Removal of pharmaceuticals from water with MXene hybrid materials

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Water is essential to everyday life and is one of the most important resources in the world. Among the vast number of pollutants, pharmaceuticals constitute a major share. In this work, we have studied the adsorption of two main pharmaceutical drugs diclofenac and paracetamol onto MXene based hybrid materials. Majority of these pharmaceuticals end up being part of the water bodies causing harm to aquatic life and other wildlife. Current methods for addressing this issue are costly and not accessible to everyone. MXene based materials may hold potential in addressing this problem.

MXenes are novel 2D-materials that were discovered in 2011. They have a structure of $M_{n+1}X_nT_x$, where M is an early transition metal, X is either carbon or nitrogen, and T represents the surface terminating groups. In this work, the MAX precursor used was Ti_3AlC_2 and through the etching process, Al was eliminated, resulting in MXene $Ti_3C_2T_x$. MXenes have garnered significant attention in recent years due to their remarkable properties. One major challenge that needed to be addressed was the development of water-resistant materials. Typically, MXene films delaminate in water, making the use of pure MXene films unfeasible in water purification applications.

The goal of this work was to produce MXene hybrid materials capable of removing pharmaceuticals from water. Five different combinations were evaluated to determine the optimal hybrid material for pharmaceutical removal. The best combination was found to be MXene: PVA: TMPyP (MPP) 8:2:1. This hybrid film was successful in removing diclofenac from the water solution. The film's pharmaceutical removal properties were tested in three different conditions: ambient conditions, under a halogen lamp, and in the dark. The best results were obtained under halogen lamp, which may be due to the photocatalytic property of porphyrin. The removal of pharmaceuticals was monitored using UV-Vis.

MPP hybrid films properties were examined using several techniques. The interlayer spacing increased according to XRD and SEM results. Further information about the chemical composition was provided by FTIR and Raman spectroscopy, which revealed that MXene's primary functional group is -O(OH). Additionally, the issue of MXene film delamination was effectively resolved with the use of this water-resistant MPP hybrid material.

Key words: MXenes, hybrid materials, diclofenac, water purification, Ti_3AlC_2

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List of abbreviations

PVA = polyvinyl alcohol

PANI = polyaniline

PVAM = polyvinyl amide

TMPyP = 5,10,15,20-Tetrakis(1-methyl-4-pyridinio) porphyrin tetra(p-toluene sulfonate)

MPP = MXene/polyvinyl alcohol/TMPyP

SEM = Scanning electron microscope

FTIR = Fourier transform infrared spectroscopy

XRD = X-Ray diffraction

UV-Vis = Ultraviolet-visible spectroscopy

1 Introduction

Water is an essential part of life and is one of the most valuable resources. However, approximately 10 % of the world's population does not have access to enough clean drinking water. Lack of clean water can lead to a number of issues, including different illnesses. More than 80 % of these illnesses are connected with absence of clean drinking water and poor sanitation. Globally, over 4500 persons die daily of preventable diseases due to the unavailability of clean drinking water. [1] There are toxins and micropollutants that influence water quality. A variety of purification techniques are used, but not yet to a sufficient level. As a result, providing clean water for everybody is ana issue that needs to be handled with utmost priority.

Various pollutants are influencing the world's water aquatic systems, including a range of pharmaceuticals. Notably, both diclofenac and paracetamol, commonly used over-the-counter drug molecules, are small, water-soluble and challenging to detect and remove from water sources. Developing a more cost-effective method for their removal would enhance accessibility for everyone. Diclofenac, a widely used nonsteroidal anti-inflammatory drug (NSAID), is consumed at rates between 195 mg to 940 mg per person.[2] Similarly, paracetamol is another commonly used pharmaceutical drug. Residual amounts of these pharmaceuticals often enter wastewater and can harm living organisms. The concentration of paracetamol in water bodies can be up to 0,134 mg/l.[3]

MXenes are inorganic 2D-nanomaterials with unique properties. MXenes are transition metal carbides, nitrides and carbonitrides.[4] Among these, titanium carbide, $Ti_3C_2T_x$, where T_x represents functional groups such as -OH, -F, -O or -Cl, is one of the most common MXene. These materials have unique characteristics including high electrical and thermal conductivity, a large active surface area, hydrophilicity, and environmental compatibility. Due to these properties, MXenes have wide a range of different applications such as in energy storage devices, sensors, flexible electronics, and water purification. They can be utilized in different forms in these applications such as powder or free-standing films.[5]

MXenes are one promising material for the removal of pharmaceuticals from water. Their morphology, characterized as a layered structure, provides advantages towards water purification. MXenes are particularly feasible for environmentally friendly water purification because MXene films can be recycled and reused, offering distinct benefits over other existing

methods. However, one main challenge is water solubility of pure MXene films, which makes them unsuitable for direct use in aqueous solutions. Therefore, some additional material is needed to enhance resistance to water solubility. Polymers or cellulose, for example, could be used to achieve this stabilization.

In this work five different polymers were utilized to evaluate the water resistance and pharmaceutical removal efficiency of MXene hybrid films. The primary objective is to investigate different compositions of MXene hybrid films in water solutions containing pharmaceuticals. Changes in pharmaceutical concentrations are monitored using UV-Vis spectroscopy. The chemical properties of materials were characterized using a range of analytical methods such as X-ray diffraction, Scanning electron microscopy, Raman spectroscopy, infrared spectroscopy, and UV-Vis spectroscopy.

1.1 Pharmaceuticals in water

Water sources are polluted with various contaminants, which can be classified into four categories: organic pollutants, inorganic pollutants, biological pollutants, and miscellaneous pollutants. Organic pollutants, such as food processing waste, fuels, and pesticides, degrade water quality and are harmful to aquatic environments. Inorganic pollutants, often originating from industrial processes and individual pollution, are typically highly toxic and pose significant risks to both the environment and human health. Biological pollutants include bacteria, molds, and viruses for example. Biological pollutants are usually less harmful than organic- or inorganic pollutants, but they still present health risks. [6] A growing problem is the presence of pharmaceuticals in the water. It has been reported that surface waters can contain up to 93 different pharmaceuticals. [7] This study focuses on the removal of two specific pharmaceuticals: diclofenac and paracetamol.

Diclofenac (Figure 1) is a widely used anti-inflammatory drug, commonly used in painkillers, treatments for inflammatory conditions, and migraine medications. The average usage of diclofenac ranges between 195 mg to 950 mg per person, varying by region. Removing or degrading diclofenac using conventional methods is challenging, with reports indicating that only 20 – 30 % of diclofenac is successfully degraded or removed during the water purification

process. [2] The concentration of diclofenac amount in water sources typically ranges between 800 – 1600 ng/ml.[8]

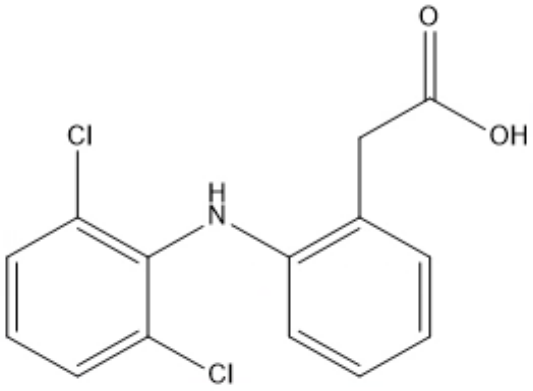

Figure 1. Structural formula of diclofenac.

Paracetamol (Figure 2) is an analgesic and antipyretic drug commonly used for pain relief, fever reduction, and in the management of chronic conditions. Its use varies by country, influenced by policy and legislation. For example, in the United Kingdom, 42 million tablets were sold in a single year, where availability is high and paracetamol can be bought from pharmacy.[9] The concentration of paracetamol in water sources varies significantly due to various factors, such as proximity to hospitals, where pharmaceutical contamination is typically higher compared to residential areas. Studies have shown that the concentration of paracetamol in water sources can reach up to 0,134 mg/l. [3]

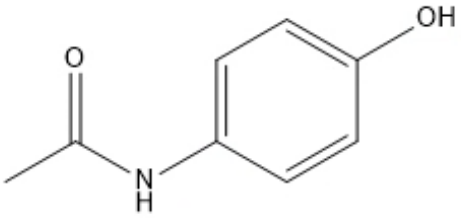

Figure 2. Structural formula of paracetamol.

