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作品名稱 **A New Method For Microplastic Removal and Optical Measurement**

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關鍵詞 **Carbon nanotubes, Microplastics, Rayleigh Scattering**

作者照片

SUMMARY

Microplastics, tiny invisible plastic pieces are piling up in the marine environment emerging as one of the many environmental issues that our planet is facing today. Researches for the removal of these particles are important because studies that have been made so far haven't come up with an effective solution. Due to the COVID pandemic, the ban legislation on single-use plastics in many states is now removed therefore the amount of plastic in the environment is increasing rapidly. Carbon nanotubes are physically and chemically stable, CNT’s got a high surface area thus having great potential for wastewater treatment. When synthesizing magnetic nanoparticles with CNTs, we had got an adsorbent material that is easy to remove from an aqueous environment via a magnet. The working principle of a spectrometer is the dimerization of the incident light when it passed through or is reflected from the sample. Rayleigh scattering is the case where the center of the scattering is much smaller than the wavelength of the light. This project aimed to detect microplastics and remove them from aqueous environments with an effective and practical method then it was aimed to determine the removal amount of microplastics by optical measurements with the developed system. Firstly, the magnetic carbon nanotubes (M-CNT) which are intended to hold onto the surfaces of microplastics was synthesized and added to the mixture of microplastics. Then the magnet within a glass tube was passed through the mixture and the environment was cleared of microplastics. A spectrometer was made to monitor this process and after its calibration, it was used to measure coffees with different concentrations. It has been shown that their concentrations can be determined by calculating the transmission values and Rayleigh scattering. In the end, it has shown that there are no micro or nano-sized plastic particles when removed with M-CNT, within the accountable range of the spectrometer that had been made. Hence the removal of the microplastics: an invisible threat for the environment has been studied by combining nanomaterials with unique surface properties in the removal process and an optical principle such as Rayleigh scattering, a new technique has been developed that can measure quickly, economically, and precisely.

1 AIM

Plastic materials are produced and used in very large quantities due to their advantages like being affordable, durable, and feasible to different applications for many sectors. This situation brings along a big environmental problem. If plastic parts are smaller than 5mm, they are called microplastic. Microplastics can be created from the breakdown of bigger plastic materials or they can be created at micro-sized in the first place to be used at cosmetics detergents etc. (Thompson et. al.,2004 (Yurtsever, 2015). As Microplastics contaminated the ecosystem they had got into the food chain and climbed as up to our plates. Microplastics, which are found on all continents, including the Arctic and Antarctica (Barnes et al., 2009; Bergmann et al., 2015), are accepted as a global environmental issue. Researches for the removal of these particles are important because studies that have been made so far haven't come up with an effective solution. In the project, it is aimed to synthesize an effective material for the removal of microplastics from environmental water sources and to develop an optical-based measurement system suitable for microplastic measurements to monitor the microplastics removal process.

The spectrometer is made for the measurements of Rayleigh scattering by using the transmission values of light.To remove different types of microplastics with these (m-CNTs) it is aimed to synthesize carbon nanotubes with Fe3O4 to form m-CNT that can adsorb microplastics due to their surface properties with nano dimensions, and that can be removed from the environment via a magnet.

2 INTRODUCTION

Figure 2.1 A) Microbeads (Oosthoek, 2020) B) Microplastics in marine environment (National Geographic Society, 2019; Breese, 2018).

Plastics, which are widely used in our daily life, are polymeric materials that provide advantages such as being lightweight, flexible, easily processible, corrosion-resistant, good electric and heat insulator, easy-to-use, and economic. Plastics which are a technological material should be used cautiously and their excessive use should be prevented. Its consumption which had been 7 million tons in total in the 1960s, became approximately 330 million tons in 2015 and it is forecasted that this consumption amount will reach 540 million tons in the 2020s (Marketing, 2012). We can classify plastic wastes into two groups such as production wastes and consumption wastes. Single plastic material can be broken down and turn into millions of microplastic particles. These particles are categorized into three main groups as nano plastics (smaller than one micrometer), microplastics (approximately <5 mm), and mesoplastics (approximately >5 mm) according to their sizes (Isobe et al., 2014). The number of plastics in the ocean offshores nowadays has been calculated around 5.25 trillion pieces and 92% of these plastics are below 5 mm (Eriksen et al., 2014). Colorless and transparent plastics or microplastics found in water resources can turn into a serious hazard as invisible garbage (Hidalgo et al., 2012). The need for disposable masks, gloves, and disinfectant bottles which has increased with the COVID-19 pandemic, exacerbates the existing plastic problem and thus, affects the environment. The prohibitions for the use of plastics such as disposable forks, knives, straws, bags, and other plastic materials in many countries cannot be applied due to pandemics. The plastic materials used have reached the seas in the pandemic. While the degradation of a disposable mask in the sea ecosystem takes an average of 450 years like all plastic types, it will never decompose, but turn into microplastics (Ak, 2020). Although it is possible to easily recognize and classify the wastes in sizes that we can see around us, microplastics can only be characterized with the help of a microscope and devices such as Fourier Transform Infrared Spectroscopy (FT-IR) (Yurtsever, 2015).

2.1 Light Spectrum

Light is electromagnetic radiation consisting of different wavelengths. The electromagnetic spectrum is obtained by sorting electromagnetic waves by their frequencies and wavelengths. Throughout the electromagnetic spectrum, we can perceive the visible light, which is only a small section of this radiation, with our eyes. If the full spectrum of white light passes through a prism, rays in different wavelengths are refracted at different angles and they create the visible light spectrum (Baker, 2009). Wavelength is the distance between two peak points of the wave. The number of oscillations per unit of time is called frequency. Violet color light has the shortest wavelength with 380 nanometers while red color light has the longest wavelength with approximately 700 nanometers (Ocak, 2012).

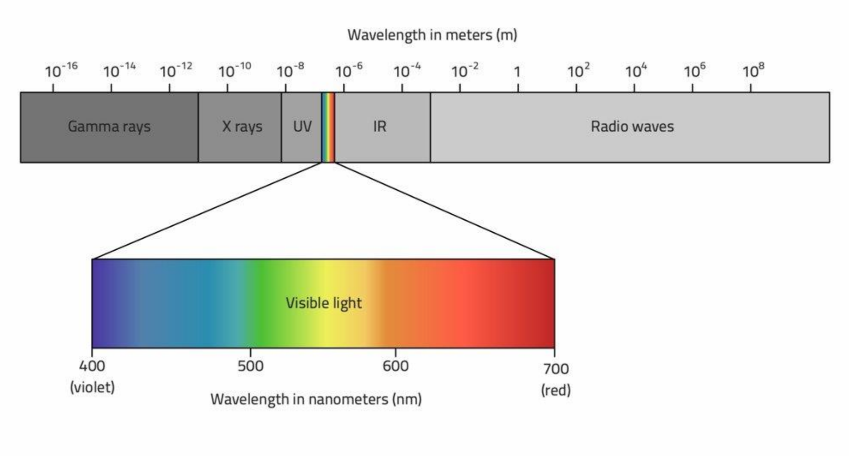

Figure 2.2 Electromagnetic spectrum (Aksoy, 2016).

2.1.1 Interference and Diffraction of Light

When two or more waves overlap and result in a new wave, this is called interference. The principle of superposition underlies the phenomenon of destructing or reinforcing each other when the waves come to the same point at the same time (Ozansoy, 2008). As a result of the interference, a new wave having new electric and magnetic field vectors is created. When the peak and trough points of waves overlap, constructive interference occurs, and a wave of greater amplitude is formed. When the peak point of a wave coincides with the trough point of the other wave, destructive interference occurs, and the intensity of the resulting wave shall be smaller than each wave or zero (Çıldıroğlu, 2010). According to the diffraction principle, only the waves in certain wavelengths in a certain direction will be protected and the rest will be destroyed as they interact with each other. The diffraction pattern created by a particular slit can be determined using the Huygen principle.

