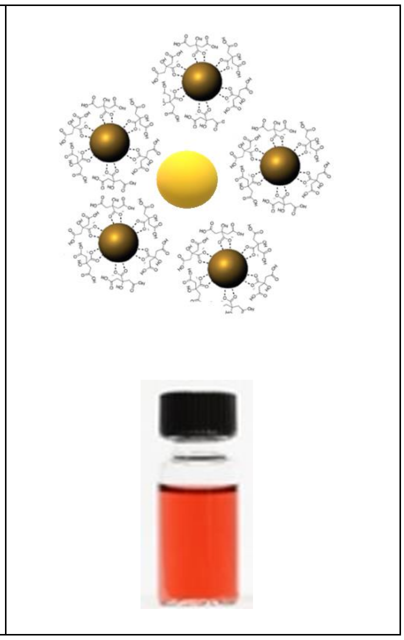


Fig. 4. Small cluster of gold nano-Particles. Red colored solution.

The gold nanoparticle solution has different colors depending on how many gold ions have gathered around the gold atoms. If it is a small cluster (Fig. 4) then the solution is red, if it is a large cluster (Fig. 3), the solution is violet. This is because the light is reflected differently depending on the size of the gold particles in the gold nanoparticle solution.

Extra information: Use of gold nanotubes in medicine

Gold nanotubes are shaped so that they have a transverse side and a longitudinal side. The longitudinal side absorbs longer wavelengths than the transverse because these sides have different surface sizes. The shape of the gold nanotubes allows them to enter between the cell walls of cancer cells. Normal cells have too little distance between them so gold nanotubes cannot get in between them. The longitudinal side can be made long enough to absorb wavelengths in the range 700nm-1100nm. When golden nanotubes absorb these wavelengths, they emit heat, which causes the cancer cells to die. This wavelength range is called the "biological window", which is a wavelength range that allows the gold nanotubes to be irradiated inside the human body without destroying other parts/tissues of the body.