It is essential to research and develop advanced water purification methods to address these challenges that diclofenac and paracetamol brings, just to mention these two. To reach this goal, to have clean water, the European Commission has established directives towards a sustainable future. One of these objectives is to achieve universal clean water and sanitation for everyone.

1.2 Water purification methods

There are currently a variety of water purification methods available as shown in Table 1. Each method has different purposes and employs selective techniques in water purification applications. However, many existing methods are associated with high cost and various disadvantages. Introducing MXene-based membranes into water purification presents one feasible alternative to traditional methods, offering the potential to enhance cost-effectiveness and availability to everyone.

Table 1. Overview of various water purification methods, including advantages and disadvantages.

Method	Example	Pros	Cons	Reference
Adsorption	Activated carbon	Availability / high efficiency	High cost	[6]
Reverse osmosis	Reverse osmosis	High efficiency / chemical free	Wastewater generation / cost	[6]
Membrane filtration	Micro-& nano filtration	Low energy consumption / versatility	Membrane fouling / maintenance	[6]
Electrical techniques	Electrochemical degradation	Good removal of metals and organic pollutants	Energy consumption	[6][10]
Biological methods	Microbial consortium	Environmentally friendly	Sensitivity to pH and temperature	[6]
MXenes	MXene membrane	Separation/ high flux rate	Laboratory scale	[4]
MXenes	MPP	Recyclable / pharmaceutical removal	Low capture rate / optimization needed	This work

There are quite a few different MXene-based methods in water purification. For example, MXene membranes offer plenty of potential applications, including enhanced flux rates and serving as separators in oil/water purification processes. Typically, MXene membranes are hybrid- or composite materials, as MXene tends to disperse into single layer sheets upon contact

with water. Through the utilization of these hybrid materials, it becomes feasible to increase various properties in water purification applications. [11]

1.3 MXenes

MXenes were discovered in 2011 as new inorganic functional 2D-material. [12] Typically, MXenes have a typical structure of $M_{n+1}X_nT_x$ (where n=1,2,3), with M representing an early transition metal such as Sc, Y, Ti, Mo, W. X representing carbon or nitrogen, also can be a combination of these two, and T is a surface group that can vary depending on the synthesis method. These surface groups can be for example -O, -OH, -F or -Cl.[13] MXenes are synthesized from a MAX phase precursor, where A stands for Al, Si or Ga.

Several different synthesis methods exist for etching the A element from the MAX phase structure to synthesize MXenes. There are quite a few different MAX phases, one most common is Ti_3AlC_2. While chemical etching is the most common approach, alternative methods such as electrochemical etching are employed. [14] Etching with hydrofluoric acid (HF) is one of the most traditional methods, but its high toxicity poses environmental concerns. More environmentally friendly method is adding lithium fluoride (LiF) and hydrochloric acid (HCl) to extract MXene flakes from the MAX precursor. Future advancements may lead to even more sustainable synthesis routes, for example, ionic liquids represent a promising solution to this issue.

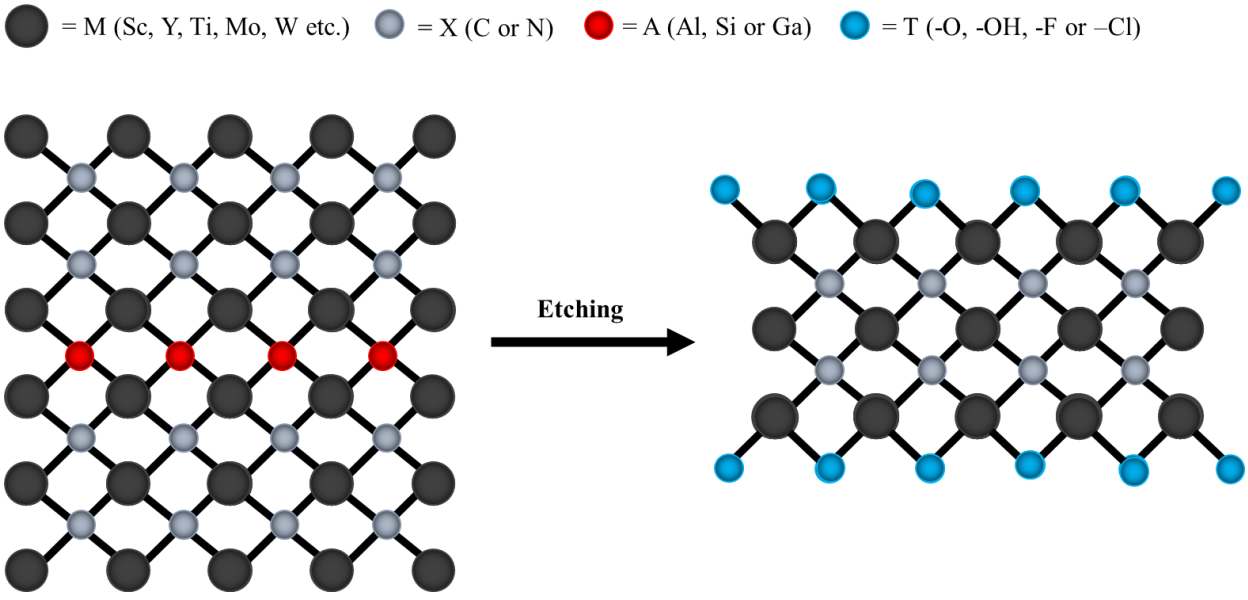

Figure 3. MAX phase synthesis to MXene, when etching the A element.

Etching results in a multilayered MXene structure as illustrated in Figure 3. The washing steps are crucial in determining the properties and composition of the MXene. The washing process of MXene solution typically involves the following steps: removal of unreacted MAX phases using water, centrifugation to obtain colloidal dispersion suitable for films, and storage of final product. Different washing methods results in different composures of formed MXene. For instance, it is not feasible to obtain multilayered MXene powder from a solution intended for film fabrication. One structure of MXene is $Ti_3C_2T_x$, which is widely used in different applications.

MXenes possess several beneficial properties. One property that has garnered significant interest in recent studies is their electrical conductivity, which is relevant in energy storage applications due to MXenes' high cycle stability and high capacity. In water purification applications, MXenes exhibit valuable properties such as mechanical strength, chemical stability, and conductivity. The mechanical strength is demonstrated by the flexibility of films. The chemical stability is beneficial as MXene hybrid materials does not delaminate in water even after weeks use.[15]

Table 2. Different MXene compositions and their applications.

MXene	Application	Reference
V_2C	Structural enhancing / as a substrate	[16]
Ti_3C_2	Photocatalyst / CO_2 reduction / water splitting / water purification / H_2O_2 production	[17]
Nb_2C	Photocatalyst for hydrogen evolution	[18]
Mo_2C	CO_2 adsorption	[19]
Ta_4C_3	Supercapacitor electrode material	[20]

Table 2 illustrates the diversity of MXenes, showing various structures and compositions that are suitable for different applications. While MXenes can be utilized in their pure form, their properties can be enhanced by making hybrid materials. This allows for the optimization of specific characteristics tailored to particular applications.

1.3.1 MXene hybrid materials

MXene-based films have certain beneficial properties. However, to enhance the properties, certain additives are required. The issue of water solubility in pure MXene films can be addressed by creating hybrid materials. In this work, the films produced are hybrid materials. Hybrid materials are composed from materials that individually do not share similar properties but together provide benefits towards wanted properties. For example, in composite materials, there are two or more components with similar properties combined to enhance the overall performance of the material. The key difference between composite and hybrid materials lies in the properties of their precursor materials. In composite materials, the precursor materials possess certain inherent properties that are enhanced when combined. In contrast, hybrid materials are composed of precursor materials that individually exhibit few of the desired properties, but together they produce beneficial properties not present in the individual components.[21]

MXene composites retain similar properties of pure MXene but exhibit certain enhancements. For instance, MXene/graphene oxide membrane is utilized in water purification applications[22]. In this composite, both materials share similar properties, resulting in improved membrane performance to using either material alone.