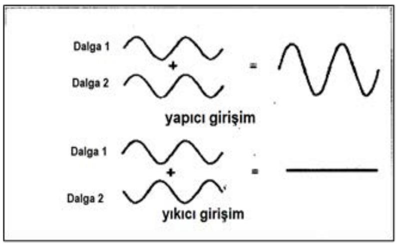

Figure.2.3 Constructive and destructive interference(Korkmaz, 2013)

2.1.2 Diffraction Grating

When the light is shined on a diffraction grating, each of the scratches represents a source and the light will not only pass straight but also exists in an intense beam depending on the range of scratches (Feynman, 1963). To find the slit width, the length of the diffraction grating is divided by the number of slits in that region. There are at least 6000-18000 lines per centimeter of the gratings used in the visible and

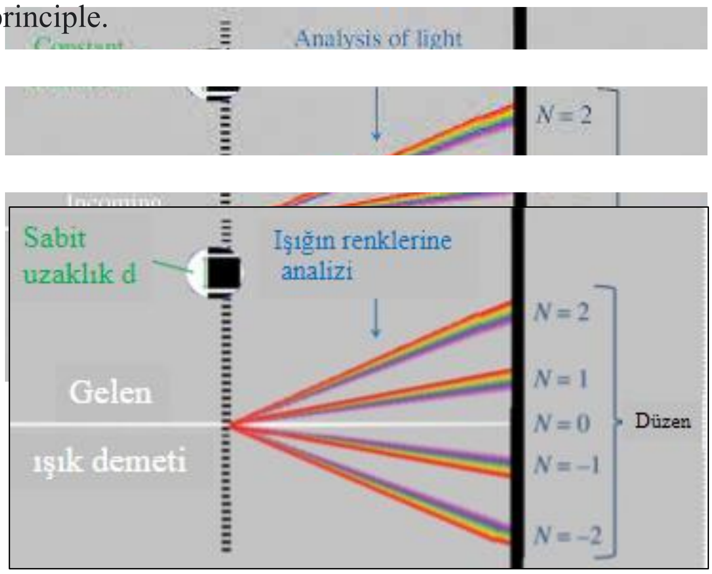

Figure.2.4 The working principle of diffraction grating, N and incident lights density is inversely proportional.

ultraviolet regions of the spectrum. The number of lines in the gratings used in the infrared region per centimeter is within the range of 700-3000.
The distance d between spaces is generally between 400 and 800 nm. For the vertical effect of the incident ray and N = 1, the violet light is directed at an angle of -24 ° and the red light at an angle of -45 °. In other words, the red light is more refracted than the violet light (Mavroukakis et al., 2019). While there is a certain ‘’d’’ space between the scratches of a diffraction grating (Figure 2.4), the ‘’constructive interference’’ will occur if there is a certain set of angles where the light progressing by refracting from each scratched surface will be in the same phase with the light refracted from any other scratched surface (Türker, 2013). DVD behaves like a diffraction grating. Transparent grooves with 1350 lines per mm, which are separate from the other layers of the disc (Figure 2.5.B), add a diffraction grating feature to the DVD.
Diffraction gratings are layers such as plane glass, etc., on which light can pass and have a large number of evenly spaced slits parallel to each other. Diffraction gratings are used to separate spectrum lines.

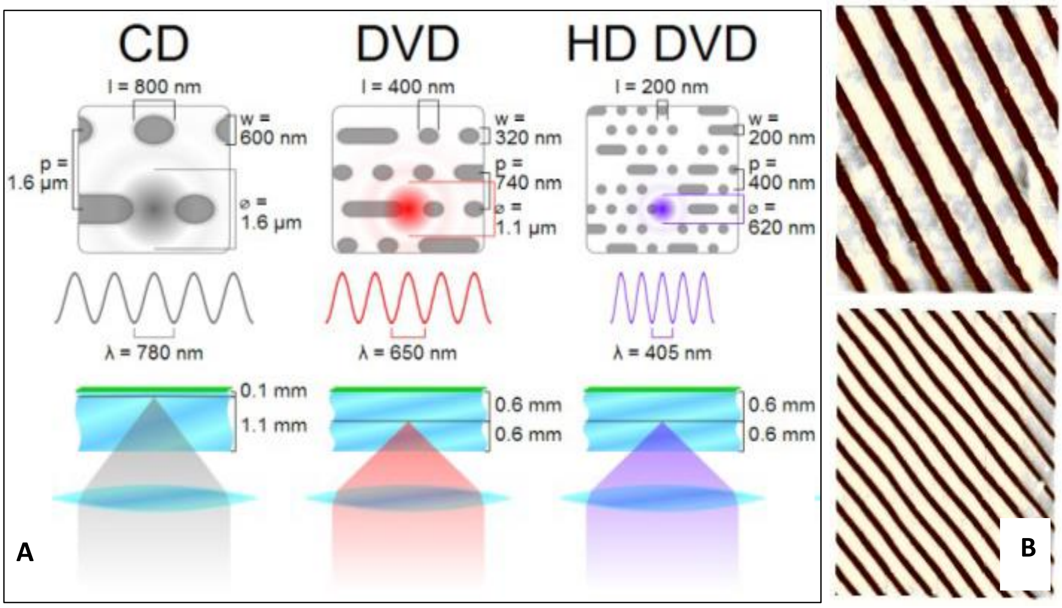

Figure.2.5a)Comparison of diffraction grating, b) Gratings on the DVDs surface (Theremino, 2014).

2.1.3 Rayleigh Scattering

Scattering is caused by variations of the refractive index of the medium on a length scale smaller than the wavelength of the light. This could be caused by the presence of impurities, defects, or inhomogeneities. Scattering causes attenuation of a light beam in an analogous way to absorption. The intensity decreases exponentially as it propagates into the medium according to:

$$\boldsymbol{I(z) = I_0 \exp(-N\sigma_s z)} \quad \textbf{(1)}$$

where N is the number of scattering centers per unit volume, and as is the scattering cross-section of the scattering center. This is identical in form to Beer's law :

$$\boldsymbol{\alpha = N\sigma} \quad \textbf{(2)}$$

The scattering is described as Rayleigh scattering if the size of the scattering center is very much smaller than the wavelength of the light. In this case, the scattering cross-section will vary with the wavelength according to:

$$\sigma_s(\lambda) \propto \frac{1}{\lambda^4} \quad \textbf{(3)}$$

The Rayleigh scattering law implies that inhomogeneous materials tend to scatter short wavelengths more strongly than longer wavelengths. (Fox,2001).

2.1.4 MIE Scattering

Light scattering arising from objects larger than the wavelength of the light is called Mie Scattering. Mie Scattering is distinct when the size of the particles is slightly higher than the wavelength of electromagnetic radiation.

Mie scattering is the direct application of Maxwell's equations to an isotropic, homogeneous, and dielectric sphere. Mie theory is a general theory for any radius, radiation of all wavelengths, and spherical particles (Seyhun, 2012).

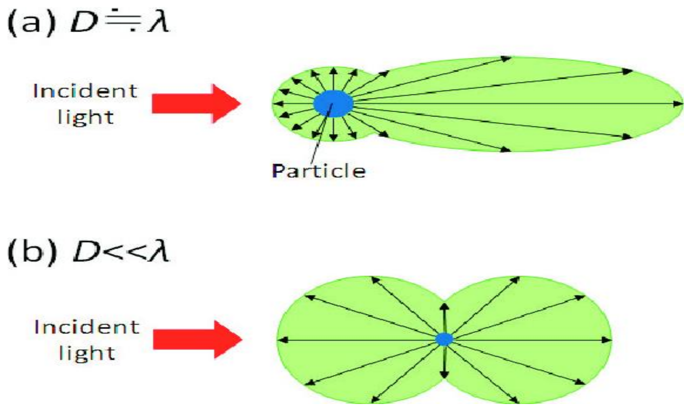

Figure.2.6 A) Mie Scattering B) Rayleigh Scattering (Mclidden,1999).

Maxwell's equations are solved by separating the variables in spherical coordinates. The incoming plane wave is expanded in Legendre polynomials so that solutions inside and outside the sphere can be paired at frontier (Mcliden, 1999).