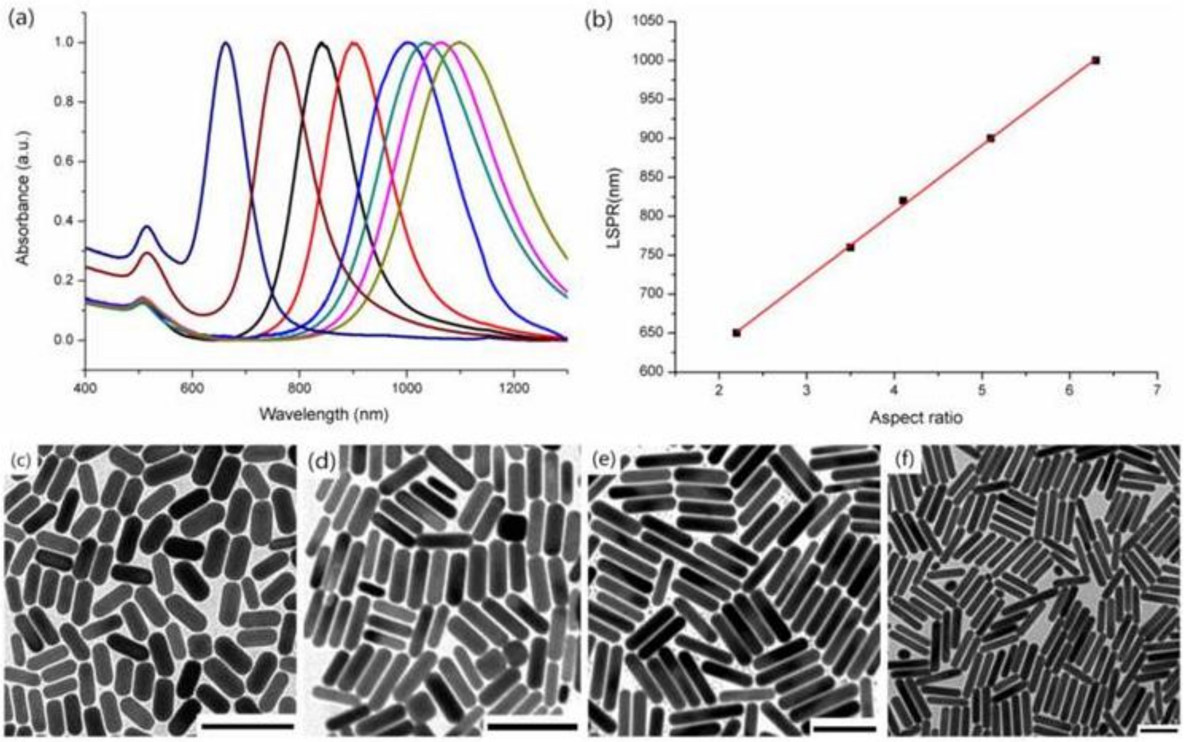


Fig. 5. Gold nanotubes and absorption spectra for different sizes of gold nanotubes. Source: *Theranostics **2015**; 5(3):251-266.*

Risk assessment

- The gold chloride solution ($HAuCl_4$) is corrosive and environmentally hazardous. Handle with care!

- Sodium borohydride ($NaBH_4$) is a corrosive, flammable, carcinogenic, and toxic substance. Handle with care!
- Trisodium citrate ($Na_3C_6H_5O_7$) is not a dangerous substance.

Risk management

- In case of skin contact or eye contact with the gold chloride solution, rinse thoroughly with water for at least 15 minutes. Call poison information center 08-331 231 when swallowing the gold chloride solution and rinse your mouth, do NOT induce vomiting!
- In case of skin contact or eye contact with sodium borohydride, rinse thoroughly with water for at least 15 minutes. Call poison information center 08-331 231 when consuming sodium borohydride. Do NOT induce vomiting!
- In case of skin contact with trisodium citrate, rinse with water and soap.

Student instructions

Laboratory demonstration

Color change of gold nanoparticle solutions

• NOTE: USE PROTECTIVE GLOVES, PROTECTIVE GLASSES AND LAB COAT!

Material:

- 2 beakers (100ml)
- Automatic pipette (100-1000µL)
- 2 measuring cylinders (20 ml)

Chemicals:

- 20 ml gold chloride solution, $HAuCl_4$ (0,25mM)
- 20 ml of trisodium citrate solution, $Na_3C_6H_5O_7$ (0,25mM)
- 0.6ml sodium borohydride solution (0.1M)

Execution:

Two students or the teacher can demonstrate this laboratory work for the rest of the students.

• Work in a fume cover!

1. Measure 20 ml of the gold chloride solution with a measuring cylinder. Pour it into a beaker.
2. Measure 20 ml of the trisodium citrate solution with a measuring cylinder. Pour it into the beaker with gold chloride solution.
3. Add 0.6ml of the sodium borohydride solution to the beaker and shake the beaker a little, what color is the solution now?
4. Measure 20 ml of the gold chloride solution with a measuring cylinder. Pour it into another beaker.
5. Measure 20 ml of the trisodium citrate solution with a measuring cylinder. Pour it into the beaker with gold chloride solution.
6. Add 0.1ml of the sodium borohydride solution to the beaker and shake the beaker a little, what color is the solution now?
7. If there is time: Repeat the experiment with different volumes of the sodium borohydride solution (but no more than 0.6ml) and observe the color spectrum.

• **NOTE:** All chemicals used must not end up in the sewage, but must be poured into inorganic waste bottle.

Risk Management:

• In case of skin contact or eye contact with any of the chemicals, rinse thoroughly with water for at least 15 minutes. Inform teacher.

9.7 Microplastics station

The images (artifacts) that were shown to the students during the microplastics station are shown below.

