ADSORPTIVE MEMBRANES FOR THE REMOVAL OF ANTIBIOTICS FROM

PHARMACEUTICAL WASTEWATER

by

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Declaration of Authorship

I declare that this thesis is my own work and, to the best of my knowledge and belief, it does not contain material published or written by a third party, except where permission has been obtained and/or appropriately cited through full and accurate referencing.

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Dedication

I dedicate this work to my beloved parents and family who have always been by my side.

Abstract

Adsorptive membranes are considered among the promising technologies that have shown competence in removing different pollutants from wastewater. They possess the dual advantage of adsorption and filtration. Pharmaceutical compounds including antibiotics are emerging contaminants of major concern because they cannot be fully removed via conventional wastewater treatment methods. Therefore, there is a crucial need for an effective technology such as the adsorptive membrane technology. In this work, an adsorptive membrane composed of Polyethersulfone (PES) with Zirconium Phosphate (ZrP) adsorbent was synthesized for the removal of Ciprofloxacin antibiotic from synthetic water solutions. Batch adsorption experiments using zirconium phosphate were conducted first to determine the optimum conditions for the antibiotic removal. Several factors were studied including the initial concentration of the antibiotic, the adsorbent dosage, contact time, pH, and temperature. The experimental data were best fit by the Temkin isotherm. Based on the adsorption batch results, the PES/ZrP membrane was synthesized by solution spin coating and tested with various adsorbent loadings to investigate the optimum ZrP loading in the membrane. The composite membrane showed a high ciprofloxacin removal reaching up to 99.7% which indicated an enhancement compared to the use of PES membrane alone (68%). Moreover, a significant improvement in the membrane's water flux (100.84 L/m^2.h) and permeability (97.62 L/m^2.hr.bar) were noticed as opposed to pure PES membrane's flux and permeability. Several characterization analyses were conducted including SEM, EDS, FTIR, XRD, and BET, which demonstrated the successful ZrP deposition in the membrane's pores with enhanced hydrophilicity properties and effective surface area. Lastly, the membrane was successfully regenerated and reused up to 5 times which indicates the potential of PES/ZrP adsorptive membrane for the removal of ciprofloxacin and at a high efficiency.

Keywords: Adsorptive membranes, wastewater treatment, pharmaceuticals' removal, antibiotics.

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List of Abbreviations

AFM	Atomic Force Microscopy
AM	Adsorptive Membrane
BET	Brunauer-Emmett-Teller
CPFX	Ciprofloxacin
DFUF	Dual-functional ultrafiltration
EDS	Energy Dispersive X-Ray Spectroscopy
EDTA	Ethylenediaminetetraacetic acid
FMWCNTs/CS	Fibrous mulit-walled varbon nanotubes/chitosan
FTIR	Fourier transform infrared spectroscopy
MF	Micro-filtration
MMM	Mixed Matrix Membrane
MWCNTs	Mulit-walled carbon nanotubes
OFAT	One Factor at A Time
PAN	Polyacrylonitrile
PANI	Polyaniline
PES	Polyethersulfone
PPCP	Pharmaceuticals and Personal Care Products
PVA	Poly (vinyl alcohol)
PVDF	Polyvinylidene Flouride
PVT	Polyvinyl Tetrazole
SEM	Scanning electron microscopy
UF	Ultra-filtration
UV-VIS	Ultraviolet–visible Spectroscopy
XRD	X-ray Diffraction
ZrP	Zirconium Phosphate

Chapter 1. Introduction

1.1. Introduction

In this chapter, a brief introduction about the emergence of adsorptive membranes and the reasons behind implementing this technology in the wastewater treatment field will be discussed. The main objectives of the study will be presented as well as the thesis contribution and organization.

1.2. Overview

Due to the very limited fresh water in the nature, many researches and studies are focused on purifying water and removing different types of pollutants to produce clean and safe or drinkable water. Various types of hazardous materials can present in wastewater such as heavy metals, pharmaceutical materials, dye materials, and pesticides. The emergence of such pollutants has been raised due to the growth in population globally, industrial activities, urbanization, and climate change which all contributed in water scarcity all around the world [1]. In addition, these hazardous materials cause a threat on human lives and the environment. For example, pharmaceutical waste materials affect the quality of drinking water resources, e.g. spreading antibiotic resistance, and they can be toxic to aquatic organisms [2]. As a result, many treatment technologies have been proposed to reuse and recycle such type of wastewaters, such as reverse osmosis, ion exchange, and adsorption [3]. The main challenge is removing the soluble micropollutants such as pharmaceutical compounds that cannot be easily removed by conventional techniques, e.g. coagulation and sedimentation and thus may discharge to the environment without treatment. Therefore, a treatment method like adsorptive membranes appear as a promising technology that has been receiving attention lately [1].

Adsorptive membrane is a membrane that has dual functions namely adsorption and filtration processes; in the literature, it is referred to as adsorptive filtration membrane [4]. This membrane basically depends on the adsorption process which is a mass transfer driven process in which the substances are bounded via chemical and physical interactions to solid surfaces. Adsorption is an easy practical approach to perform, offering flexibility in the design and good resistance to toxic substances. Most importantly it is a reversible process, since the adsorbents can be regenerated by

desorption processes which is considered a cost-efficient process. The effectiveness of adsorbents used depend on their morphology and chemistry [5]. As such, reserachers have been attracted to study many types of adsorbents such as nano size adsorbents and bio-adsorbents. However, adsorption surface from certain disadvantages such as agglomeration and difficulty in regeneration. For example, the most common adsorbent which is widely used is activated carbon, but it suffers its regeneration as being costly, which encouraged researchers to find alternative cost-efficient adsorbents [2].

The use of membrane technology in filtration processes has been significantly developed over the years. It is known that microfiltration (MF) and ultrafiltration (UF) can only eliminate some viruses and suspended solids, while nanofiltration and reverse osmosis can remove heavy metal ions and fluorides but result in fouling problems and high operating pressure [6]. Due to the drawbacks and high cost of conventional water purification methods, the investigation of more effective operations or even integration of alternatives has been a great area of research over the past years [5]. This resulted in the emergence of a combination between membranes and adsorption processes to overcome some of these drawbacks faced when the preceding approaches were used individually and thus exploit the benefits of both [1]. The membrane technology basically depends on three principles: adsorption, sieving and electrostatic phenomenon. The adsorption mechanism in the membrane separation process relies on the hydrophobic interactions of the membrane and the solute (analyte) [3].

Adsorptive membranes, also called modified membranes, have many advantages such as high removal rate and efficiency, low operating pressure, high permeability flux, regeneration, and less space requirements [4]. Additional characteristics may include favourable hydrodynamic, acceptable reusability, and small footprint [7]. Polymers and powders with adsorption capability are inserted in the membrane to reduce leakage and recovery problems. These adsorptive membranes are also characterized by high affinity for ions and molecules, as they combine ions by chelation bonding, complexion, or ion exchange [4]. Moreover, the large surface area and redundancy of adsorption sites are important factors for the efficiency of adsorption and removal of pollutants from wastewater. For instance, cellulose acetate/Mg-Al layered double hydroxide nanocomposite adsorptive membranes were used to remove pharmaceutical compounds from wastewater such as diclofenac sodium and tetracycline [8]. Moreover, an

adsorption hybrid membrane composed of powdered activated carbon and PES membrane support [9], and PVDF membrane with carbon nanotubes layers were also used for removing pharmaceuticals [10]. Such reported experiments in literature which discusses the effectiveness of this technology, shows the promising potential of implementing adsorptive membranes.

1.3. Thesis Objectives

The main objectives of this thesis are outlining and presenting the mechanisms, synthesis, types, and various applications of adsorptive membranes. Applying this technology is a broad topic that needs thorough understanding before presenting the essential aim of the thesis, which is implementing it in the removal of pharmaceutical compounds from wastewater. Removal of pharmaceutical materials using adsorptive membranes has not been studied or investigated extensively before as the conventional methods. Therefore, the main objectives of this thesis are:

- Studying the removal of Ciprofloxacin from wastewater as a model for pharmaceutical compounds using Polyethersulfone membranes, and Zirconium Phosphate as an adsorbent by performing batch tests.