2.2 Absorption of Light

Light can be absorbed by atoms, ions, and molecules. The absorption of radiant energy by a substance is explained by the particle feature of the radiation, that is to say, photons (Altınışık, 2004). This energy conveys electrons from low-energy orbitals (ground state) to high-energy orbitals. Electromagnetic radiation absorbed during its transition from one energy level to another is measured by Spectrophotometry (UV-Visible, IR, X-ray), Colorimetry, Atomic Absorption Spectroscopy, NMR Spectroscopy, ESR (Electron Spin Resonance) Spectroscopy (Spectral Methods, t.y.). This measurement is taken by measuring the difference between the intensity (I0) of the light sent on the atom, ion, or molecule and the intensity (I) of the transmitted light. The colors perceived by the human eye are reflected light that is not absorbed by objects (Ocak, 2018).

2.2.1 Beer-Lambert's Law

According to the Beer-Lambert law, the concentration in the sample can be determined by looking at the absorbance values. The absorbance of the solution increases with the increase of the light intensity.

$A = \varepsilon\, b\, c$ (4)

Beer-Lambert law in optics refers to the absorption of light as a result of its interaction with the material. Beer-Lambert law: The amount of light passing through a solution is inversely proportional to the distance covered by the light in the solution and the solution concentration logarithmically, and the amount of light absorbed is directly proportional.

Lambert's law: The intensity of the beam passing through a homogeneous absorbing medium decreases exponentially with the increase of layer thickness:

$$I = I_0 \times e^{-kd} \quad (5)$$

I = intensity of the passing beam I0 = intensity of the incident beam k = absorption coefficient d = thickness of the layer.

Beer's law: The intensity of the beam depends on the concentration of the substance it passes through:

$$I = I_0 \times e^{-kc} \quad (6)$$

I = intensity of the passing beam I0 = intensity of the incident beam k = absorption coefficient c = concentration.
The permeability (T) of the solution is the ratio of the intensity of the passing beam (I) to the intensity of the incident beam (Io).

$$T = \frac{I}{I_o} \quad (7)$$

However, more commonly permeability is expressed as a percentage:

$$T(\%) = 100\frac{I}{I_0}$$

$$A = \log_{10}\frac{I_0}{I}$$

$$A = -\log_{10} T$$

2.3 Spectrophotometer

The process of measuring the amount of substance in the solution by using the amount of light that passes through the solution or the amount of light shined by the solution is called photometry while the devices used in the measurement is called photometer. The spectrophotometer is a device that separates and sends a part of the light beam on the sample to be analyzed by using filters, and they can make this selection through slits (Spectrophotometer, 2012).

2.4 Microplastics

The first completely synthetic plastic ''Bakelite'' $(C_6H_6O.CH_2O)_x$ was created by Leo Baekeland in 1907. The invention of bakelite gave way to the development of new plastics that are still produced today, such as polystyrene, polyester, PVC, polyethylene, and nylon. The fact that plastics are durable light-weight and flexible has led them to be preferred in the production of many products, and the fact that they are cost-effective has led them to be preferred especially in disposable products.
Despite the production of 381 million tons of plastic waste annually, recycling only 9% of the disposable plastics gives rise to environmental pollution. (Great Britain's Royal Statistical Society, 2018). Depending on the type of plastic and where it drops, it can take days or even hundreds of years for wares to break down into very small pieces, and even after that, the plastic is likely not biodegradable.

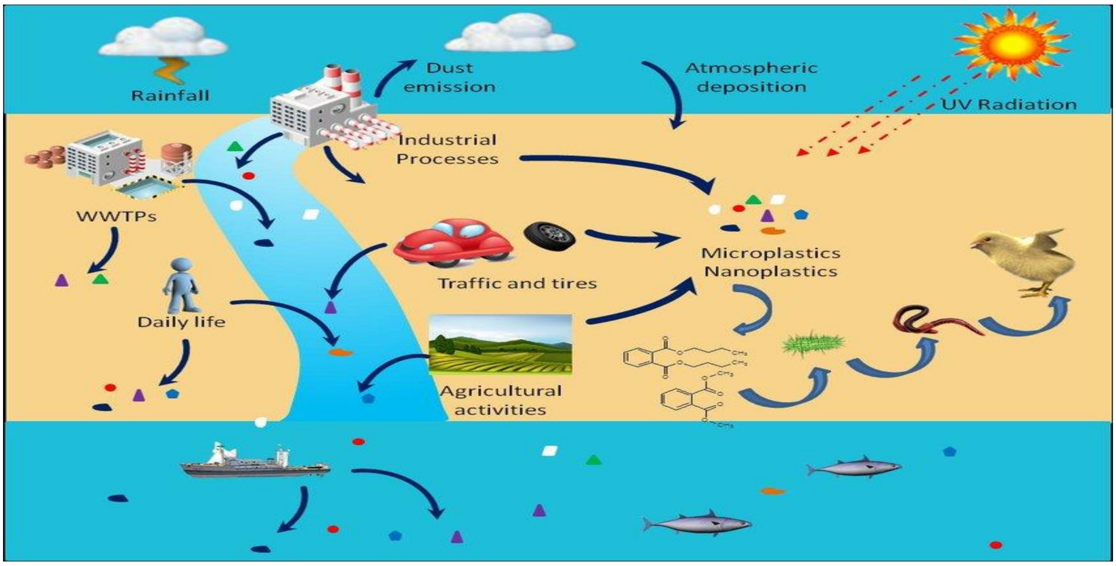

Figure.2.7 Microplastic sources and how they get into the environment (Schnug, 2020).

Plastic waste entering the environment becomes fragile and breaks down into small pieces by winds, waves, and photodegradation effects. Plastic parts smaller than 5 mm that pollute the environment are called ‘’microplastics’’ (Thompson et al., 2009). Microplastics that are formed in this way with the effect of the medium are called ‘’secondary microplastics’’. Microplastics can be specially produced in small sizes and these microplastics are called primary microplastics. Microplastics are smaller than two millimeters and they are made of polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), or nylon. In general, they are used in self-care and beauty products and they represent some of the most common examples found in natural ecosystems. These products create approximately 100.000 microplastics in their single-use (Condor Ferries, 2020). Microplastics can enter sea environments in different ways (Figure 2.8). Synthetic textiles, which form 35% of the microplastics found in the ocean with the highest rate, can produce a synthetic piece up to 1900 fibers by washing a single piece of clothing (Browne et al., 2011). The reason for this is the mechanical and chemical stresses to which the fabrics are exposed during the washing process in the washing machine. Your installation conveys the water that you spend from your washing machine to a wastewater treatment plant. These fibers which are too small for the facility to filter, are discharged with treated wastewater and eventually, conveyed to the oceans.

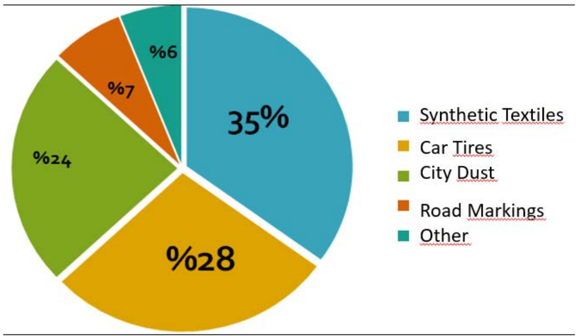

Figure.2.8 Microplastic types in the marine environment (Armstrong, 2019).

In a monthly sampling study conducted on our Mediterranean coasts in 2016, it was reported that more than half of the 1137 fishes in total from 28 species had microplastic particles in their digestive system. It has been observed that the type of particles found in the digestive systems of these fishes at the most is the textile fiber, which is thought to come from particle-type washing machines found (Guven et al., 2017).

These small-sized plastics in the aqueous environment are swallowed by living creatures in the ecosystem and accumulate in the tissues and organs of organisms that do not have enzymes to digest synthetic polymer (Wang et al., 2019). These plastic parts in nature can also affect human health. In addition to the additives used in the production phase of plastics, toxic chemicals that are absorbed from nature accumulate and increase as climb up the food chain (Boddy, 2017).