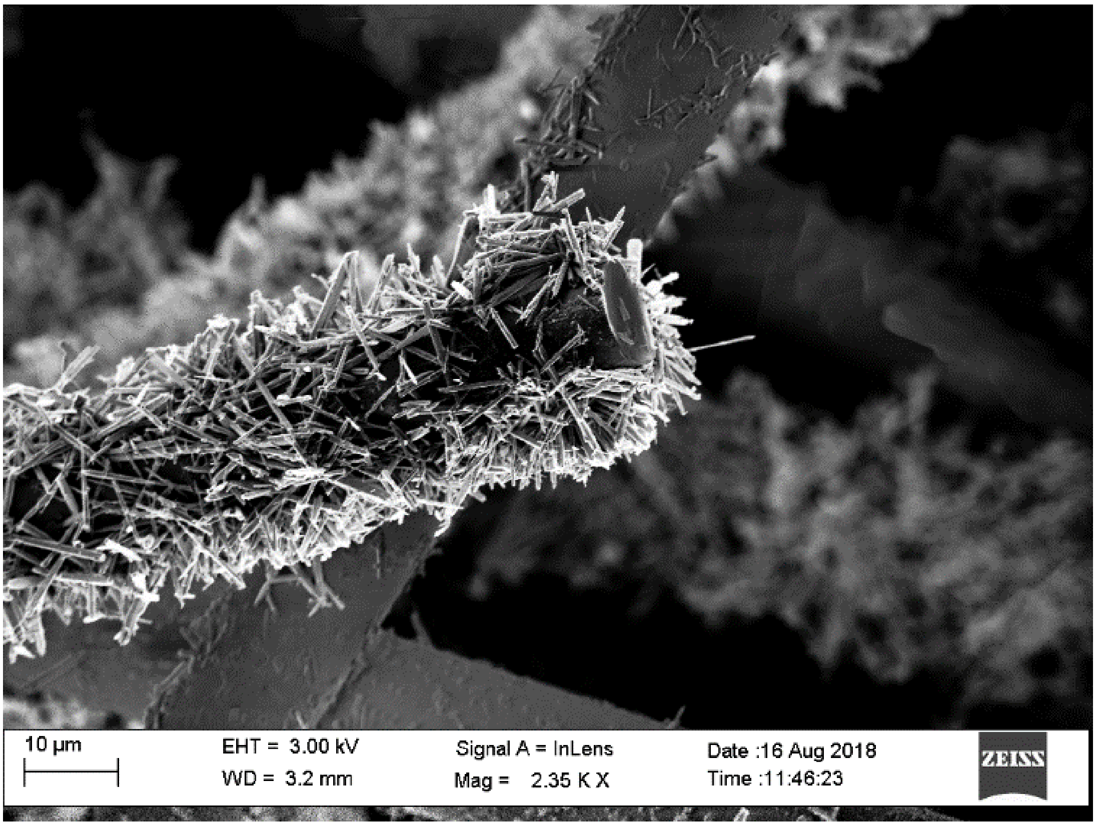


Fig. 1. The Scanning Electron Microscopy image of ZnO nanorods that were shown to the students during the microplastics station.

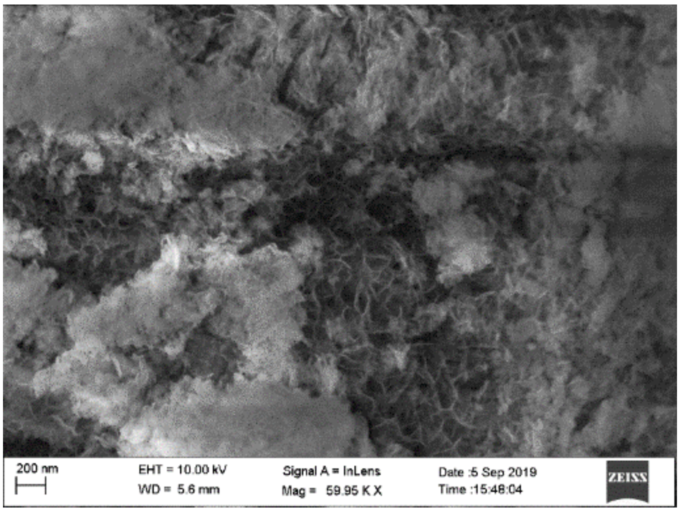


Fig. 2. The Scanning Electron Microscopy image of the first (failed) experiment trying to synthesize ZnO/Fe^0 that was shown to the students during the microplastics station.