MXene hybrid materials are usually created with polymers, which generally do not share properties such as conductivity with MXenes. However, when combined, they can form materials with enhanced properties. For example, adding polyvinyl alcohol (PVA) with MXene results in a hybrid film that is no longer vulnerable to water degradation. Polymers are an excellent choice for this purpose because they usually possess hydrophilic functional groups, which interact well with the common surface groups of MXenes (-OH, -O, -F) [23]. MXene hybrid materials have many possible applications, including use in water purification.

2 Experimental

2.1 Purpose of work

The purpose of this work was to develop a MXene hybrid film capable of removing pharmaceuticals from water. As previously mentioned, pure MXene films are water soluble. Therefore, finding the right composition to manufacture MXene hybrid material to achieve water resistance was one main goal, because most of the experiments are done in water solution. To achieve this, various polymers and additives were tested. Once a promising combination of hybrid materials was identified, optimization of parameters was required. Comprehensive characterization using different methods were conducted to understand the materials properties and differences in the films.

The second goal was to remove pharmaceuticals from water after identifying the optimal composition for MXene films. Diclofenac and paracetamol were two main substances used to evaluate the effectiveness of MXene hybrid materials in pharmaceutical removal. The degradation of these pharmaceuticals was monitored using UV-Vis spectroscopy, as both compounds exhibit intense UV-Vis absorption peaks. The high sensitivity of this technique allows for the detection of small amounts of pharmaceuticals and enables precise measurement of the differences in pharmaceutical degradation compared to reference samples.

2.2 Chemicals

The chemicals used in the synthesis of MXenes included hydrochloric acid (37%, Sigma), lithium fluoride (Sigma), MAX phase (Carbon Ukraine), and lithium chloride (Sigma). To enhance the properties of MXene films, various polymers were incorporated: polyvinyl amide (BASF), polyvinyl alcohol (Sigma), polyaniline (synthesized in-house from aniline, Sigma), and porphyrin TMPyP (TCI). The pharmaceuticals tested were paracetamol (Sigma) and diclofenac (TCI). For filtration, a 0.1-micron polycarbonate filter membrane from Merck was used.

2.3 Synthesis of MXene and composite films

2.3.1 Synthesis of MXene colloidal solution

$Ti_3C_2T_x$ (MXene) was synthetized by etching Ti_3AlC_2 (MAX phase) (particle size <40µm) with 12 M HCl and 2,3 M LiF. Specifically, 0,5 g of Ti_3AlC_2 was slowly added to a 10 ml mixture of HCl/LiF solution to mitigate heat generation. The resulting solution containing Ti_3AlC_2 was stirred at 500 rpm for 24 hours with elevated temperature of 45 °C in an oil bath as illustrated in Figure 4. After a 24-hour reaction period, the solution was allowed to cool down to room temperature.

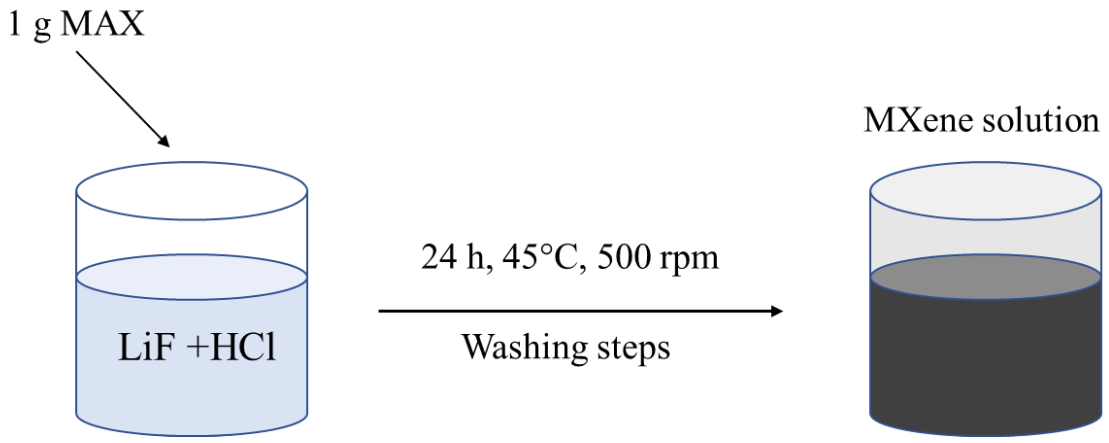

Figure 4. Protocol for $Ti_3C_2T_2$ (MXene) synthesis from Ti_3AlC_2 (MAX phase) precursor.

MXene solution was washed sequentially with 1 M HCl, 1 M LiCl, and with distilled water. 40 ml of each washing agent was used in the following order: once with 1 M HCl, three times with 1 M LiCl and three times with distilled water. After the addition of each washing agent, the solution was centrifuged for 2 minutes at 4200 x *g*. After washing steps, the MXene solution was ultrasonicated for 1 hour at a controlled temperature (maintained below 30 °C). The sonicated solution was then centrifuged for 1 hour at 2058 x *g*. Subsequently, the colloidal solution was obtained and transferred in a storage bottle which was protected with argon to prevent oxidation. Finally, 1 ml of solution was extracted from the bottle to determine concentration of solution (mg/ml).

2.3.2 MXene films

After obtaining the MXene solution, films were fabricated using suction filtration. A specific concentration and volume of MXene solution were placed in the filtration system (as illustrated in Figure 5), and vacuum pressure was applied to achieve approximately 80 mbar of pressure. Typically, the MXene films produced in this work contained 40 mg of MXene at a concentration of 1 mg/ml. Vacuum filtration was initiated, and 2-3 ml of MXene was added to obtain the first layer of film. Filtration continued until a total of 40 ml of MXene solution was added. Once all the water had been removed, the formed film was on top of filter paper. The product was then left to dry for 24 hours to the exicator before further use.

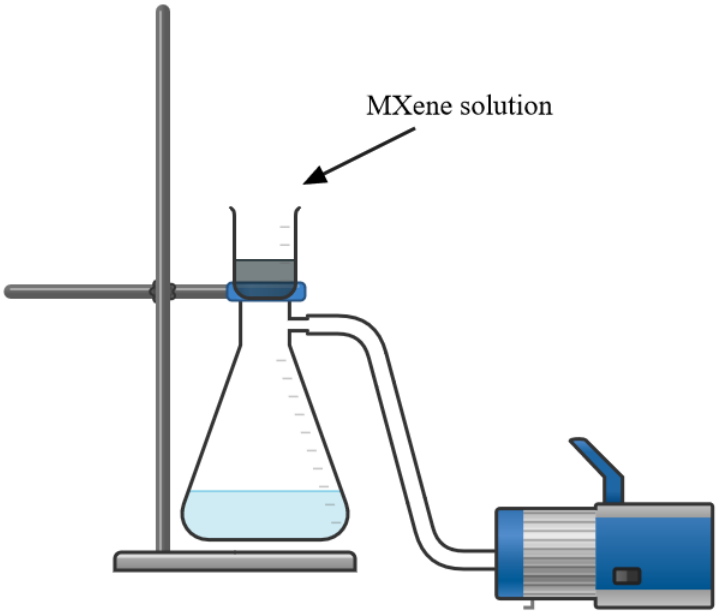

Figure 5. Filtration setup: The Mxene solution is poured onto filter paper, and water is drawn through the system with the assistance of a vacuum. The materials remain on the 0.1-micron polycarbonate filter, resulting in the formation of the film.