2.5 Carbon Nanotubes (CNT)

The element carbon has two natural allotropes in nature and these are diamond and graphite. Both forms display unique physical characteristics in terms of hardness, heat conductivity, lubricating behavior, or electrical conductivity. The discovery of fullerene in 1985 made a breakthrough in synthetic carbon allotropes. Then, the discovery of carbon nanotubes by the Japanese physicist Sumio Iijima in 1991 and the discovery of graphene in 2004 was made (Hirsch, 2010). A cylindrical rolled-up state of graphene is called a nanotube. The diameter of a carbon nanotube is specified in the nanometer value, and it is also known that the diameter of a nanotube exceeds 1 micrometer. This proper structure of carbon nanotubes can have a great impact on semiconductor physics due to the very small and excellent and unusual electronic characteristics of the carbon atom (Yetim, 2012). These 1-dimensional materials, which are structurally included in the zero-dimensional fullerene family, have proper geometric, electronic, mechanical, and optical characteristics that enable them to be suitable for many applications. It has properties such as high tensile strength, flexibility, good heat conductivity, large surface area, low heat expansion coefficient. There are two types of carbon nanotubes as single-walled and multi-walled (Liew et al., 2014).

2.5.1 Single-Layer Carbon Nanotubes

Single-layer carbon nanotubes (SWCNTs) are structures that are formed by rolling the graphene sheet structuring at an atomic thickness and may have a diameter of 1 nm nanometer and a length in the range of 1-100 microns (Yetim, 2012, Liew et al., 2014). Single-layer carbon nanotubes can exist in three forms. These are the armchair, chiral, and zigzag-shaped, and this property is related to how graphene turns into a cylinder (Scoville, 2008). For single-walled nanotubes, each atom is on two surfaces, inside and outside the nanotube. When this feature is combined with the ability to attach any chemical type to its sidewalls, this provides an opportunity for unique catalyst supports. The electrical conductivity of carbon nanotubes can also be used in the search for new catalysts and catalytic behavior (Foley, 2006).

2.5.2 Multi-Layer Nanotubes

Multi-layer carbon nanotubes (MWCNTs) are formed from tubular graphene surfaces that share the same center and cover each other (Liew et al., 2014). Multi-layer nanotubes are structurally classified into two groups. In the 'Russian Doll' model, a carbon nanotube contains one more carbon nanotube in a carbon nanotube (the diameter of the inner nanotube is smaller than the outer nanotube). In the 'parchment' model, a graphene layer is wrapped around itself more than one. Multi-layer nanotubes have many properties similar to single-layer nanotubes, but in multi-layer nanotubes, outer nanotubes protect the inner nanotubes against chemical reactions that may occur due to external materials. Besides, the tensile strength of multilayer nanotubes is higher than that of single-walled nanotubes (Scoville, 2008).

The large surface area and high absorbency of CNTs make them ideal candidates for use in air, gas, and water filtration. Researchers and companies are conducting studies on carbon nanotube-based air and water filtration devices. These filters have been reported to kill bacteria as well as block small pieces (Foley, 2006).

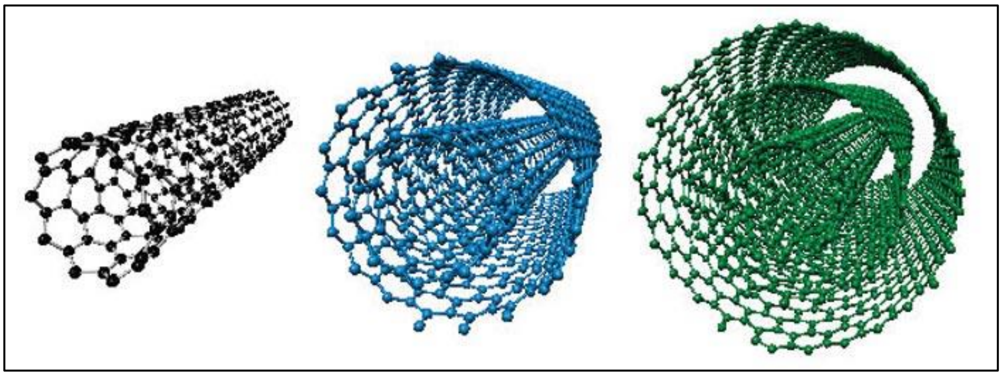

Figure.2.9 Carbon nanotubes single, double and three-walled. (Dumé, 2013).

2.5.3 Magnetic Carbon Nanotubes and Their Use in the Removal of Environmental Pollutants

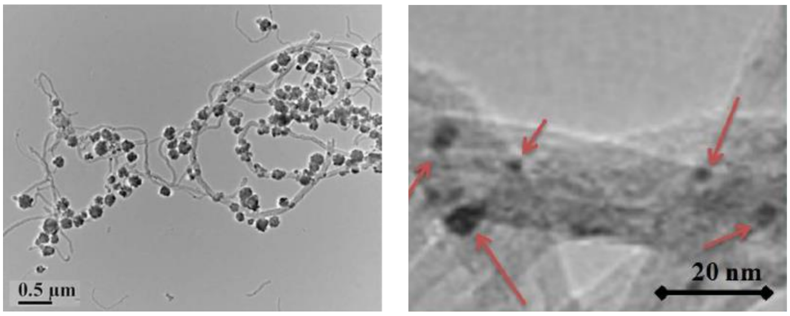

Figure 2.10. Image of synthesized material of CNT and Fe_3O_4 NP's at electron microscope (TEM) (Saber-Samandari vd., 2016; Sadegh vd., 2018).

Due to their characteristics such as having high specific surface area, porous structure, surface properties, high chemical stability even in acidic, basic, and high salt concentrations or environments with high temperatures, CNTs have a great potential in cleaning wastewater. Besides, they provide advantages with their mechanical properties such as high elasticity coefficient and tensile strength (Kim et al., 2010; Yin et al., 2019). In the classical methods used to remove waste from aqueous environments, removing the adsorbent from the media is a difficult stage and in general, time-consuming methods such as filtration or centrifugation are used. Also, filter clogging and adsorbent losses may occur in the filtration method. For all these reasons, magnetic separation processes are more advantageous than conventional methods as it is conducted in a shorter time with low cost and in an easy way. Magnetic nanoparticles (NP) such as Fe_3O_4 can be easily separated from the medium when a magnetic field is applied to the adsorption medium. Adsorbent materials formed by combining magnetic NP and CNTs can also be used effectively in removing organic and inorganic environmental wastes from aqueous environments (Saber-Samandari et al., 2016; Sadegh et al., 2018; Samadishadlou et al., 2017). Some examples of electron microscope images of such nanomaterials are given in Figure 2.10.

3. MATERIAL AND METHOD

3.1 MATERIALS AND DEVICES USED

Materials used to complete our experiments in the project: cool white LED, 9V battery, plastic tub 1x1cm, 3D printer (Ender brand), laser removed from a laser, DVD, USB camera, paper sandpaper, plastic materials (Pet bottles, plastic covers), filter paper, carbon nanotubes (short COOH functional multi-walled carbon nanotubes Nanograph, Turkey), Fe_3O_4, magnet, Lego parts, high-intensity discharge sodium lamp.

DVD: To prepare the diffraction grating, the disc was divided into two and the aluminum covering was removed with the help of tape. A piece was cut from the desired half and placed in front of the camera.
Web Camera: A camera with a USB port capable of shooting 1080p was used.
Theremino program: The software calculates the intensity of the light striking each pixel and in this way, it can measure the amount of radiation for each color.
Spectrometer (Ocean USB-400 model), Assay balance (Denver Instrument, SI-234A), Ultrasonic bath (Hydro brand).