- Developing a synthesis procedure for adsorptive membranes.

- Testing the potential of using PES/ZrP adsorptive membranes for the removal of pharmaceutical compounds from wastewater.

- Characterizing the synthesized PES/ZrP membrane and the pure PES membrane by different analyses such as: SEM, FTIR, XRD, and BET.

- Applying analytical techniques and different isotherm and kinetics' models to describe the adsorption process.

1.4. Research Contribution

This research work has contributions in the filed with regard to the following aspects:

- Helping understand the importance of removing emerging contaminants from wastewater, and the need of clean drinkable water sources.

- Providing information regarding adsorptive membrane technology, their working mechanisms, and fabrication techniques.

- Discussing the different applications of using adsorptive membrane and the advantages this technology may bring.

- Proposing an alternative technique for the removal of pharmaceutical materials from wastewater by using PES/ZrP adsorptive membrane after synthesizing it in the laboratory.

- Comparing the use of adsorptive membrane technology with adsorption and membrane filtration processes performed separately.

- Presenting challenges and future outlooks.

1.5. Thesis Organization

After this introduction, Chapter 2 provides background information and literature review about adsorptive membrane mechanisms, different applications, and various fabrication techniques. In addition to reviewing some conventional methods for removal of pharmaceutical compounds from wastewater and their limitations that directs the attention towards adsorptive membranes utilization. Chapter 3 presents the materials and instrumentations used throughout the experimental work, in addition to the experimental set-up and procedures followed in batch adsorption tests and adsorptive membrane synthesis and testing. Furthermore, chapter 4 presents the results obtained from the various tests and analyze them with giving the appropriate explanation based on literature review. This chapter is divided into several sections that includes batch adsorption results' analysis, adsorption isotherms, membrane analysis, and membrane characterization such as XRD, FTIR, BET, and SEM. Finally, conclusions are provided in chapter 5 with essential recommendations that would be beneficial for future work.

Chapter 2.   Background and Literature Review

In this chapter, a general overview about adsorptive membranes is presented. This helps understanding their mechanisms toward removal of pollutants specifically removal of pharmaceutical materials. Also, the different types of adsorptive membranes will be discussed based on their classifications, and their various applications in removal of metals, dyes, and pharmaceutical compounds. Moreover, this chapter also presents the main fabrication techniques of this type of membranes, and the challenges faced accompanied with future outlooks.

2.1. Mechanism of Solutes Removal by Adsorptive Membranes

Generally, the removal of solutes from wastewater by adsorptive membranes consists of two mechanisms: rejection and adsorption. Once the water-containing solutes comes in contact with the active layer of the membrane, the solutes with sizes greater than the membrane's pore size gets rejected by molecular sieving and do not pass. The solutes that have smaller sizes will pass through the active layer and get attached to the support layer which acts as microspheres adsorptive material. They will then react/attach and create a tight internal complex and produce a permeate of filtered water from adsorptive membrane that satisfies the required standards [6]. Thus, the system can differentiate both small and large solute molecules. For instance, in a study done by Xuan Zhang [6] arsenic contaminants were removed from aqueous solution by an adsorptive polymeric membrane with iron oxide (Fe_3O_4) microspheres installed in the support layer. The small sized arsenic metal ions pass through the membrane layer, get to the support layer, and attached to the Fe_3O_4 to form a tight internal spherical complex. As a result, filtered water permeate is produced. This process is illustrated in Figure 2-1.
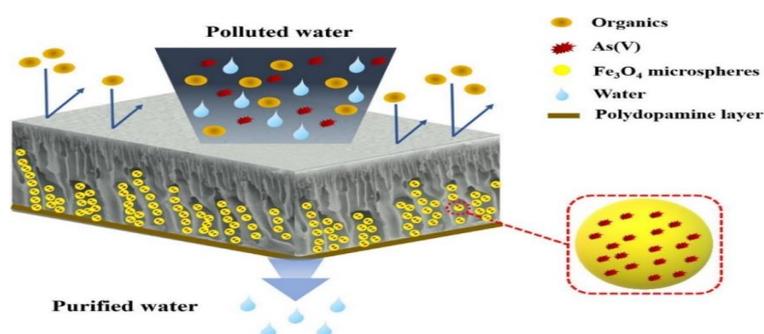
Figure 2-1: Removal of various pollutants by adsorptive membrane [8]

Most commonly, MF and UF membranes are chosen because of their high permeability of water, low pressure requirement, and low cost. It was observed that enhancing the performance of the membrane can be done by increasing the functional adsorption sites reasonably. Therefore, adding hydrophilic nanoparticles can enhance the water flux efficiently [6]. However, addition of nanoparticles should not be done excessively to avoid damaging the membrane's structure and hindering its performance. It is thus usually recommended to have less than 6 wt% of the adsorbent in the membrane matrix [6].

2.2. Classification of Adsorptive Membranes

Adsorptive membrane technology can be an economic and efficient method for the treatment of different wastewater contaminants. More specifically for those contaminants which their removal efficiency depends on surface interactions controlled by the functional groups on the adsorbents' surface. The preceding properties play a crucial role in determining the capacity, efficiency, selectivity, and reusability of the adsorbent [11]. Hence, there are various types of adsorptive membranes, including the ion-imprinted membranes, where a particular ion is added as a template and then eluted out in the preparation procedure of the membrane. Other types of membranes include polymer or inorganic particles in the matrix and called mixed matrix membrane (MMM). Adsorptive membranes are also found in ultrapure water production, and sulfur removal from fuel [4]. The pore size of adsorptive membranes is in the range from nanofiltration to microfiltration scopes. The adsorbents used that have high adsorption capacity usually include hydroxyl, amino, carboxyl, and sulfonic groups [4].

Adsorptive membranes can be classified either based on the preparation technique used to add the adsorbent to the membrane or based on the location of the adsorbent.

- **Classification based on polymeric type**

Polymeric membranes are commonly utilized in microfiltration, ultrafiltration, and nanofiltration due to their low cost and ease of fabrication. This is a promising technology, however, commercialize practical adsorptive membranes are very limited and restricted to such inactive polymers as nylon, polyethylene, and polypropylene. Therefore surface modification is needed to prepare the inert polymer, which can be done by the addition of inorganic and organic adsorbents to enhance their affinity

toward contaminants [12]. The organic adsorbents are introduced into the membrane by grafting, blending, and assembling, while the inorganic adsorbents are added directly or after modification [4]. These methods are used when dealing with the reactive monomers such acrylamide, acrylic acrylonitrile, acid, and those having the epoxy group. Other methods may include the attachment of several dye chemicals to the hydrophilic polymeric membranes such as polyvinylbutyral and cellulose acetate membrane [12].

Natural Polymers

Biopolymers or natural polymers are among the major materials used in adsorption of dyes, heavy metal ions, and other contaminants, even at low concentrations. They are fabricated using renewable and biodegradable materials due to the presence of nitrogen and oxygen in their chemical structure [13]. For example, chitosan which is a polysaccharide biopolymer with high content of hydroxyl and amine functional groups derived from chitin, a natural biopolymer available in crustaceans shell, is widely used in adsorptive membranes. Its privilege comes from the high binding capacity, ease of accessibility, and unique properties [5]. The main advantageous properties of chitosan are its degree of acetylation, solubility, molecular weight, biodegradability, and various bioactive aspects [14]. Its main drawback is the low solubility when using it in an aquatic environment with a pH less than 6.5. Therefore, some reagents such as glyoxal and formaldehyde can be used as cross-linkers to prevent any solubility problems and enhance the mechanical characteristics of chitosan as a sorbent. Using chitosan-based membranes is a common practice as it is the most preferred method of adsorption due to excellent kinetics, improved reusability, and practicality of scaling up [5]. It has an excellent performance in heavy metals removal from wastewater because of the amine functional group that forms surface complexes with several metal ions [15].