2.3.3 Hybrid films

Hybrid films can also be fabricated using the same technique employed for MXene films. To enhance the water resistance of MXene films, different molecules with various properties can

be added. One approach to modify properties of MXene films was addition of polymers, which can increase flexibility and reduce water solubility. In this work, several different polymers were tested: polyaniline (PANI), polyvinyl alcohol (PVA), and polyvinyl amide (PVAM). Additionally, porphyrin (TMPyP) was used to potentially enhance the photochemical properties of the films. The properties of the films can be further modified by incorporating different molecules with beneficial functional groups. Various combinations were tested to identify the most suitable composition for water purification.

From the results it can be seen that MPP-hybrid film (MXene-PVA-Porphyrin) has quite extraordinary properties compared to other films made. Therefore, the focus shifted to optimizing the parameters for MPP-hybrid film. Table 3 presents the different combinations of MXene: PVA: TMPyP (MPP) that were tested. The optimal results were obtained with the MXene: PVA: TMPyP ratio of 8: 2: 1 as discussed in the results section.

Table 3. Optimization of MPP-hybrid material, with different amounts of TMPyP.

MXene (mg)	PVA (mg)	TMPyP (mg)	Name
40	10	8	MPP8
40	10	6	MPP6
40	10	5	MPP5
40	10	4	MPP4
40	10	2.7	MPP2.7
40	10	2	MPP2

2.4 Characterization

XRD measurements were done using PANanalytical Aeris powder X-Ray diffractometer. Measurement angle for XRD was set between 4 – 80 degrees. UV-Vis spectrums were measured by Agilent Cary 60 spectrometer. Measurements were conducted in a quartz cuvette over a range of 180- 800 nm. Raman spectra were measured by Renishaw Quontor. Raman measurements were performed using a 532 nm laser with a 20x objective. FTIR measurements were made by Brucker spectrometer utilizing the diamond ATR method. SEM images were obtained using Thermo Scientific Apreo.

2.5 Removal of pharmaceuticals

The removal of pharmaceuticals was monitored using UV-Vis spectroscopy. To ensure reliable data, tests were conducted under consistent parameters. The testing procedure was as follows: 1) A quarter of formed film (film size approximately 41 mm in diameter) was cut and placed in a 5ml closed bottle. 2) 3 ml of diclofenac or paracetamol solution was added to the bottle. 3) After waiting 24 hours, the solution was measured using UV-Vis spectroscopy.

Diclofenac and paracetamol were the two pharmaceuticals tested. The concentration of both solutions was optimized through trial and error. The main challenge was the sensitivity of the UV-Vis technique. At higher concentrations, the spectrum was not readable. After testing, the most optimal concentrations for UV-Vis analysis were determined to be 10 mg/ml for paracetamol and 20 mg/ml for diclofenac.

Figure 6. Testing setup for removal of pharmaceuticals from water. The film is placed at the bottom of the vial, and a pharmaceutical solution is added on top of the film. Vials are capped to prevent water evaporation.

3 Results

3.1 General results

In this work, several different polymers were tested to achieve the desired properties, including water resistance, removal of pharmaceuticals, and potential photochemical reactions. Figure 7 illustrates various hybrid materials that were evaluated. Different combinations were used to produce specific hybrid films. Preliminary results were obtained for each combination, with the MPP film identified as the most promising option for further investigation. Although all hybrid films demonstrated water resistance, some were less effective in removing pharmaceuticals. The MXene/PANI film showed some potential for pharmaceutical removal, but further studies are required.

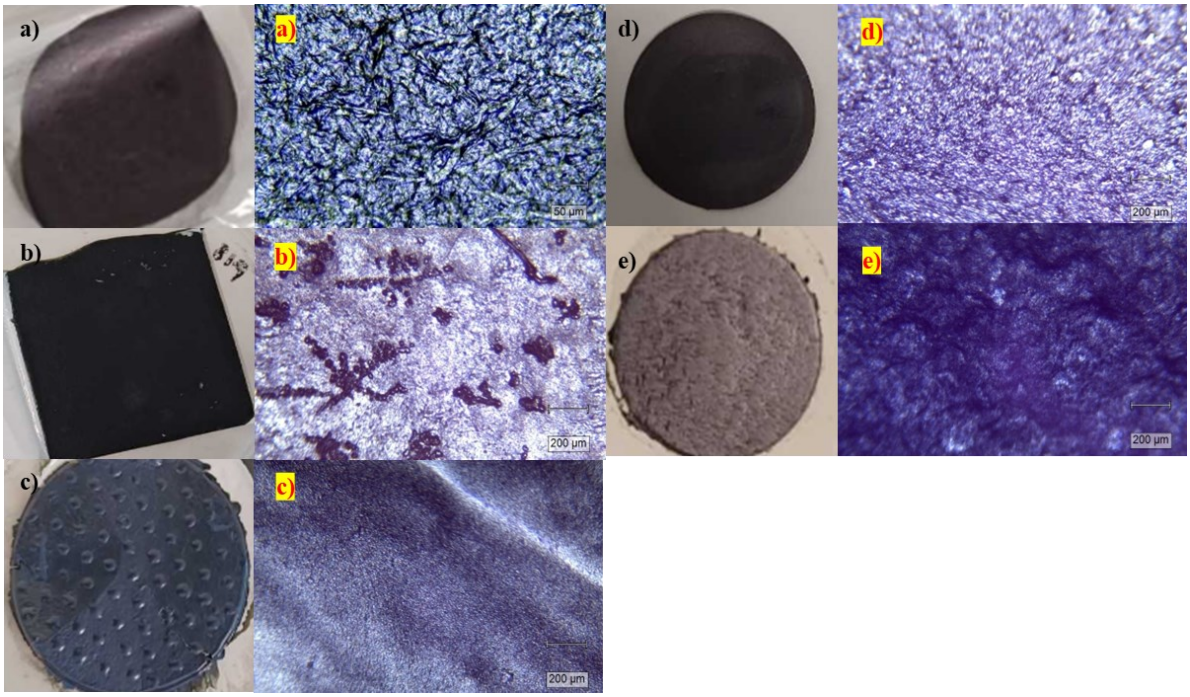

Figure 7. Different MXene based films produced in this work and their respective Raman image showing morphology a) MXene film b) MXene/PVAM film c) MXene/PVA film d) MXene/PANI film e) MPP film.

Different combinations of MPP are presented in Table 3. The focus of the results is on MPP5 hybrid film, which has optimized parameters. This film is compared to MXene film using various characterisation techniques to achieve better understanding of material's composition and properties.

3.2 X-Ray diffraction

X-Ray diffraction (XRD) is a powerful tool to detect and determine the purity of MXene and identify any impurities. The XRD pattern can indicate whether there is an unreacted MAX phase present or if the reaction has proceeded, forming a single to few-layer MXene solution and subsequently towards films. As shown in Figure 8, MXene film exhibits only (00*l*) peaks, which is typical for 2D materials.[24] Specifically, the main (002) peak at 6.9° indicates an interlayer spacing of 1.3 Å at MXene films.

The MXene/PVA hybrid film exhibits a similar (002) peak, and the presence of PVA is evident around 20°.[25] The XRD pattern of the MPP5 film shows differences, indicating that TMPyP affects interlayer spacing. According to Bragg's law, a smaller angle corresponds to a larger interlayer spacing. In Figure 8a, the MPP5 film shows an angle of approximately 4.1°, indicating an interlayer spacing of 10.7 Å. Similar to MXene/PVA film, a peak around 20° is attributed to PVA.