3.2 Method

3.2.1 Constructing and Calibrating the Spectrometer

To construct the spectrometer firstly, using the Tinkercad software a box is designed and printed 3D, in which the optical parts of the instrument were placed. The box was printed black to prevent light reflections within the box and it is rectangular shaped, with a length of 20 cm and a width of 8 cm. A thin 1 mm slit was open to one of the small faces. The slit allows only a parallel beam of light to enter through wide. Inside the box, a camera with diffraction grating glued in front of it is placed.At the other side of the slit, the incoming light is firstly gathered by a lens and then passed through the sample. (figure)

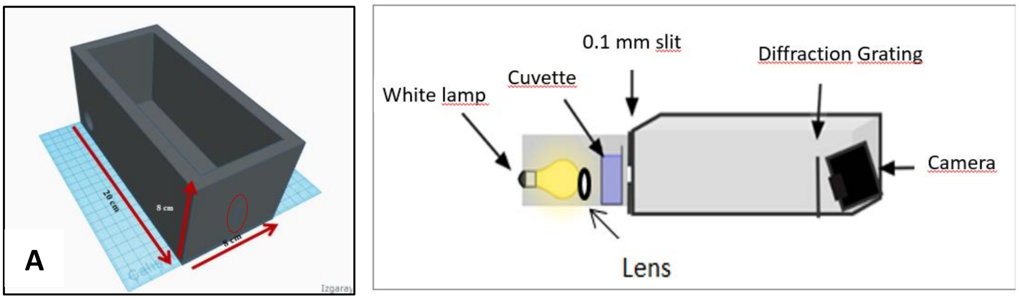

Figure.3.1 a) The 3D design of the spectrometer that has been made with TınkerCad, b) Schematic representation of the spectrometer(Original).

After designing the spectrometer, it is necessary to establish the relationship between the wavelengths falling on the camera pixels and the pixels. Determining which wavelength falls on which pixel is important for calibration. Therefore, the spectrometer was calibrated using a sodium lamp connected with an electronic ballast. The sodium line D is known to be around 589 nm. Based on this information, the spectrometer wavelength range was determined.
Following the calibration with the sodium lamp, the sample spectrum of the white LED was taken with the industrial ocean USB-400 model spectrometer to control the accuracy of the spectrum of the white LED light source used in the spectrometer and it was compared with the spectrometer done.

3.2.2 Taking Measurements from Different Samples with the Spectrometer

Optical transmittance measurements of different samples were taken to test the spectrometer designed. In these measurements, the percentage of optical transmittance was calculated with the equation (I/Io* 100).
Io refers to the light intensity measurements taken while there is water in the bathtub and I refers to the light intensity measurements taken while there is a sample in the bathtub.
First, measurements were taken by diluting yellow, blue, and red food dyes.
To demonstrate that the spectrometer that we obtained after color measurements can be also measured using Rayleigh scattering, coffee particles dispersed in water were used. In this manner, the existence of very small scatterers in the wavelength range (400-700 nm) in the

liquid can be detected. For this, 0.05-0.1-0.15-0.2-0.3 gram coffee weighed in the balance was prepared by mixing with 40 mL of water, and its transmission values were measured in the spectrometer. Equation 1 and Equation 2 were used to calculate Rayleigh scattering. In Equation 1, it is specified that the light intensity will decrease in proportion to the number of scatterers, and the ratio of the scattering cross-section to the wavelength is given in Equation 2. When we combine these two equations, we can obtain with Equation 10 that the light intensity depends on the wavelength.

$$I=I_0\exp(-kN\,(1/\lambda^4)\,l) = I_0\exp(-c\,(1/\lambda^4)) \qquad (10)$$

In this equation, the number (N) of scattering centers per unit volume, scatterer dimensions, length of the bathtub (l) and the function of parameters related to the light will a coefficient. In the coffee sample, the number of N and therefore, the c value is expected to increase depending on the coffee concentration.

3.2.3 Magnetic Carbon Nanotube (m-CNT) Synthesis

Fe_3O_4 nanoparticles (Fe_3O_4 NP) displaying ferromagnetic property were used in the preparation of magnetic featured carbon nanotubes (m-CNT) and COOH-functional tip, short and multi-walled CNTs (CNT-COOH) were used as CNT. Magnetic nanoparticles (50 mg) and CNT-COOH (200 mg) were dispersed in a mixture of 40 mL deionized water and ethanol (1:1, volume ratio). The mixture was ultrasonicated for 1 hour and stirred at room temperature for 96 hours. A 200 nm filter membrane was used to remove the solution from the solid precipitate and dried in a vacuum at 50°C for 16 hours (Sadegh et al., 2014; Sadegh et al., 2018). m-CNT preparation steps are given in Figure 3.2.

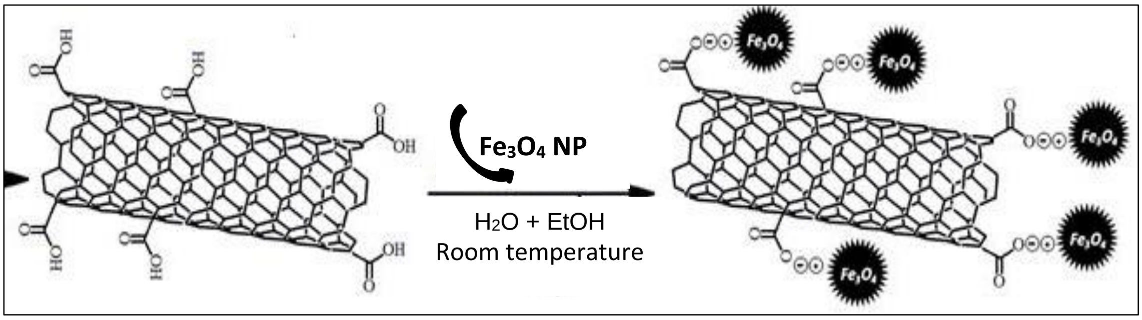

Figure.3.2 m-CNT 's synthesis reaction (Sadegh vd., 2014; Sadegh vd., 2018).

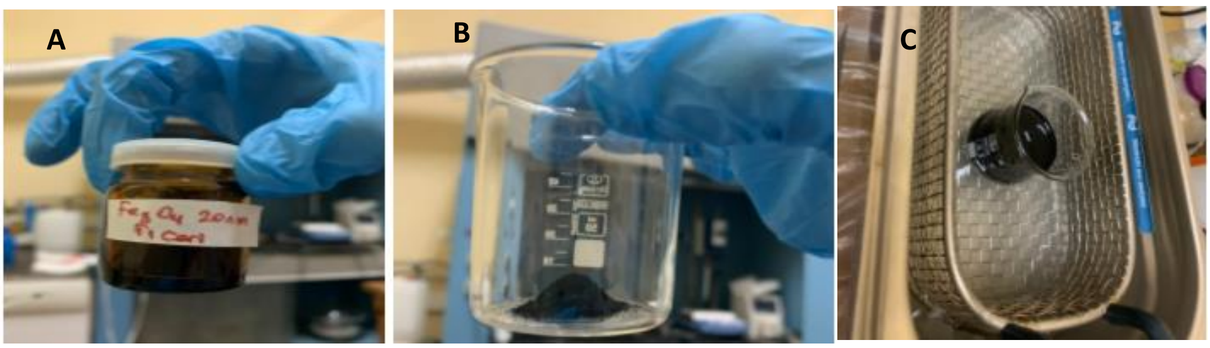

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Figure.3.3 a) Fe_3O_4 NP, b) 200 mg CNT-COOH c) CNT-COOH ve Fe_3O_4 NP in Ultrasonic bath

3.2.4 Obtaining Microplastics

Toothpaste and facial cleansing products containing primary type microplastics were used in the project. To separate the plastic microparticles from cosmetic products, the product was first dispersed in water and then, transferred into a syringe. Microplastics in the injector were

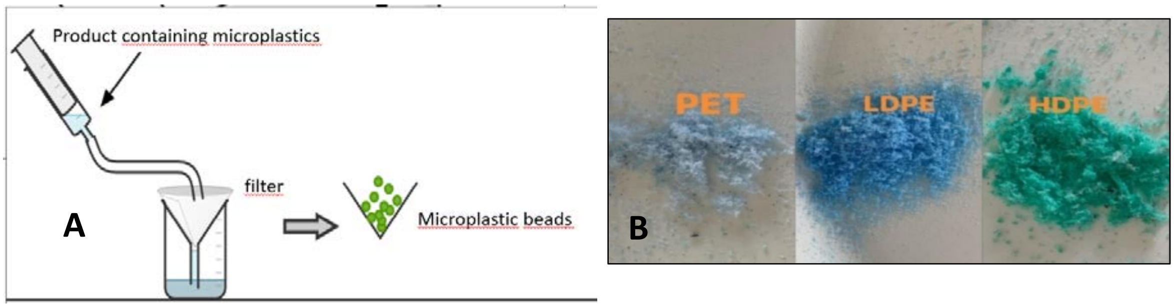

Figure. 3.4 a) The schema of how the microbeads obtained from cosmetics b) Different types of secondary microplastics obtained with sandpaper

obtained by filtering with the help of a filter paper (Figure 3.4.a). Secondary type microplastics were obtained by sanding disposable plastic covers containing PET, HDPE, and PP (Figure 3.4.b).