Many previous studies used chitosan as powders, flakes, or gel beads forms [16]. However, chitosan membranes was also prepared as flat or hollow fibers form for adsorptive separation purposes, but yet preparing pure chitosan membranes is a challenging issue and have limitations because of its poor mechanical strength and chemical stability [17] [18]. In order to improve the mechanical resistance of chitosan flat membranes, chitosan can be applied as thin film composites to act as a good support or can be embedded in compatible nano biomaterials [5]. Moreover, other drawbacks

are attributed to the coating process, which could be be either nonuniform or incomplete coating or non-stick coated chitosan. As a result, mixing other polymers with chitosan can be considered to overcome these issues and enhance the chemical stability and mechanical resistance [12].

Synthetic Polymers

Polyacrylonitrile (PAN) is considered one of the preferred synthetic polymers used for manufacturing of UF and MF adsorptive membranes due to their cost-effectivity, outstanding solvent stability, and great mechanical resistance. This membrane can be synthesized by many methods. Some researchers successfully fabricated an adsorptive ultrafiltration membrane from synthesized polyvinyltetrazole-copolyacrylonitrile (PVT-co-PAN) using the non-solvent induced phase separation technique [19]. It has been proven that addition of PVT can change the pore size, charge, and hydrophilicity of the membranes [18]. Thus, PVT makes the membrane more hydrophilic and negatively charged.

Other synthesized polymers used in blended membranes include polyurethane with cellulose acetate, which were typically used for removal chromium (VI) from aqueous solutions [19]. Cellulose acetate is a common filtration membrane due to its hydrophilic nature, good fouling resistance, and cost efficiency [20]. Some disadvantages of using cellulose acetate-based membranes attributed to the low chemical, mechanical, and thermal strengths. These properties can be improved by using polyurethane which provides good mechanical, chemical and thermal features. This polymer is a heterogeneous matrix consisting of an alternating array of soft and hard sections. The soft parts are flexible and soluble in water like polyether polyols, while the hard parts are rigid and non-soluble in water [21]. As a result, the synthetic polyurethane-cellulose acetate blend membrane appeared to be an effective costly and efficient material for removal of contaminants from water. The scanning electron microscope (SEM) micrographs for this membrane is shown in Figure 2-2 which indicates spongy structures that partly packed with dense cellulose acetate having various pores on the surface which facilitates the water flux rate [22].

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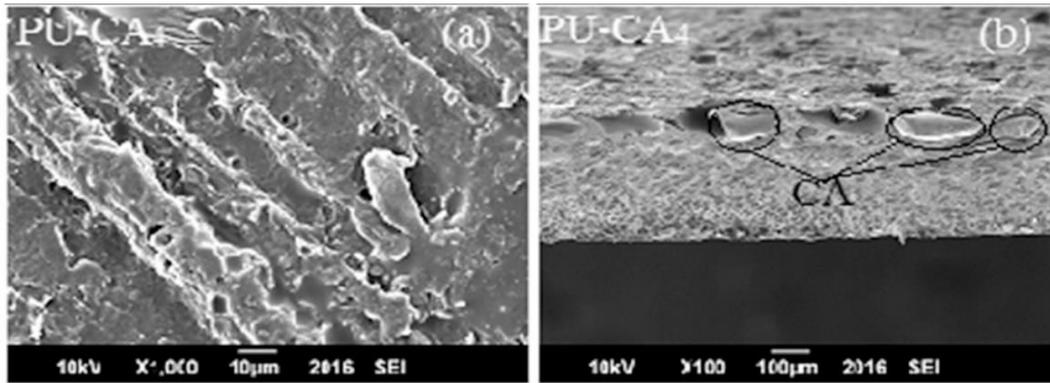
Figure 2-2: SEM images of PU-CA blend membranes [21]

Polyethersulfone (PES) is a widely used commercial material in manufacturing polymeric membranes due to its several outstanding characteristics including superior chemical and thermal stability, excellent mechanical strength, and applicability in a broad range of pH (2–12). On the other hand, despite all the wide uses of PES it has some disadvantages such as fouling issues caused by nonpolar solutes adsorption, and hydrophobic particles or bacteria which leads to shorter membrane lifespan. In addition to other problems like biocompatibility associated with aggregation, and its inert state in water. Therefore, membrane modification of common polymers or membranes to produce adsorptive membranes would be a reasonable alternative to overcome such constrains [23].

In the recent decades, significant attention on developing polymeric nanocomposites have increased, where the size of the filler material is in nanometres [24]. However, the composite is not necessarily in nanoscale, as it can be micro or macroscopic. Such advancement resulted in exceptional combination of the nanomaterial's properties which include the size, mechanical traits, low concentrations required to effect change in polymeric matrix, and ease of manufacturing since they can be manufactured as conventional polymer composite. Nanocomposite technology shows significant improvements in biodegradability, and great enhancement in mechanical, thermal, and electrical characteristics. However, implementing nanotechnology in mixed matrix membranes manufacturing has some challenges including the strong possibility of fine particles to agglomerate, and the difficulty in determining the composition, strength, and functionality of the interfacial area. Also, during the degassing process, the air might get entrapped while pouring the highly viscous material in the mold [24] and thus

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affect the structure of the material. Therefore, this technology has the potential to be a promising method in the adsorptive membrane field but still requires further investigations to benefit in water purification applications due to the above constrains.

Using nano-adsorbents is a promising technology for solutes removal with low molecular weights caused by the high surface area, plentiful adsorption sites, and fast kinetics [25], [26]. Nevertheless, nanoadsorbents are made as fine powders which results in such issues in separation processes as regeneration, high cost and some potential toxicity troubles from leaching into water bodies [27]. Combining the advantages of nano-adsorbents and UF membranes and overcoming their disadvantages in water purification remains a challenging issue. Furthermore, several nano-adsorbents have been studied to modify polymeric membranes, such as MWCNT, PANI/Fe$_3$O$_4$, graphene oxide nanoplates, and activated carbon [28], [29], [30], [31].

- **Classification based on adsorbent type**

Adsorptive membranes are also classified into four main categories depending on adsorbent type within the membrane. These are mostly under the category of mixed matrix membranes (MMM).

The MMM is the most common types of adsorptive membranes due to the ease of its preparation and method of adsorbent agglomeration and lumping when its content is high within the membrane matrix. In general, adsorbents in a polymer matrix type possess a lower adsorption capacity and a longer equilibrium time [4]. The MMM is a hybrid type of membrane developed from the single polymer membranes in which an inorganic material is fixed with the polymer matrix. The MMM can have selective separation and filtration ability to remove suspended materials, microorganism, micro-contaminants in one step [32]. The MMM of silica, polysulfone, and cellulose acetate was used to remove silver ions [33]. membrane was used Removal of lead and nickel cations was considered using zeolite nanoparticle infused onto polysulfone membrane by hydrothermal process [34]. Thus, in principle these hybrid membranes are based on mixing the inorganic materials acting as adsorbents to the polymer membrane by certain methods. For example, two preparation techniques including the immersion of pre-treated polyvinylidene flouride (PVDF) films in zinc oxide (ZnO) suspension, and blending the ZnO nanoparticles with PVDF solution before the casting films process

have been investigated [35]; the immersion method requires the need of surfactants as a pre-treatment of the PVDF films.

Polysulfone is a well-known polymer used in preparing the MMM polymeric membranes due to its bright properties including the low cost, high mechanical strength, stabilitiy, wide range of operating pH, practicality, and diversity of active functional groups. Usually, polysulfone is combined with nanomaterials or ceramic materials to enhance the properties of the membranes. For example, organoclay embedded polysulfone nanocomposite membranes were used for arsenate ion (AsO_4^{-3}) removal from polluted surface water [36]. This resulted in significant enhancement of pure water flux, roughness, surface hydrophilicity, and mechanical strength of the membranes which increased with increasing organoclay concentration from 0 to 2.0 wt% [36].