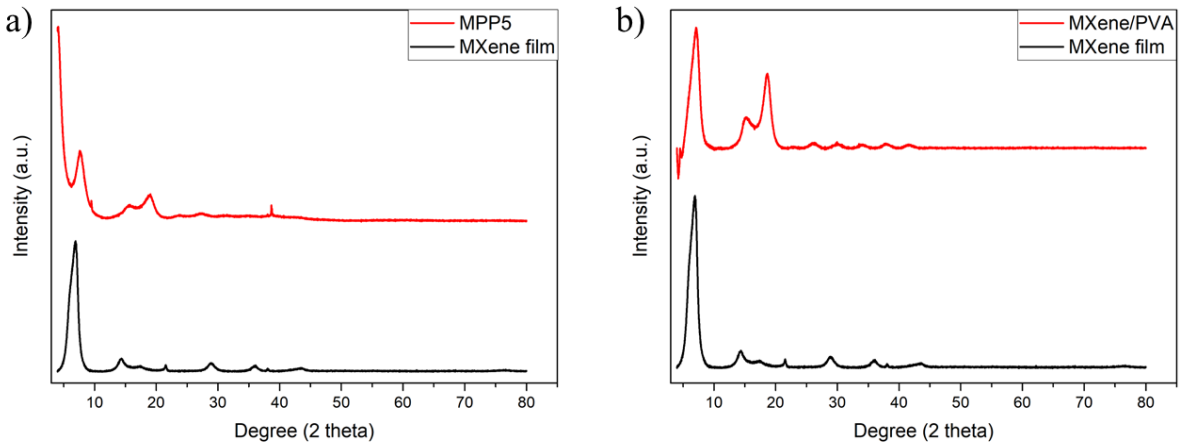

Figure 8. XRD-results from a) MPP5 and b) MXene/PVA, MXene film is used as reference in both cases.

3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to study the morphology of the films. Cross-sectional images of MXene and MPP5 films are shown in Figures 9 and 10, respectively. These visualizations support the previous XRD data. As seen in Figure 9, the space between MXene layers is smaller. When PVA and TMPyP are added to the structure, particularly TMPyP, interlayer spacing increases, as observed in Figure 10.

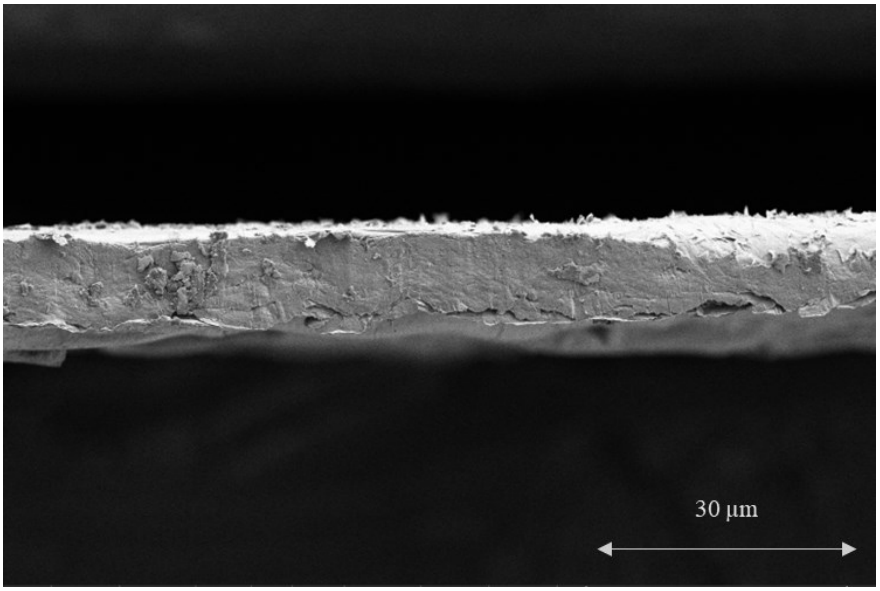

Figure 9. SEM-image from MXene film.

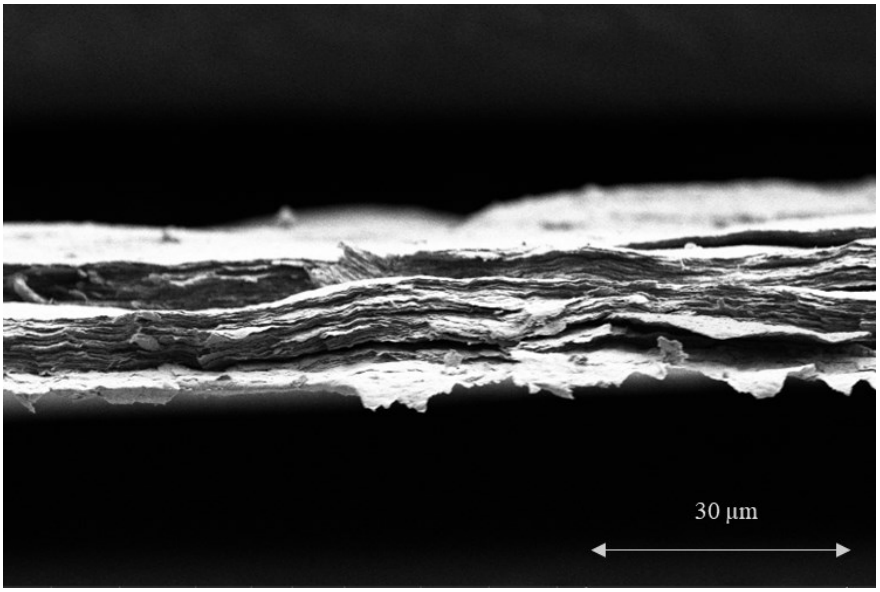

Figure 10. SEM-image from MPP5 film.

3.4 Raman spectroscopy

Raman spectroscopy provides valuable insights into the characteristics of materials. From Raman spectra, we can determine MXene's functional group (T_x) and characterize material's properties. Raman spectroscopy is particularly useful due to its non-destructive nature. When combined with a complementary technique as Fourier-transform infrared spectroscopy (FT-IR), it offers a comprehensive understanding of material's properties.

Figure 12 shows Raman spectra from three different spots, as indicated in Figure 11. Two spots are from MPP5 film, and one is from MXene film. The Raman spectrum of the MXene film (Figure 11c) displays two broad peaks in the range of 1100-1700 cm^{-1}, corresponding to D and G peaks of graphitic carbon.[26] Peaks at 580 cm^{-1}, 622 cm^{-1} and 725 cm^{-1} indicate carbon vibrations, while the peak at 404 cm^{-1} correspond to the functional group T_x, specifically -O(OH).[27]

From Figure 12, we can observe that the spectrum measured from the black line of the MPP5 film exhibits similar peaks to those of the MXene film. This indicates that the black line of MPP5 film is a defect, consisting of stacked MXene within the hybrid material.

The Raman spectrum of the MPP5 film exhibits notable differences compared to the spectra of the previous ones. TMPyP is detected as multiple peaks in the 2500 to 3000 cm^{-1} range. This is the primary distinction between MPP5 and MXene films. These peaks are absent in the MXene film. Additionally, the -O(OH) T_x group peaks present in the MXene film are not observed in the MPP5 film. The peak at 2900 cm^{-1} likely corresponds to PVA.[28]

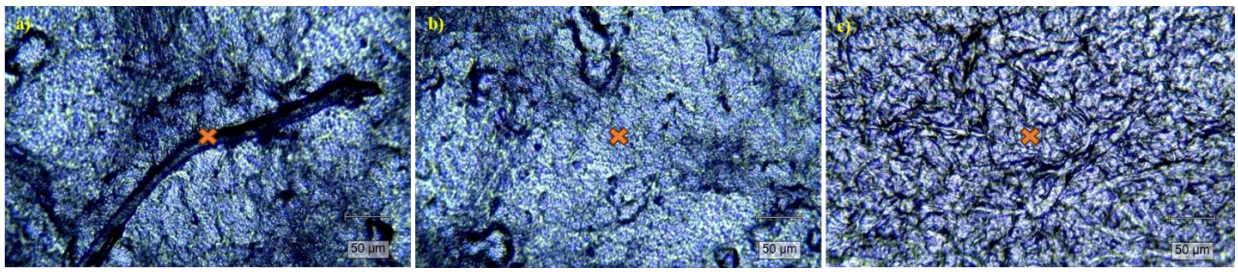

Figure 11. Raman measurement spots for a) MPP5 defect b) MPP5 c) MXene film.