3.2.5. Removal of Microplastics with Magnetic Carbon Nanotubes

Aqueous mixtures were prepared with different amounts of microplastics obtained with the help of sandpaper. 1 g, 30 mg, and 20 mg microplastics, respectively were added to 150 mL, 75 mL, and 15 mL water in the beaker. The synthesized m-CNTs were added with microplastics to these mixtures containing microplastics in a one-for-one amount and the microplastics were removed by mixing with the help of a glass tube that contains a magnet inside it (Figure 3.5).

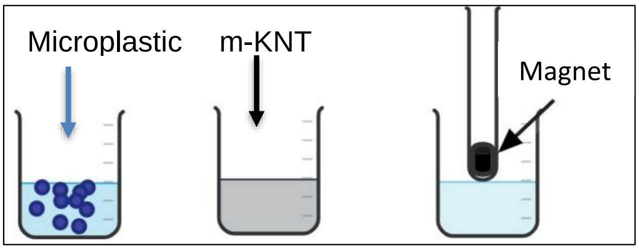

Figure.3.5 Schematic representation of m-CNT addition and magnetic removal from aqueous suspension containing microplastics.

3.3. Projects Time Chart

Work	Months				
	October	November	December	January	February
Literature Review	X	X	X	X	X
Preparation for Experimental Process via Online Meetings		X	X	X	X
Experimental Preparation			X	X	X
Collecting and Analyzing Datas			X	X	X
			X	X	X

4. RESULTS

4.1 Constructing and Calibrating the Spectrometer

After the main body was printed from the 3D printer, a connection between the spectrometer

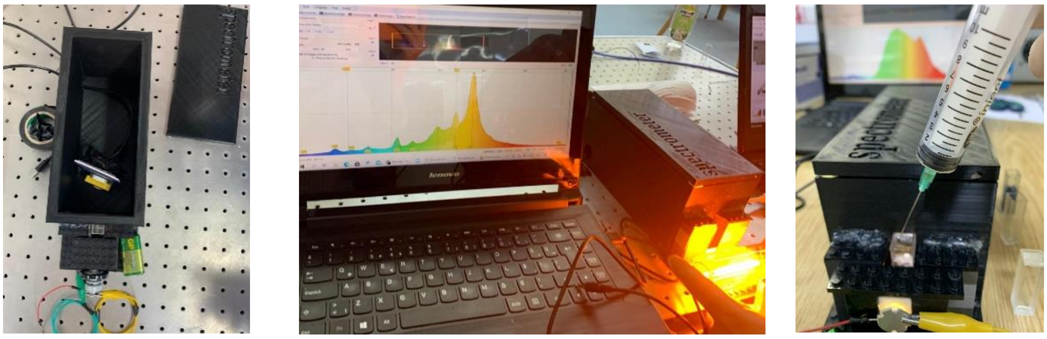

Figure 4.1 Constructing and connecting the spectrometer with the Theremino software (orijinal).

And Theremino software was established and measurements were initiated (Figure 4.1).

As seen in Figure 4.2.A, the peak points in the measurement of the spectrometer taken with the sodium lamp are at wavelengths of 589.0-589.6 nm. Thus, the theoretically expected value was obtained and our spectrometer was calibrated.

Then, the spectra obtained from the white LED light source in the industrial spectrometer and the spectrometer constructed in the project were compared. As can be seen in the chart given in Figure 4.2.B, these spectra were found to be compatible with each other. It is thought that the difference between the measurements may arise from the difference in light intensity sensitivity in the pixels of the webcam used or from the different structures of the diffraction gratings used. Web camera spectrometers have 720×1080 pixels and their sensitivity will be limited since each pixel have a value between 0-255. However, since the measurements depending on the wavelength and the changes in light intensity will be measured proportionally in the method we use, this spectrometer is sufficient for measuring the microplastic removal which is the goal of the project.

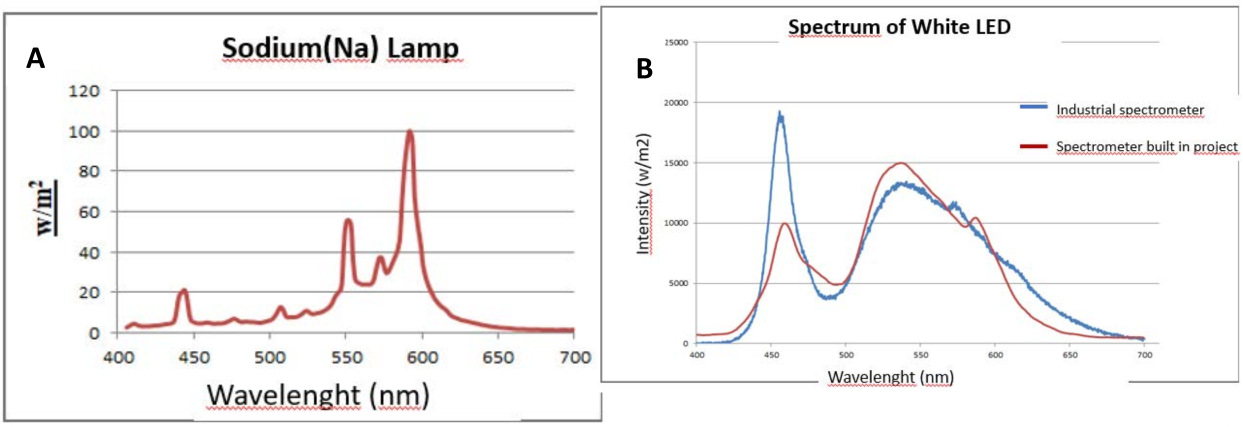

Figure.4.2 Spectrum of the sodium lamp, b)Comparison of the White LED s spectrum taken with an industrial spectrometer.

4.2 Taking Measurements from Different Samples with the Spectrometer

To pursue the operation of the spectrometer, the measurements were first taken with food dyes and compared with the literature. Measurements were taken by diluting yellow and blue food dyes. In these measurements given in Figure 4.3, it was observed that the optical transmittance for yellow color increased approximately above 500 nm while the optical transmittance decreased below 500 nm, and the same transmission curve was obtained in the literature. The spectrum which was taken from the blue color also displayed a behavior compatible with the literature (Figure 4.3). These measurements indicate that the spectrometer can also be used for color determination

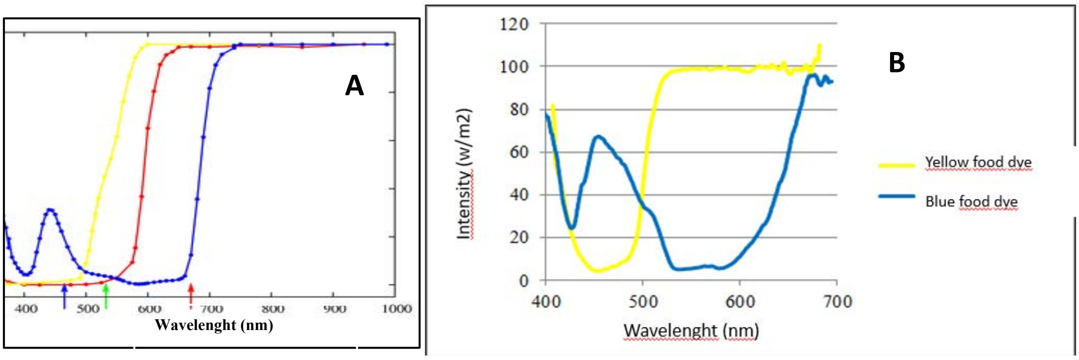

Figure.4.3 a) Spectrums of yellow blue and red food dyes. (Cleyet, 2005), b) Projede yapıl an spektrometrede farklı renklerdeki gıda boyalarının verdiği spektrumlar.