It is important to mention that fabrication of mixed matrix membranes requires an inorganic additive to the matrix in order to boost the selectivity of the membrane in the direction of a targeted species, reducing fouling, and increasing hydrophilicity. However, these additives should be selected wisely to avoid cost burdens or complexity in the manufacturing. As a result, selection of inorganics additives is based on their performance, size, complexity in production, and cost. Moreover, the selection of base polymer also plays a vital role in the performance of the membrane. As Polysulfone (PSF) is a thermoplastic polymer that is characterized by toughness and good stability at elevated temperatures, Polyvinyl-pyrrolidone (PVP) on the other hand is a pore former which enhances diffusion and increases the mechanical stability [37],[38]. Therefore, they are more suitable candidates to be used as base matrix with additives.

Mixed matrix membranes propose alternate materials that merge both promising selectivity benefits of the inorganic particles and economical capabilities of polymers. Several studies have been conducted to predict the MMM performance based on the ideal and the non-ideal models [39]. The ideal morphology model is composed of a system with two phases, with the inorganic fillers and the polymer matrix present without defects or distortion at the interface. However, it is hard to achieve this ideal model due to the imperfect filler−polymer adhesion that resulted in imperfect morphologies or three-phase systems. These membranes contain organic−inorganic interface flaws. Interface defects have three major categories: interface voids, rigidified polymer layer around the inorganic fillers, and particle pore blockage. As the polymer's

chains cause clogging and blockage of the filler pores which prevents the passing of the material to be purified [39]. The models should be able to evaluate the permeability and selectivity for MMM morphologies. Other important parameters that affect the functioning of the mixed matrix membrane include: the particle pore size and distribution, particle dispersion, polymer characteristics, and interactions [40]. Figure 2-3 shows the comparison between the ideal MMM model structure which has the dispersed phase and the polymer matrix and the nonideal structure.
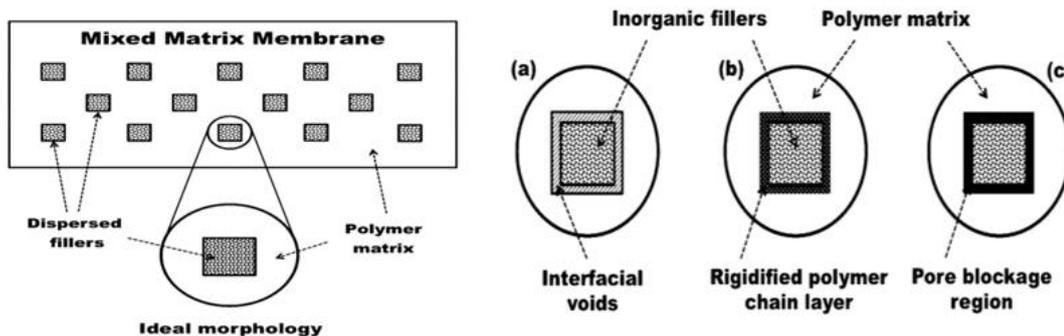
Figure 2-3: Schematic diagram with ideal and non-ideal MMM structures [41]

In mixed matrix membranes, the polymer is the continuous phase, and the inorganic filler is the dispersed phase. The polymers in the continuous phase are typically characterized by their glass transition temperature and polarity, while the selection of the dispersed phase depend on the pore size, structure, and surface polarity. Block copolymers type is generally preferred as it offers advanced function and nanostructured membranes [41].

Depending on the physical state of the polymer, the MMMs can be also classified into three main categories, namely solid−polymer, liquid− polymer, and solid−liquid−polymer mixed matrix membranes. Solid−polymer MMMs are the most common type, in which zeolitic and nonzeolitic inorganic materials are used as fillers [40]. Zeolites are porous crystalline silicates with a complex crystallographic structure giving rise to specific molecule-sized pores [42]. Zeolitic MMMs can be fabricated using rubbery and glassy polymers as a polymer matrix. On the other hand, carbon molecular sieves, nonporous and porous silica nanoparticles, and metal oxide nanoparticles are known types of nonzeolitic fillers. Due to the recent advancements, many alternative fillers have emerged like: carbon nanotubes, graphene, layered silicates, and metal organic frameworks (MOFs) with numerous desired properties [40].

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A new review by Yin and Deng [43] specified four types of MMMs depending on the structure and filler location in the hybrid membrane structure; these include thin film nanocomposite, conventional nanocomposite, thin film composite with nanocomposite substrate, and surface located nanocomposite. In this context, the MMM will be discussed based on their filler type. In this regard, MMM have four main categories: inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs and hybrid filler-based MMMs [44].

Inorganic filler based MMMs

In this case, the inorganic fillers get attached to the support materials via covalent bonds, i.e. van der Waals forces or hydrogen bonds. These fillers are made via such processes as sol gel, ion sputtering, thermal plasma synthesis, flame synthesis, mechanical alloying/ milling, and electrodeposition. These adsorptive materials significantly improve the performance of the membrane. For instance, it was shown that the addition of ZnO particles in polyether sulfone (PES) membranes improved dye rejection from 47.5% to 82.3% [45]. Also, Goh et al. [46] added graphene oxide layers on polyamide imide (PAI) or polyether imide (PEI) hollow fiber membrane through the instant dip coating technique; such material was used for removal of salt and divalent ions from water. In addition to using it with PES membranes as nanoplates for the removal of dyes with a rejection of 99% [30]. The high efficiency is attributed to the improved hydrophilicity because of the acidic groups (e.g., carboxylic acid and hydroxyl) affixed on the surface accompanied by adding graphene oxide to the polymer membrane [44]. The advantages of using this type of adsorptive membrane include improving flux, selectivity [47], disinfection purposes, and preventing membrane fouling [44]. Carbon nanotubes and metal organic framework as polymer fillers were also investigated due to their high porosity, and good thermal and chemical resistance [48].

Organic filler based MMMs

These advanced adsorptive membranes contain organic fillers such as cyclodextrin, polypyrrole, polyaniline (PANI), and chitosan beads, which can be added by the methods of blending and phase inversion. They are more preferred than the inorganics one as they have more functional groups which make them adaptable and capable to

attach to the substrate through chemical reactions. Moreover, they successfully bound themselves with hydrophobic surfaces producing antifouling, highly hydrophilic adsorptive membranes. For example, PANI nanofibers were blended to produce synthesized nanocomposite membrane in polysulfone polymer with superior permeability, antifouling capacity, and water flux [49]. This type of membrane was successfully applied in the removal of the protein Bovine serum albumin from water [49].

In addition, an adsorptive membrane was prepared from blended β-cyclodextrin polyurethane into polysulfone matrix for removal of Cd^{+2} ions from water. The addition of this organic filler to the membrane increased the permeability by facilitating wider pores on the surface, greater hydrophilicity, and higher cadmium rejection that reached up to 90%. However, some drawbacks were reported in this technique due to the rougher and less mechanically stable mixed matrix membrane [50].

Biomaterial-based MMMs

Using biomaterials in adsorptive mixed matrix membrane is considered a new technology that has shown promising results due to high permeability, antifouling property, and mechanical reinforcement effect. Several biomaterials were considered for the removal of several pollutants from wastewater. For example, aquaporin filler in amphilic triblock polymer vesicles were investigated for the removal of urea, glucose, glycerol and salt from water [51]. The use of plant waste as biofiller in polyethersulfone to produce an adsorptive mixed matrix membrane used for the removal of cationic dyes from water was reported [52]. Three kinds of plant wastes, including tea waste, banana peel, and shaddock peel were used with a rejection that reached up to 95%. These biomaterials incorporation in membranes resulted in increasing the membrane's porosity to 80–85% and the thickness of the membrane in comparison with pure PES membrane. Consequently, this adsorptive membrane removed the cationic dyes efficiently from water with excellent membrane reusability by obtaining high dye recoveries. This study's adsorption performance can be maintained in a larger membrane scale with dead-end operation [52].