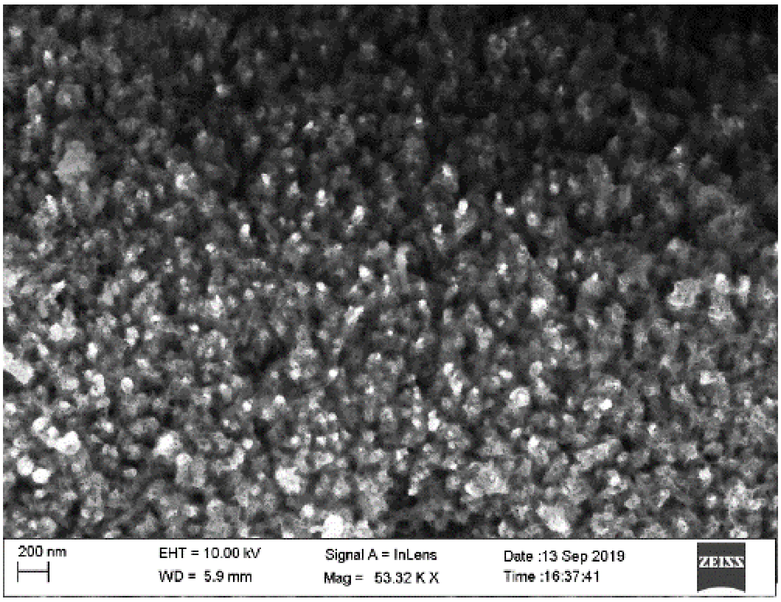


Fig. 3. The Scanning Electron Microscopy image of the fourth (successful) experiment trying to synthesize ZnO/Fe^0 that was shown to the students during the microplastics station.

Fig. 4. Degradation of methylene blue with $ZnO/SnO/Fe^0$ – sample. The 7th sample (right) was taken after 2h and 15min. This was shown to the students during the microplastics station.

Fig. 5. Degradation of methylene blue with ZnO – sample. The 7th sample (right) was taken after 2h and 15min. This was shown to the students during the microplastics station.

9.8 Peak intervals and integration results

Table 1. The peak intervals and the integration of the peaks for polystyrene before degradation.

Polystyrene before degradation	**Peak interval**	**Area under peak**
$-OH_{PS}$	3131,239 - 3746,566	1,6881000501884
$C = O_{PS}$	1660,118 - 1759,921	0,669022327575
Reference peak $_{PS}$ $(C - H)$	1484,138 - 1498,12	0,88290208178

Table 2. The peak intervals and the integration of the peaks for polystyrene after degradation.

Polystyrene after degradation	**Peak interval**	**Area under peak**
$-OH_{PS}$	3131,239 - 3746,566	6,314201126099
$C = O_{PS}$	1660,118 - 1759,921	0,4381883057535
Reference peak $_{PS}$ $(C - H)$	1484,138 - 1498,12	0,397668729

Table 3. The peak intervals and the integration of the peaks for polypropylene before degradation.

Polypropylene before degradation	**Peak interval**	**Area under peak**
$-OH_{PP}$	3008,776 - 3718,241	1,2969651324498
$C = O_{PP}$	1654,092 - 1849,96	0,61039387184905
Reference peak $_{PP}$ (CH_2)	2711,177 - 2735,525	0,181981016272

Table 4. The peak intervals and the integration of the peaks for polypropylene after degradation.

Polypropylene after degradation	**Peak interval**	**Area under peak**
$-OH_{PP}$	3008,776 - 3718,241	3,572790282585
$C = O_{PP}$	1654,092 - 1849,96	0,4415087712613
Reference peak $_{PP}$ (CH_2)	2711,177 - 2735,525	0,200355695722