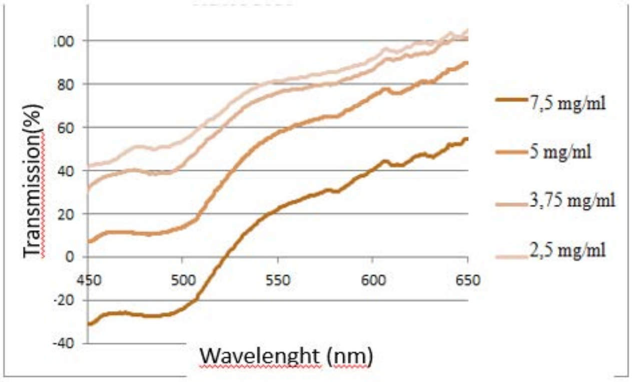

Figure 4.4 Transmission graph of coffees with different concentrations.

The transmitted light chart created from transmission measurements taken from coffee samples prepared in different concentrations is given in Figure 4.4. The results obtained indicated that the concentration was inversely proportional to the light transmitted through the sample, as expected. Rayleigh's calculation made using Equation 1 is given in Figure 4.5.

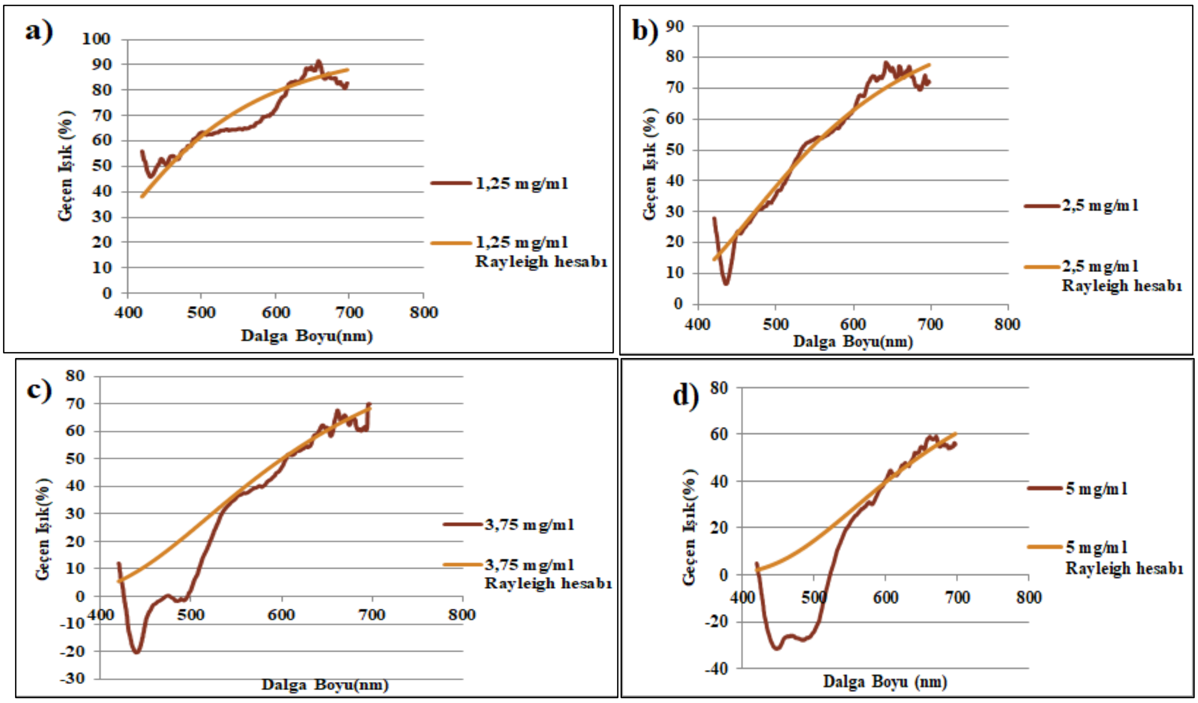

Figure.4.5 Transmission of light through different concantrations of coffee solutions and Rayleigh scattering calculations. a) 1,25 mg/mL b) 2,5 mg/mL c) 3,75 mg/mL d) 5 mg/mL

As can be seen in Figure 4.5 for coffee samples prepared at concentrations of 1.25, 2.5, 3.75, 5 mg/ml, the measurements taken with Rayleigh's calculation complies with a certain wavelength range. In the regions where the light intensity is very low, this concordance deteriorates. Therefore, the concordance in the regions with high light intensity has been taken into consideration. At the end of the experiments, it has been realized that the number of coffee particles dissolved in water can be used for Rayleigh scattering. The coffee concentration and the c coefficients shown in equation 10 are given in Table 4.1. As expected, the concentration and c coefficients were found to be proportional. This ratio was determined as 2.4x1010 (nm4xmL/mg).

Tablo 4.1. coefficient of c relative to the coffee concentraition

Coffee Concentration (mg/mL)	Coefficient of c	c / coffee concentration (nm^4xmL / mg)
1,25	$3x10^{10}$	$2,4x10^{10}$
2,5	$6x10^{10}$	$2,4x10^{10}$
3,75	$9x10^{10}$	$2,4x10^{10}$
5	$12x10^{10}$	$2,4x10^{10}$

According to the results, the amount of coffee added up to a concentration of 15 mg/mL (0.6 g coffee, 40 mL water) for a 1 cm bathtub can be determined with the spectrometer made. If the size of the bathtub is reduced, higher concentration values can be measured than this concentration.

4.3 Removal of Microplastics and Their Optical Measurements

Mixtures of obtained microplastics and m-CNTs in a beaker are given in Figure 4.6.A. 1g microplastic/150 mL water; microplastics first float on the surface in the media prepared as 30 mg microplastic/75 mL water and 20 mg microplastic/15 mL water. Then, when the medium interacted with a magnet, microplastics held onto the m-CNT surface and separated from the medium along with the mobilization of m-CNTs (Figure 4.6.B).

Figure.4.6 A)Steps of Magnetic Separation. B) The picture of accumulated microplastics on the magnet after the magnetic separation from the water.

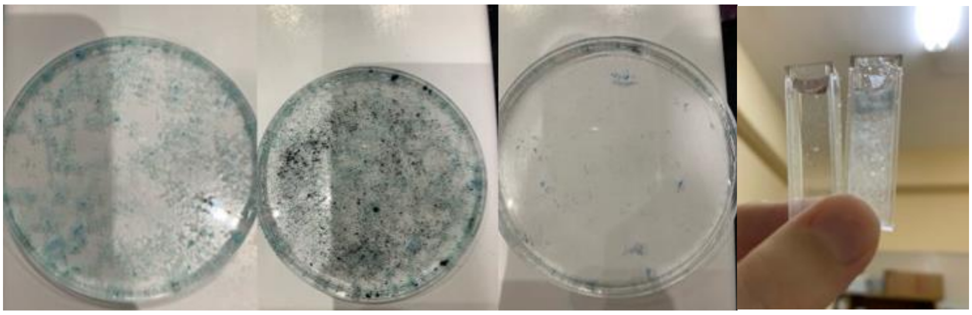

Figure.4.7 A) The sample containing HDPE microplastics B) Suspension where m-CNT is added. C) Sample after the microplastics are removed D) Cuvettes with samples before and after the microplastic removal.