Hybrid filler based MMMs

Hybrid filler based MMMs represent the latest mixed matrix membrane technology where two fillers (independently or in composite) are added to the continuous phase. For instance, Daraei et al. [29] studied the combination of iron (II, III) oxide and polyaniline in polyethersulfone matrix to achieve 85% of Cu (II) removal from water with excellent reusability and durability. In addition, the novel hybrid material chitosan-montmorillonite was injected in the polyethersulfone matrix as nanosheets and was used for the removal of dyes from wastewater discharge; the system resulted in high flux recovery that reached about 92% and enhanced mechanical properties [53].

As mentioned earlier, to maintain the UF performance, nanoadsorbents content in the matrix should be less than 6 wt% to prevent the formation of leaky interfacial voids and defects. However, the main problem was the unsatisfactory adsorption capacity. Another issue for the mixed matrix membrane was the rigidified polymer layer covering the surface of nanoadsorbents, which may decrease the number of adsorption active sites and thus hinder the performance [54]. The preceding problems led to developing other type of adsorptive membranes following their preparation techniques, these membranes are discussed below.

2.3. New Trends on Adsorptive Membranes Preparation Techniques

- **Pore-filled adsorptive membrane**

This type was developed to overcome the disadvantages of the mixed matrix adsorptive membrane (MMM). It basically depends on trapping nanostructured adsorbents into the finger-like pores of UF membranes, instead of blending the membrane matrix. This technology proven to result in simultaneous removal of several contaminants from water due to the dual functions of rejection and adsorption. For instance, $Zr(OH)x$ nanospheres were added to the finger-like pores of polyethersulfone membrane preserved by polydopamine coating [54]. This membrane showed good adsorption efficiency for lead ions. Moreover, it showed ease in reusability and regeneration with no comprising in the mechanical strength, yet lower permeability than MMMs [54]. This adsorptive membrane was synthesized by two processes. Firstly, the hollow porous nanospheres were inserted in the finger-like pores during reverse filtration, and secondly the polydopamine coating which was used to seal it in the cavities of the UF

membrane. This results in a membrane with adsorption ability and ultrafiltration properties [54]. Figure 2-4 compares schematically the blend membrane formed from nano adsorbents embedded in the membrane matrix, and the dual-functional ultrafiltration (DFUF) membrane of the type pore-filled adsorptive membrane.
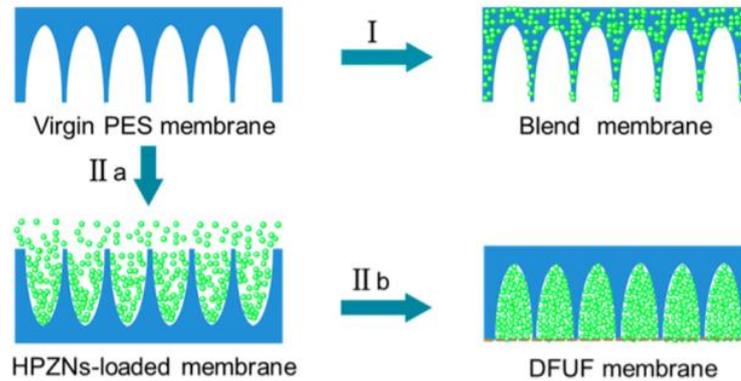
Figure 2-4: Schematic representation of the novel adsorptive membrane types [55]

- **Surface adsorptive membrane**

Surface adsorptive membranes are the membranes in which the adsorbent particles are added to their surfaces by different means and depending on this method of fabrication they can be furtherly subcategorized into four types. These methods include coating, depositing, grafting, and assembling. They are characterized by excellent adsorption capacity and short equilibrium time [4].

The surface coated adsorptive membrane is prepared by two steps. Firstly, the adsorbent particles get stacked on the membrane surface by dipping and filtering, then coated by the polymer layer by crosslinking or coating [55]. This may provide better adsorption capacity and contaminants removal efficiency than MMMs. It also called the sandwich structure [56]. On the other hand, the surface-deposited adsorptive membranes can be produced by filtration deposition which can produce a highly ordered layered graphene oxide membrane [57]. In addition, the hydrothermal technique can also be applied in the deposition of zeolite on ceramic membranes [58], while the vapor deposition polymerization method can be used to immobilize Polyrhodanine on the inner surface of anodic aluminium oxide membrane [59].

The surface-grafted adsorptive membranes are fabricated by grafting or by the photo-induced postsynthetic polymerization technique which relies on immobilizing the

adsorbents on the membrane surface by a covalent link. The photo-induced postsynthetic polymerization method has advantages such as enhancing the chemical and physical interface interactions between the material and the membrane. While avoiding the formation of voids is a big challenge in MMMs. This type of membrane was studied for the removal of Cr(VI) from water; the results showed improved interaction between metal-organic framework particles and the polymer chains in the membrane [60]. However, it suffers limitations in applications, complications in the process, and harsh reaction conditions [4].

The surface assembled adsorptive membrane is fabricated by assembling polyelectrolyte using electrostatic interaction. This technique depends on alternating electrostatic adsorption of polyanions and polycations onto porous substrates utilizing the layer-by-layer approach [61]. For instance, polyethersulfone ultrafiltration membranes can be modified by a thin polyelectrolyte multilayer film via varying deposition of poly(allylamine hydrochloride) and poly(acrylic acid) [61]. This type can suffer from detachment of the assembly layer during functioning which is also a drawback of the surface-deposited adsorptive membranes [4]. To sum up the adsorptive membrane types mentioned, Figure 2-5 illustrates schematic representation of the way the adsorptive material is added to the membrane.
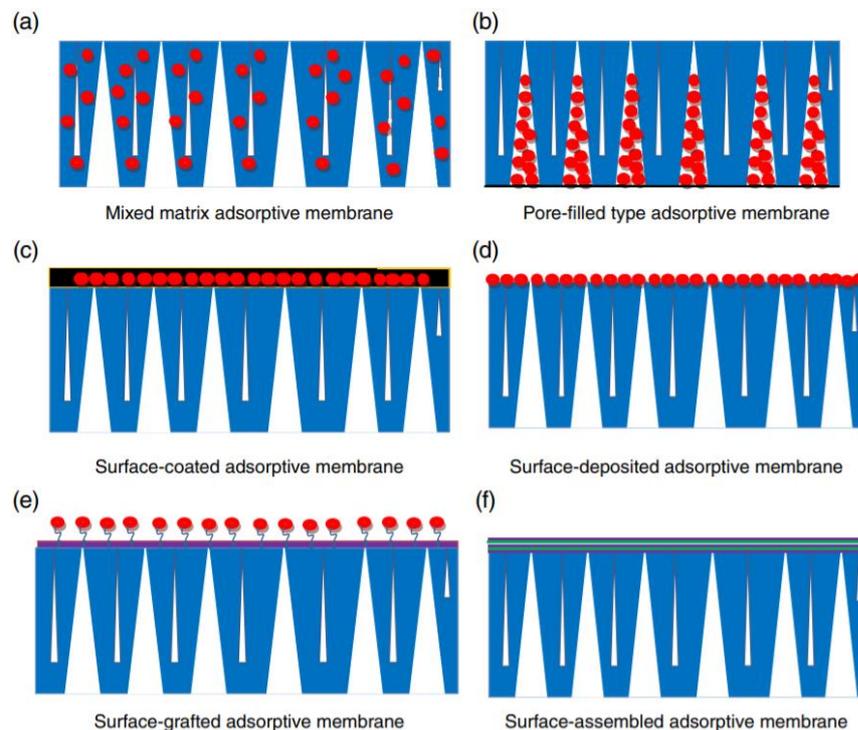
Figure 2-5: Schematic representation of types of adsorptive membranes [6]

2.4. Applications of Adsorptive Membranes

2.4.1 Removal of dye materials

Dyes are chemical compounds that can get attached to surfaces or fabrics to impart colour. Many types of synthetic dyes have industrial extensive applications such as textile, plastic, paint, paper, printing, food processing, and cosmetic industries [62]. There are more than 100,000 distinct types of dyes produced with more than 100 tons/year discharged in water streams globally [63]. Therefore, the wastewater containing dyes needs to be treated as they are toxic, carcinogenic, and poses a serious hazardous threat to aquatic living organisms and humans [64]. The conventional treatment methods typically in practice are physico-chemical processes that employ adsorption, oxidation [65], and chemical precipitation [66]. Coagulation, biological oxidation, and membrane filtration are also used but each method has its limitations and drawbacks in application [64]. These drawbacks can be avoided by the use of adsorptive membranes.