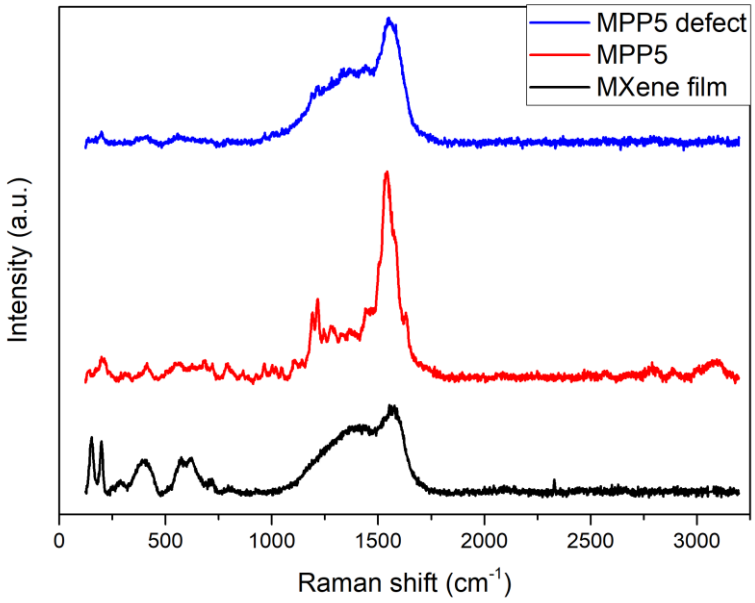

Figure 12. Raman measurements from MXene, MPP5 and MPP5 defect.

3.5 Infrared spectroscopy

The chemical composition of materials was analysed using Fourier-transform infrared spectroscopy (FT-IR) with attenuated total reflection (ATR). A diamond probe was employed for the measurements. While the diamond probe provides excellent resolution, it also introduces strong lattice bands in the 2300-1900 cm^{-1} region [29]. Consequently, these wavelengths have been excluded from the graph in Figure 13.

There were no differences in the FT-IR spectra between sides of either the MPP or MXene films, indicating homogeneity throughout the films. While the spectra of both MXene and MPP5 exhibit similarities, there are some differences. Figure 13 shows that both films share similarities. The broad peak around 3450 cm^{-1} corresponds to the stretching vibrations of O-H groups. The primary peaks of MXene film appear at 1665 cm^{-1}, associated with stretching of C=O, and at 600 cm^{-1}, corresponding to the stretching of Ti-O. [30]

The MPP5 film exhibits additional peaks not found in the pure MXene film. Specifically, the peak 2940 cm^{-1} is attributed to the asymmetric stretching of CH_2 from PVA. Other PVA-related

peaks are observed at 1640 cm^{-1} and 1140 cm^{-1}, which can be due to water absorption and C-O stretching, respectively. Additionally, the peak at 820 cm^{-1} is assigned to C-C stretching. [31]

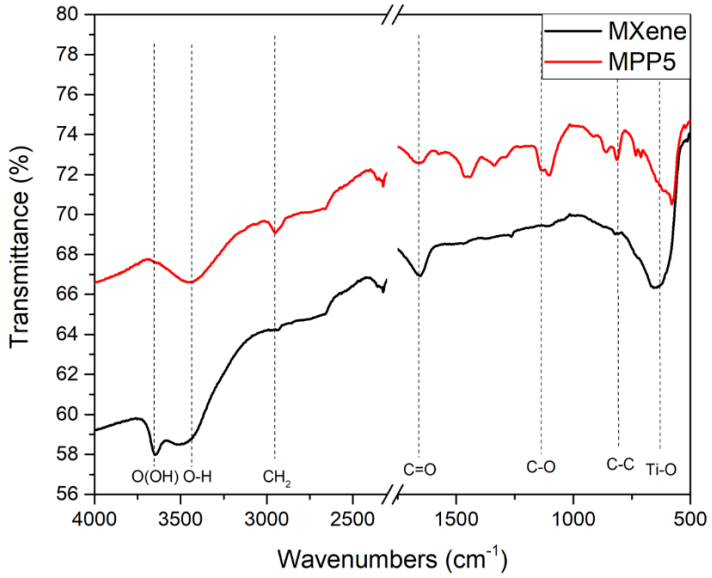

Figure 13. FTIR spectra from MXene -and MPP5 films.

Combining FT-IR with Raman spectroscopy provides a more comprehensive understanding of film's characteristics. Raman spectroscopy identified the functional groups T_x as $-OH_2$. In the FT-IR spectra of the MXene film, an additional peak at 3600 cm^{-1} is evident, likely due to free $-OH_2$-groups in the MXene film. These $-OH_2$-groups are bonded when TMPyP and PVA were added, and in MPP5 spectra we can see that there is no longer this characteristic peak. $-OH_2$-groups are presumably connected to the matrix with hydrogen bonds from TMPyP and PVA.

3.6 UV-Vis

UV-Vis spectroscopy was the main characterisation technique to monitor the removal of pharmaceuticals from water solutions. This method is fast, reliable, and repeatable allowing for precise detection of changes in pharmaceutical concentrations. Initially, it was essential to establish reference spectra for both diclofenac and paracetamol, as shown in Figure 14.

Diclofenac exhibits a primary absorption peak at 274 nm [32], while paracetamol shows a primary peak at 243 nm [33]. As pharmaceuticals are removed from the water solution, their concentration decreases, resulting in a reduction in the absorbance of their characteristic peaks compared to the reference spectra.

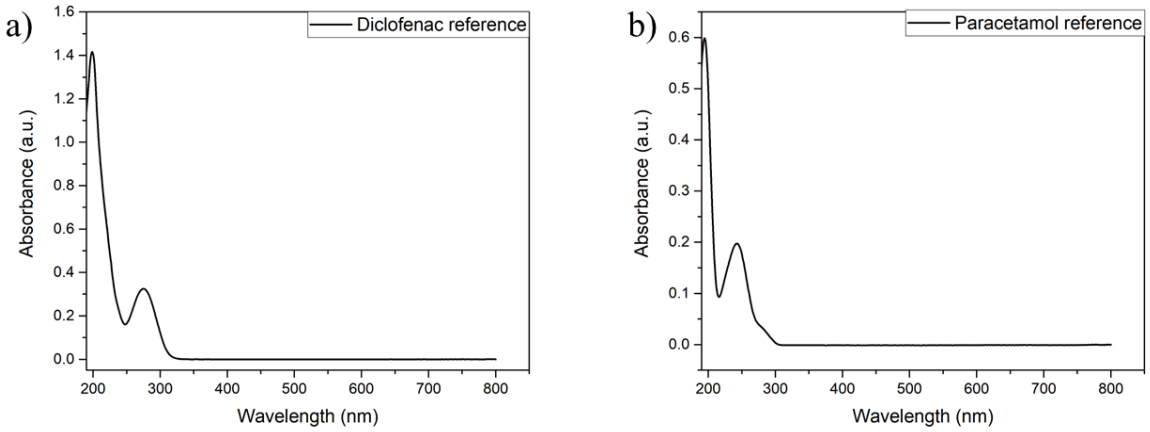

Figure 14. UV-Vis spectra from a) diclofenac reference and b) paracetamol reference.

Several different hybrid materials were tested for their efficacy in removing pharmaceuticals from water. Two main issues were encountered during these experiments: the pharmaceuticals were not adequately removed, and the hybrid materials lacked stability in water. Figure 15a demonstrates a partial removal of diclofenac solution for the first time, whereas Figure 15b shows that paracetamol removal was less effective. The peaks at 425 nm and within the 200 – 250 nm, originating from TMPyP (see Figure 16a), may interfere with the sample, possibly resulting in partial removal of paracetamol, but less efficiently than diclofenac. A significant issue with these results was the excessive amount of TMPyP in the MPP film, which led to its dissolution back into water solution. Consequently, further optimization of the film was necessary.