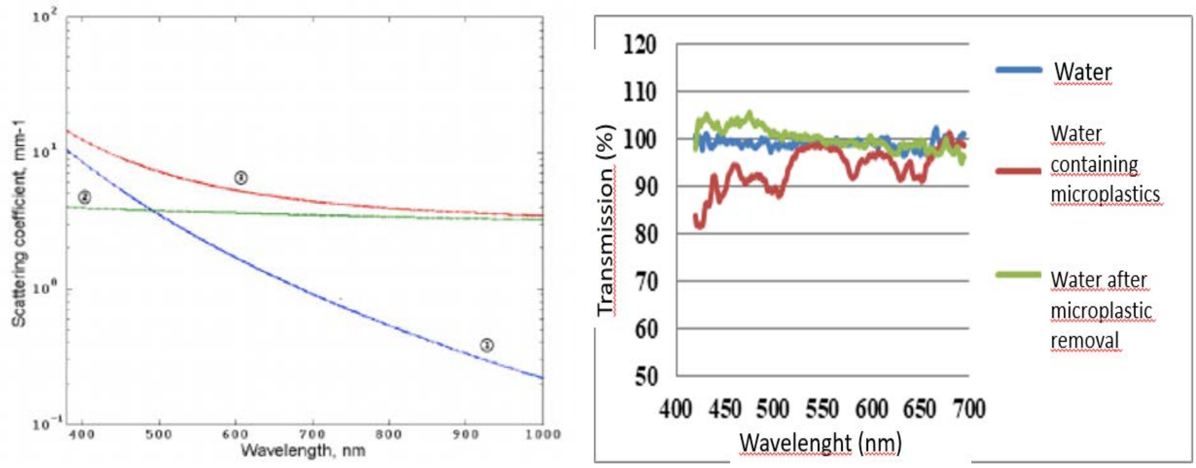

Figure.4.8 A)Rayleigh scattering (1),Mie scattering (2),Combination of Mie and Rayleigh scattering equations (3) (Petrov,2012). B) Transmission display chart where before and after plastics were removed from water.

As shown in Figure 4.8 A, the wavelength-dependent change in Mie scattering is very small, and thereby, we can expect to see the same reduction in wavelengths in the entire spectrum in scattering with wavelengths or greater. However, it can be expected that the scattering will

decrease and the optical transmission will increase as the wavelength increases in Rayleigh scattering. Therefore, there will be a slope in the transmission curve depending on the wavelength. Since the scattering coefficient decreases at high wavelengths (Figure 4.8 A (1)), the transmission will increase. In the combination of Mie and Rayleigh scatterings, a reduction in transmission value at all wavelengths as well as an increase in transmission depending on wavelength are observed. In the measurement taken as shown in Figure 4.8.B, the fact that the transmission is less at low wavelengths and higher at high wavelengths in the plastic-containing liquid demonstrates that the liquid contains micro and nano-sized plastic parts.
When Figure 4.8 B is interpreted, it can be thought that if the entire spectrum is decreasing in the transmission chart, the particle sizes will be at the level of micrometers or above, but if a curved optical transition is observed, there will be nano-sized microparticles. For this reason, Rayleigh scattering has been examined in detail. The measurements, which were taken after the microplastics were removed from the aqueous environment indicate that there are no micro or nano-sized particles in the range of values that the spectrometer can measure

5 CONCLUSION AND DISCUSSION

In The m-CNT material intended to hold on to the surfaces of microplastics was synthesized and added to the solution containing microplastics and then, the microplastics were cleaned by gently sweeping a strong magnet placed in the glass tube in the aqueous environment. A spectrometer that can measure quickly, economically, and precisely was constructed to measure whether or not the water sample was free of microplastics was built and then, it was calibrated. In addition to calculating Beer-Lambert's law with the spectrometer, scattering of light by small particles in the solution was calculated with Rayleigh scattering in the project.

In the project, it has been demonstrated that the spectrometer made in consequence of the measurements taken with different colors of food dyes can be used to determine color in liquid samples. Besides, the measurement of coffee solutions taken in different amounts demonstrated that the dimensions of the dissolved coffee particles were smaller than the micrometer size and the coffee concentrations can be determined by calculating the transmission values and Rayleigh scattering. It has been observed that measurement up to 10 mg/mL concentration can be taken in a 1 cm bathtub. As the light intensity will decrease substantially after this value, the measurement results are inconsistent. In Mie scattering, the variation depending on the wavelength is very small, so we can expect to see the same degree of reduction in wavelengths across the entire spectrum in scattering with wavelengths or greater. However, it can be expected that the scattering will decrease and the optical transmission will increase as the wavelength increases in Rayleigh scattering. Therefore, there will be a slope in the transmission curve depending on the wavelength. Thus, it can be thought that if the entire spectrum decreases in the transmission chart, the particle sizes will be at the level of micrometers or above, but if an inclined transmission is observed, there will be nano-sized microparticles. For this reason, Rayleigh scattering has been studied in detail. The investigation of coffee concentration with Rayleigh scattering is not available in the researched sources. It is planned to make a scientific publication on this subject.

In their study conducted in 2019, Grbic et al. developed a method to bring magnetic properties to plastics by using their hydrophobic surfaces with the help of magnets and refine them from the medium. They ensured magnetic recovery by binding hydrophobic iron nanoparticles to plastic. By applying this principle to a simple method, they achieved to recover 92% of polyethylene and polystyrene grains of 10−20 μm and 93% of microplastics larger than 1 mm (polyethylene, polyethylene terephthalate, polystyrene, polyurethane, polyvinyl chloride, and polypropylene) from seawater.

their study published in 2019, Nakajima et al. recognized the importance of a device that can remove various types of microplastics quickly, simply, and efficiently when evaluating the current microplastic treatment methods with the help of density difference. Thus, they developed a simple device with the help of the small glass separator without valves, Utermöhl mechanism. The new device easy to clean and transport can remove microplastics from sediments. With this simple device, they achieved to treat 94-98% of <1.000 µm microplastics (polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, and polystyrene).

In the experimental setup, the measurements taken after the microplastics were removed from the aqueous environment demonstrated that there were no micro or nano-sized particles in the range of values that the spectrometer made in the project could measure. The cost calculation for the spectrometer obtained is given in Table 5.1. The spectrometer made is very cost-effective with a cost of approximately 20 $.
Furthermore, the m-CNT produced by using raw materials obtained from domestic sources is very cost-effective and has been synthesized practically and easily.
Table. 5.1 Cost Table.

Substances for m-CNT	Cost ($)
Multi walled CNT	8.08
Fe_3O_4 NP (100 mg)	0.36
Ethanol (40ml)	0.24
Total	9.40

Materials for Spectrometer	Cost ($)
Lego Pieces	1
9 V Battery	2
Optic Lens	1
3D Print	4.90
1080 p Web Cam	9.50
White LED	1.99
Total Cost	20.40

In conclusion, the process of cleaning the microplastics could be measured cheaply, easily, and practically by using Reyhleigh Scattering as a different measurement method. For microplastics, which is a global problem, we think that a cost-effective method providing an advantage with the easy application has been developed.

6 .RECOMMENDATIONS

• To clean microplastics from massive aqueous environments, a refining machine can be developed where first organic materials are filtered and then, m-CNTs are continuously added and they can be removed with the help of magnets.
• The developed system can be installed on ships to clean the microplastics in the ocean.
• It is known that the number of microplastics mixed into the ecosystem from washing machines and thereby, their effects are high. This treatment process can be applied to the sewage drain of washing machines.

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This project aimed to detect microplastics by optical measurements and remove them from aqueous environment with magnetic carbon nanotubes (m-CNTs). The process of cleaning microplastics could be measured cheaply, easily, and practically by using Rayleigh scattering method. The developed system has high potential for engineering application to clean microplastics in the aquatic environments.