The attention is directed on using biosorbent materials due to their lower cost, as they can be obtained from renewable resources, and they are environmentally friendly [67]. For instance, Chitosan-based membranes are being extensively investigated, due to its hydrophilicity, biodegradability, and high affinity to dyes and some metal ions [68]. Examples of applying adsorptive membranes for the removal of dyes include: the removal of Bezactiv Orange V-3R dye with a chitosan membrane with montmorillonite (MMT) filler which is a clay mineral characterized by good biocompatibility, biodegradability, and excellent mechanical properties [69]. The results showed that the adsorption increased with increasing the content of MMT in the membranes [70]. Similarly, Reactive Black 5 and Reactive Red 49 dyes were removed by a nanocomposite adsorptive membrane based on chitosan–montmorillonite nanosheets added to the polyethersulfone membrane matrix. It is a hybrid type adsorptive membrane with a finger-like structure that showed excellent performance, excellent hydrophilic nature, competent mechanical strength, and great thermal stability [53].

The main attribute of the adsorption depends on surface interactions, thus the functional groups on the adsorbent surface play significant part in this adsorption process. For instance, Polyethersulfone nanofiltration membranes were synthesized by blending O-carboxymethyl chitosan/Fe_3O_4 nanoparticles by phase inversion for the removal of

Direct Red 16 dye [71]. This modified mixed matrix adsorptive membrane in flat sheet form, showed greater pure water flux and permeation in comparison with the unfilled membrane. The dye removal was motivated by the negative charge of the membrane surface created from the addition of the nanoparticles in the matrix [71].

Overall, functional groups determine the effectiveness, selectivity, and reusability of the membrane produced. Also, larger surface area and adsorption sites enhances the removal of contaminants from wastewater [72]. Moreover, despite all the applications that used chitosan, it has some drawbacks like getting swollen in water and losing its physical structure, in addition to its low mechanical strength [73].

2.4.2 Removal of heavy metals

Heavy metals are dispersed in the environment by natural processes such as volcanic eruptions, erosion, agricultural activities, and industrial activities. The heavy metals present in water can have many adverse health effects on humans [74]. For example, Arsenic cause nausea, vomiting, damaged blood vessels, and abnormal heartbeat [74], while Cadmium can cause cancer, anemia, and hypertension [75]. Recently, the use of adsorptive membranes for metals removal become an efficient technique that combines many advantages such as low energy consumption, and improved permeate flux [12].

Adsorptive membranes can be modified to contain reactive functional groups such as -NH_2, -SO_3H, and -COOH groups, via ion exchange or surface complexation. These functional groups are essential for metal ions attachment, thus, removed when contacting the membrane surface regardless of the pore sizes that are larger than the metal ion size [12]. Adsorptive membranes are porous membranes with functional groups on their external and internal surfaces. The functional groups can bind with heavy metal ions by surface complexation or ion exchange mechanism [76]. This ion exchange mechanism occurs when the adsorbent has the active sites with free electrons or an electric charge after which an electrostatic interaction between the adsorbent and the substance occurs [12]. Hence, heavy metal ions are removed from the wastewater when they approach the membrane surface even if their size is much smaller than the membrane's pore size. This is a preferred technology over traditional porous membranes which remove particles by size exclusion only depending on the pores size [76].

Examples of utilizing adsorptive membranes for the removal of heavy metals include: the removal of Cd(II), Cu(II), and Ni(II) metal ions using chitosan adsorptive membranes with polysulfone polymer and applying the phase-inversion method to achieve ultra-filtration which have shown high removal efficiency [5]. Also, Copper ions were removed by a highly porous adsorptive membrane of chitosan hollow fiber membrane with cellulose acetate blended [77]. Moreover, fabricating a rougher membrane surface to increase water permeability can be achieved by adding hydrophilic nanoparticles. Abdullah et al. [78] fabricated polysulfone/hydrous ferric oxide nanoparticles ultrafiltration mixed matrix membranes for removal of lead (Pb^{2+}) from aqueous solutions. As it was shown that with increasing the loading of the nanoparticle, many characteristics were enhanced. The membrane became more hydrophilic to attract more water molecules to the surface and thus increase the permeability of the adsorptive membrane [78].

Many factors need to be considered to decide whether the adsorptive membrane is suitable for this kind of operation or not; these include the mechanical strength, water permeability, adsorption capacity, surface charge alteration, water flux, and ions selectivity. For instance, adding nano-sized adsorbents in adsorptive nanocomposite membranes showed enhancements in adsorption capacity and selectivity, and affinity for targeted metal species. However, when the loading exceeds the optimum loading the mechanical strength can be diminished [79]. Therefore, the optimum loading needs to be determined to enhance the characteristics without overdoing to avoid an opposite response [79].

2.4.3   Removal of Pharmaceutical Compounds

One of the current concerns that poses threat to humans and the ecosystem is what's called 'emerging organic contaminants' (EOCs). This term covers the newly discovered compounds in the environment such as pharmaceuticals and personal care products (PPCPs) [80]. Pharmaceuticals, as medicines or drugs, are chemical compounds used for many purposes such medical diagnosis, cure, treatment, or prevention of diseases for humans and animals [2]. These substances are the main focus of this thesis since they are an essential category of emerging environmental contaminants, which recently led to increased concerns as huge amounts are being discharged ending up in surface waters and wastewaters. These pharmaceuticals are excessively consumed by modern

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societies these days, such that they find their way to the environment through sewage treatment plants or direct discharge from the skin while swimming or bathing [81]. Many pharmaceuticals do not completely degrade after application, therefore their metabolites and unchanged forms are excreted when entering the ecosystem [82]. Pharmaceutical residues are continuously introduced to the aquatic environment as traces at very low levels in the ng L^{-1} or µg L^{-1} range [83]. This enabled the use of different technologies to detect these compounds at such levels [82]. This continuous input or inadequate removal at treatment plants shifted the focus towards this type of contaminants [81].

These pollutants have been released to the environment for so long, however the attention to their harmful effects has been brought only in the recent years. This is due to development of analytical testing instrumentation that enabled the detection and studying of such substances [84]. Many efforts have been focused on removing these contaminants as they become a public health concern affecting negatively the water quality, impacting drinking water resources, and the ecosystem [85], in addition to the potential chronic health problems related to long term consumption of mixtures of these compounds all through drinking water.

Most common pharmaceuticals

- **Analgesics/anti-inflammatories:** These are pain-relief drugs that include narcotic analgesics, non-narcotic analgesics, and non-steroidal anti-inflammatory drugs which affect the peripheral and central nervous systems to ease the pain associated with most diseases. The most common non-narcotic analgesics include acetaminophen and aspirin, while the narcotic analgesics are morphine, codeine, methadone, and oxycodone. As for the NSAIDs, ibuprofen, diclofenac, mefenamic acid, indomethacin, and naproxen are examples of this type [80]. Acetaminophen (paracetamol) is the most known non-opioid analgesic prescribed for mild to moderate pain that is usually detected in high concentrations in wastewater effluents in European countries (0.08–13.8 µg/L) [81].