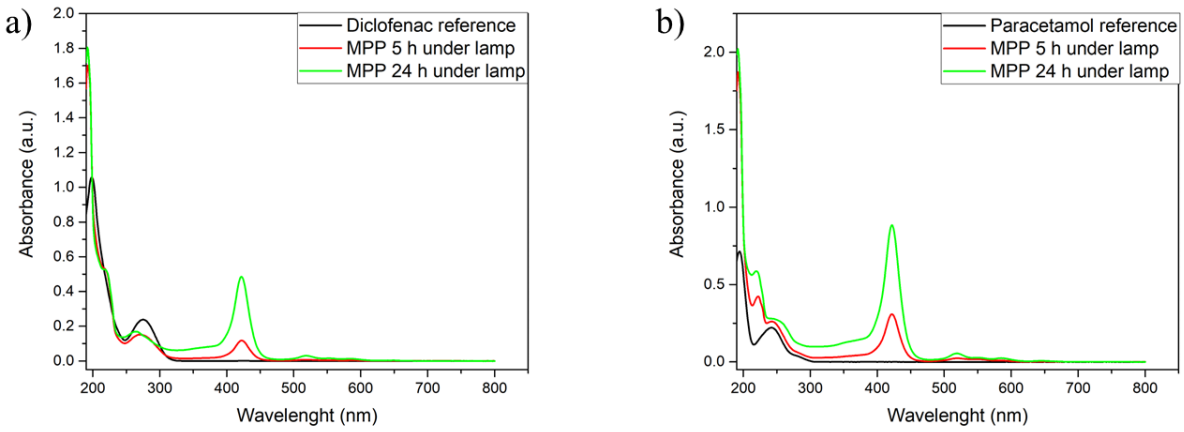

Figure 15. UV-Vis spectra from the first trial with MPP hybrid film. MPP contains 30 mg of MXene, 9 mg of PVA and 6 mg of TMPyP. a) MPP in diclofenac reference for 5 h and 24 h. b) MPP in paracetamol reference for 5 h and 24 h.

Before optimization of MPP film, the role of TMPyP was evaluated independently. A water solution containing the same amount of TMPyP as used in the MPP film was tested for its reactivity with pharmaceuticals. Diclofenac and paracetamol solutions were added to the plain TMPyP solution. As shown in Figure 16b, TMPyP exhibits a higher reactivity with diclofenac compared to paracetamol. This differential may be attributed to charge interactions, given that TMPyP is positively charged, and the diclofenac salt used is negatively charged. This charge disparity likely facilitates the interaction between TMPyP and diclofenac. However, the use of plain TMPyP as a removal agent for pharmaceuticals is not feasible due to its high cost and the residual contamination it leaves in the water.

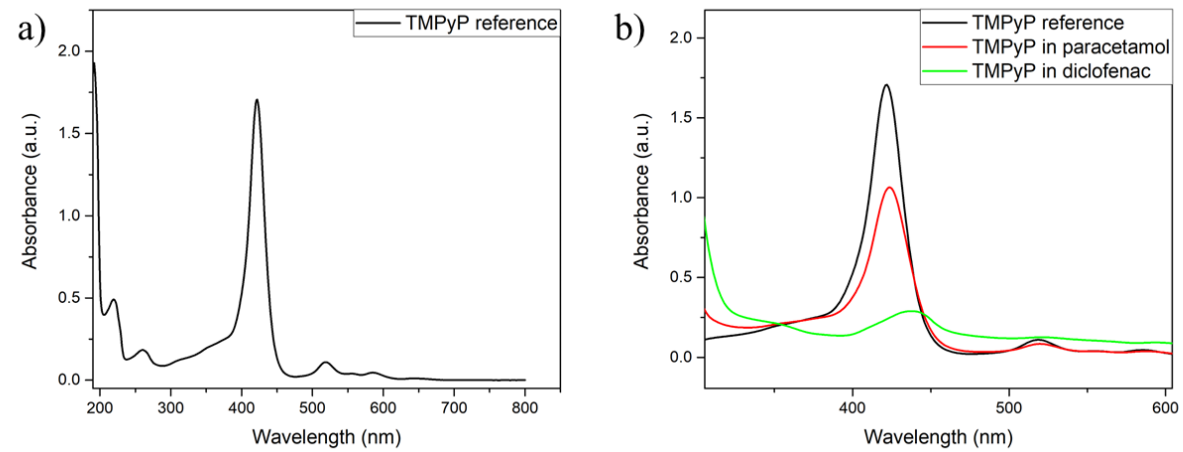

Figure 16. UV-Vis spectra from a) TMPyP reference in water solution and b) from TMPyP in paracetamol and diclofenac water solutions.

Table 5. Optimization of MPP-hybrid material, with different parameters and results what happens in water solution containing pharmaceuticals.

MXene (mg)	PVA (mg)	TMPyP (mg)	Result
40	10	8	Excess of TMPyP
40	10	6	Excess of TMPyP
40	**10**	**5**	**Optimal**
40	10	4	No removal
40	10	2.7	No removal
40	10	2	No removal

The amount of TMPyP was identified as the problem and necessary optimization of the TMPyP content in MPP films is needed, as detailed in Table 5. Figure 17a-c illustrates that a smaller amount of TMPyP (2 – 4 mg) results in no removal of diclofenac. In contrast, Figure 17d demonstrates that an excessive amount of TMPyP in the MPP film leads to the appearance of a characteristic peak at 425 nm. Nevertheless, it also indicates that some diclofenac can be removed under these conditions.