- **Antibiotics:** These are antimicrobial compounds with the ability to hinder and destroy bacterial and fungal growth. Antibiotics are used for many purposes

such as treating human diseases by killing the bacterial and fungal pathogens, and alsoanimal diseases as veterinary drugs [86]. They were first introduced in the late 1930s as natural and synthetic antibiotics. This type of pharmaceuticals is called "pseudo-persistent" which means that they are continuously entering the environment with permanent presence. Antibiotics are classified into more than 10 categories like fluoroquinolones, β-lactams, aminoglycosides, macrolides, tetracycline, and sulfonamide [80]. Tetracycline (TC) is one of the most encountered pharmaceutical contaminants [8].

- **Cardiovascular pharmaceuticals (β-blockers/diuretics):** These pharmaceuticals are anti-hypertensive drugs which are used to treat high blood pressure. There are many kinds pharmaceuticals that falls under this classification such as β-blockers, calcium channel blockers and diuretics [80]. These pharmaceuticals are among the most consumed type worldwide due to the increase of this disease among individuals from different ages and genders [84].

- **Psychostimulants:** This type includes the common stimulant which is caffeine. It is a metabolic stimulant for the central nervous system to reduce physical exhaustion and promote alertness. Caffeine can easily find its way to surface water and wastewaters due to its common usage [80].

- **Estrogens and hormonal compounds:** hormonal compounds are an important class of pharmaceuticals due to their serious effects. Estrogen is either natural like estriol, estradiol, and estrone that are emitted from human beings. While the synthetic estrogen 17α-ethinylestradiol is used for contraception, it causes dangerous impacts to the environment like the feminization of male fish, changing DNA identity and immune cell number, and hinders the ability to breakdown pollutants [80].

- **Antiepileptics:** This is a type of drugs that are used to prevent sudden repetitive stimulation of the brain that triggers seizures and its complications like in epilepsy [87]. Their main function is blocking the voltage gated sodium channels or producing chemicals to stop the repeated simulation [87]. These

drugs including carbamazepine are commonly found in PPCPs wastewater effluents [80].

- **Antihistamines:** Histamine is an important chemical messenger in physiological responses, allergic inflammation, and immunomodulation [88]. Antihistamines are the medicines used to treat these effects and relieve the symptoms of allergies such as fever, rash, sneezing, and any reactions to insect bites or stings [89]. Examples of the pharmaceutical compounds in such medicines include ranitidine and famotidine [85].

- **Antidepressants:** These medications relieve symptoms of depression and anxiety disorders by adjusting the chemical imbalances of neurotransmitters in the brain responsible for mood and behavior changes [90]. An example of antidepressants is benzodiazepines [85].

Pharmaceuticals' consumption statistics worldwide

Generally, pharmaceuticals industry is a thriving sector with a growing continuous increase in consumption driven by the need to treat ageing-related and chronic diseases. In addition to the continuous development in clinical practices and science discoveries [91]. Moreover, the current lifestyle, nutrition, and modernity have resulted in a tremendous increase in many diseases like diabetes, high blood pressure, cholesterol, cancer, and psychological illnesses like depression. As a result, the market has endured a substantial growth during the past two decades with pharmaceuticals' revenues of 1.25 trillion U.S. dollars in the end of 2019 worldwide. This was a more than triple increment from 2001 [92]. In addition to the global spending estimate on medicines that experienced an increase in 2020 of 29-32% from 2015 [93]. Therefore, statistically the consumption of medicines in 2020 is estimated to reach 4.5 trillion doses, up 24% from 2015 levels. As more than half of the population over the world consume more than 1 dose per person per day in average [93]. The medicine spending in 2020 distributed by countries, product type, and disease area is shown in Figure 2-6. Furthermore, this industry is always expanding as medicines are continuously researched and developed, as in 2017 nearly 7000 medicines were under development from several categories worldwide [94]. This makes it one of the largest industries globally.

Pfizer is one of the leading companies in the pharmaceuticals industries. It is a multinational corporation headquartered in New York City established in 1849. Today, Pfizer manufactures pharmaceutical products for plenty of medical sectors such as cardiology, immunology, and neurology. In 2019, their total revenues was about 52 billion U.S. dollars worldwide [95]. This shows the great impact of this sector and how threatening the pollution that can be caused by such public consumption.
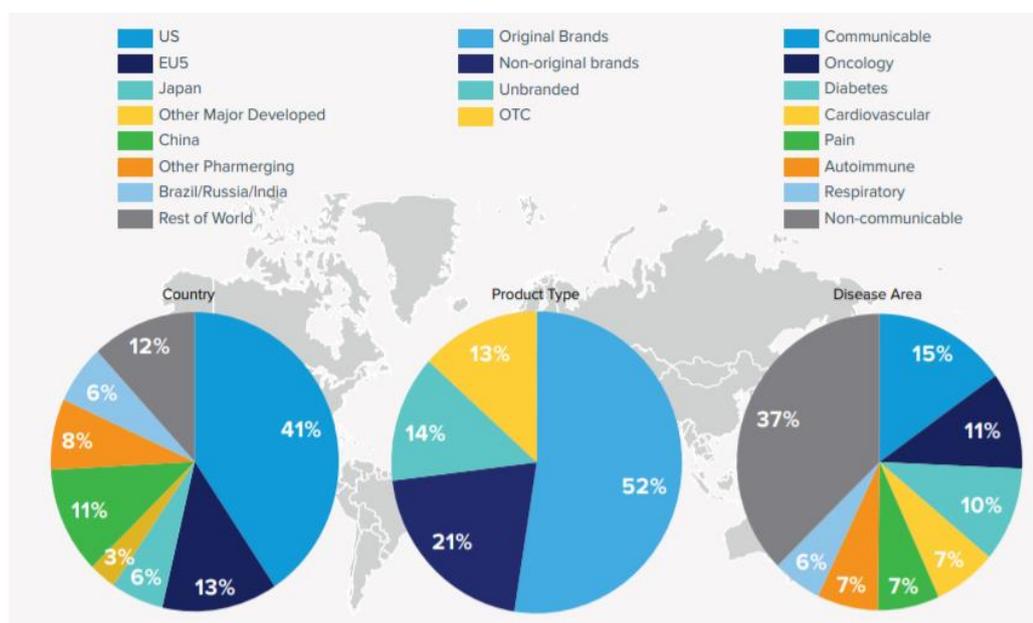
Figure 2-6: Medicine Spending by countries, Product Type and Disease Area [93]

Technological advancement and pharmaceutical detection

The sudden attention that has been brought to pharmaceuticals contamination has resulted from the advancement of technological analysis techniques. This has allowed the detection and examination of pharmaceutical traces present in water at low concentrations that was neglected before. These techniques include: Gas chromatography with mass spectrometry (GC-MS) or tandem mass spectrometry (GC-MS/MS), liquid chromatography with mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS/MS). These technologies allowed the determination of compounds to the ngram/L level in water and wastewater. The liquid chromatography analysis is effective in measuring more polar and highly soluble compounds like Tetracycline, while the gas chromatography is used for more volatile compounds like Aspirin [96].

Occurrence of pharmaceuticals

Despite the awareness and acknowledgement of this issue, most countries if not all do not have routine monitoring programs for testing pharmaceuticals in drinking water or wastewater. This is due to practical difficulties like the high cost associated with implementing such tests in reality with a large scale. In addition to the lack of available analytical equipment and laboratory infrastructure that would encompass the diverse categories of pharmaceuticals and their metabolites. Therefore, the data available for pharmaceuticals' occurrence in surface water and drinking water is usually obtained from targeted research projects and specific investigations. However, such research projects provide an estimate about the situation of pharmaceuticals presence in the environment [96].