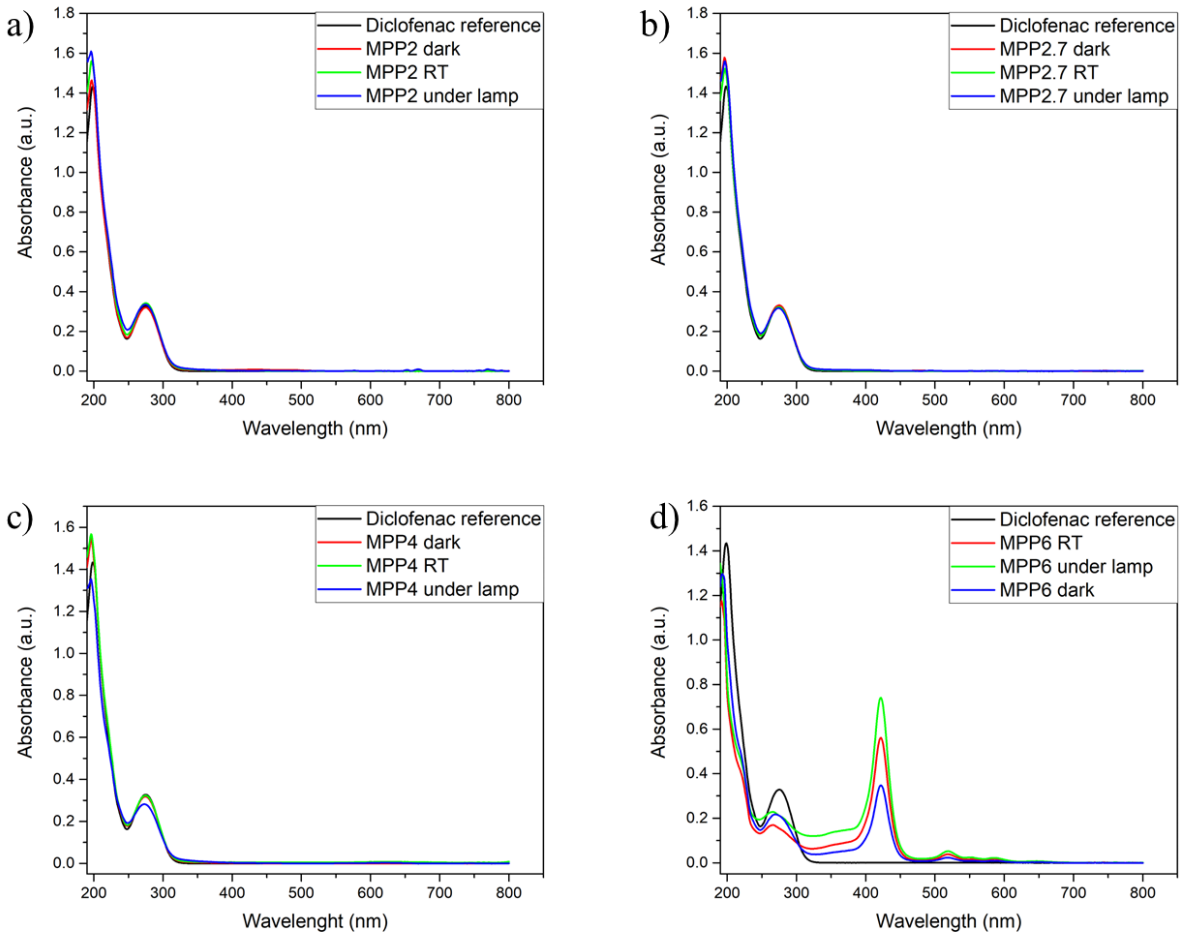

Figure 17. UV-Vis spectrum from a) MPP containing 2 mg of TMPyP, b) MPP containing 2.7 mg of TMPyP, c) MPP containing 4 mg of TMPyP, d) MPP containing 6 mg of TMPyP. All samples were tested under three different circumstances: Room temperature and light (RT), under halogen lamp and in dark, for 24 h.

The most optimal MPP film was MPP5, which contained 5 mg of TMPyP. In Figure 18a, the characteristic peak of TMPyP at 425 nm is absent. Additionally, Figure 18b shows that the MPP5 film effectively removes diclofenac from the solution. The removal efficiency was tested under three different conditions: at room temperature and light, under halogen lamp, and in dark. The results in Figure 18b indicate that the halogen lamp condition led to the highest removal rate of diclofenac. This enhanced removal may be attributed to the photocatalytic properties of TMPyP.

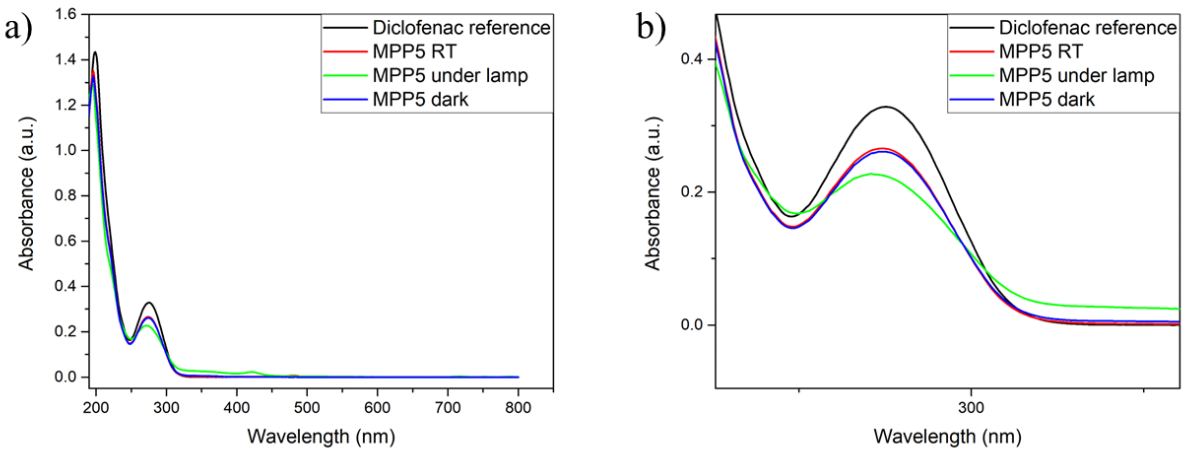

Figure 18. a) UV-Vis spectra from MPP5 film in diclofenac. b) Magnification from the main UV-Vis peak of diclofenac. Three different circumstances: Room temperature, under halogen lamp and in dark, all for 24 h.

The amount of captured diclofenac in the MPP5 film was analysed using UV-vis spectroscopy. The MPP5 film was immersed in pure water and left for 24 hours. Subsequently, the UV-Vis spectrum of water was measured to detect any diclofenac that had dissolved from the film. As shown in Figure 19, the presence of diclofenac in the water indicates that it can be released from the MPP5 film and collected for further usage.

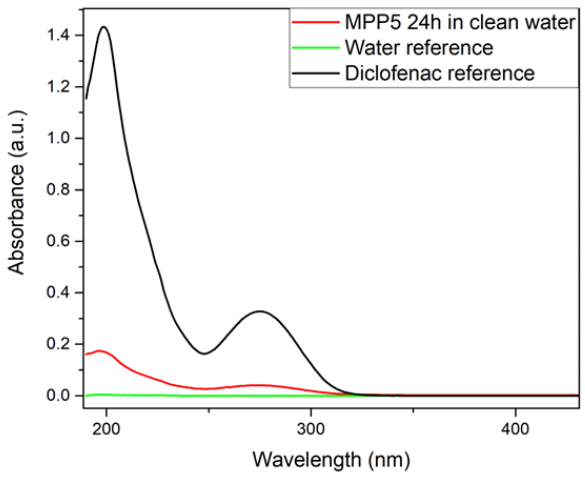

Figure 19. UV-Vis spectra from washed MPP5 film after 24 h in clean water.

4 Future prospects

This subject has plenty of potential for further research. Firstly, numerous optimizations of these films can be undertaken. In this work, only the porphyrin (TMPyP) content was varied, and only one type of porphyrin was utilized. Testing other potential polymers could also enhance the properties of the hybrid film. Future advancements may include more environmentally friendly synthesis routes, further improving the feasibility of this water purification method.

Additionally, it would be beneficial to test different pharmaceuticals now that the optimal synthesis route for MXene hybrid films has been found. Determining the reactive pharmaceutical core would provide deeper understanding of the range of pharmaceuticals that can be removed. Hormone removal such as estradiol, could also be tested with these MXene hybrid films.

Applications in other areas could be examined, such as combining electrochemistry with this material to degrade pharmaceuticals. Another potential future direction is transitioning from laboratory-scale experiments to large-scale applications, such as in wastewater treatment plants.

A critical consideration for the future is the recycling and end-of-life handling of these materials. While these materials are recyclable and can remove pharmaceuticals, it is important to investigate the reuse potential of the captured pharmaceuticals. As demonstrated in Figure 19, certain amounts of pharmaceuticals can be removed, but exploring reusability of this captured material would be advantageous.

5 Conclusions

In this work, an MXene hybrid film was successfully synthesized and fabricated using a specific synthesis route and filtration method. Various hybrid materials were tested for their efficacy in removing pharmaceuticals from water. After several trials, the MPP hybrid film showed the first preliminary success in pharmaceutical removal. The TMPyP content in the MPP hybrid film was optimized to ensure that excess TMPyP did not appear in the UV-Vis spectra. The optimal MPP5 film was tested in three different conditions: at room temperature and light, under halogen lamp, and in the dark. In all three cases, pharmaceutical removal was successful and highest removal observed under the halogen lamp, likely due to the photocatalytic performance of TMPyP.

The MPP5 hybrid film was characterized using several techniques. XRD analysis indicated an increase in interlayer spacing when TMPyP was added. SEM images supported this finding. Raman spectroscopy revealed that the functional groups present in MXene was the -OH_2 group. FTIR analysis showed the disappearance of these functional groups upon the composition of the MPP film and suggested the presence of different chemical bonds in the hybrid film. UV-Vis spectroscopy was the primary method for monitoring the removal of pharmaceuticals. Following optimization and characterization, removal of diclofenac was successfully achieved as discussed above. It was possible to cleanse the film of pharmaceuticals and quantify the extent of removal.

Overall, the goals of this work were successfully achieved. However, further optimization is necessary, particularly in understanding the kinetics of the removal process. Additionally exploring the reuse potential of removed pharmaceuticals should be considered for future research.

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