For instance, studies has showed that Analgesic (acetaminophen, ibuprofen), and antibiotics like Ciprofloxacin had the highest occurrence in aquatic environment in countries like Spain [97]. While other studies found various pharmaceutical compounds in tap water at concentrations from ng to µg per litre in many European countries such as Italy, Germany, and Netherlands [98]. In addition, phenazone was found with the highest concentration as 400 ng/L in Berlin's drinking water coming from groundwater source that was contaminated with sewage [99]. Finally, between 15 and 25 pharmaceuticals were detected in treated drinking water worldwide, and more than that have been found in untreated water sources linked with the highest occurrence of the most consumed compounds by individuals [96].

Additionally, the level of these compounds in the aquatic environment is affected by many factors including: their consumption pattern and use, the percentage of wastewater collected, the characteristics of the processes used for wastewater treatment, and the regulations implemented. These are characteristic of each population and each country, however the consumption trend is somewhat similar worldwide as a result to the globalization of the pharmaceutical industries [97]. Moreover, the occurrence is affected by the seasonal changes in annual consumption rates and the excretion rates. These are strongly influenced by an individual's age, gender, nutrition, thyroid function, hypoxaemia, and mental state [100].

Fate of pharmaceutical compounds before entering the environment

Most pharmaceutical compounds get metabolised to phase I or phase II metabolites before leaving the body with the urine and getting exposed to the environment [101]. Drug metabolism is the chemical alteration that the drug experiences inside the body to produce drug metabolites. These metabolites can be inactive, similar, or distinct from the original drug (parent drug) when it comes to toxicity or therapeutic activity [102]. Phase I reactions are basically oxidation, reduction or hydrolysis that produces more reactive and toxic substances than the original drug. While phase II reactions involve conjugation (addition of glucornic acid, sulphate, acetic acid or amino acid) that produces inactive compounds. All these reactions alter the physical and chemical behaviour of the substances because metabolism results in more water solubility [101].

The responsible part of the body for drug metabolism is the liver that produces specific enzymes (cytochrome P-450 enzymes) that coverts the drugs to these forms to decrease its side effects [102]. This is mostly affected by the metabolic rate in humans, when it is higher the excretion rate as parent compound becomes low [100]. This is valid for pharmaceutical substances like diclofenac, ibuprofen, and carbamazepine. On the other hand, Atenolol and naproxen get excreted unchanged due to their low metabolic rate in humans [100]. As a result, not only the parent drug opposes a major concern in water treatment but also their metabolites. Moreover, this metabolic rate does not necessarily indicate the substance's lifetime in the aquatic environment, as it can have a high metabolic rate in humans but still show high persistence in water [100].

The fate of the pharmaceutical substances basically depend on what happens in the sewage treatment plants after exertion from the body. As there are three possibilities for their fate:

1) The drug or metabolites that are completely biodegradable, get decomposed by microorganisms to carbon dioxide and water like the case of aspirin [103].

2) The less persistent drugs or metabolites based on the lipophilicity or other binding possibilities like penicillin, can be degraded partially and the rest of the substance will remain in the sludge. These substances can find its way to the environment if the sludge is used for agricultural purposes [103].

3) The very persistent, polar, and non-binding to solids drugs or metabolites such as Clofibrate does not get removed by sewage treatment plants. Therefore, it reaches the aquatic environment by effluents discharged to surface water, and harm the aquatic organisms [103].

As a result, efficient treatment methods for wastewater must be found that can remove all types of pharmaceutical compounds and their metabolites to avoid their presence in the aquatic environment.

Sources of pharmaceutical compounds in water

Tests and research have reported that traces of pharmaceuticals at ng L^{-1} or µg L^{-1} levels van be found in the water cycle, including wastewater, surface waters, groundwater, and drinking-water. These pharmaceuticals threats to cause pharmacological effects due to their active ingredients [96]. Understanding the source of the problem can assist in reducing the size of the issue and in finding solutions. Human and veterinary applications are the main sources of pharmaceuticals in the environment mainly introduced by excretion followed by the transport in sewage [100]. In addition to the direct improper disposal of unwanted or expired drugs from households in the sewage without consent about the consequences [100].

Furthermore, the sources of pharmaceuticals in water are related to many industrial activities such as pharmaceutical industry waste and hospital waste disposal [85]. As waste from pharmaceutical industries disposed of at landfills, hospital effluents, and patients' exertion can introduce these compounds into the environment [101]. Besides the rapid growth that the pharmaceutical industries have been experiencing which lead to more waste and consumption [84]. Moreover, the insufficient removal from wastewater is also a source since water effluents are discharged into rivers or surface water that can reach groundwater along with drinking water via seepage from contaminated streams. In addition to sludge being used as soil fertilizer in farms, these substance can reach all environmental compartments [103]. The flow of pharmaceuticals in the environment and their different routes is demonstrated in Figure 2-7.
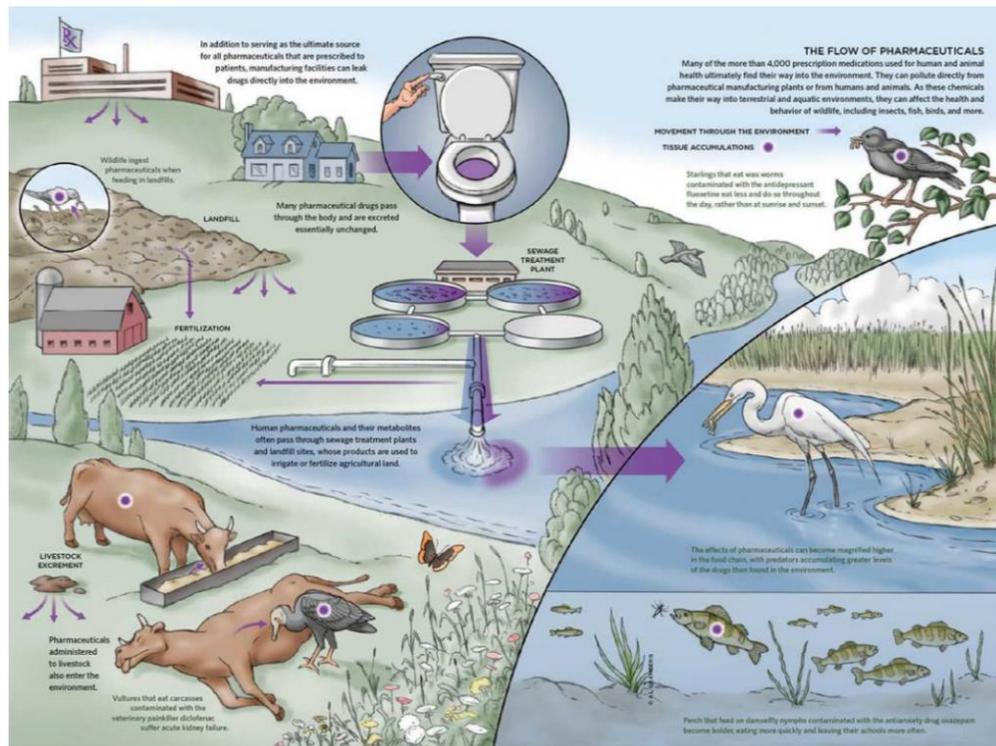
Figure 2-7: Flow of Pharmaceuticals in the environment [104]

Harmful effects of exposure

Pharmaceutical substances may be present in the aqueous environment at traces or low concentrations; however, the accumulation of these biologically active substances can find its way to potable water which can be threatening to human health. Besides being dangerous to aquatic organisms [103]. Research has shown that some of the pharmaceutical compounds are mutagenic, carcinogenic and embryotoxic [103]. Also, another major concern is bacterial resistance or antibiotic resistance. As Antibiotics are used to kill susceptible infecting bacteria, so these bacteria develop antibiotic resistance to resist the effects of the medicine and survive to infect humans [103]. Such bacteria that get exposed to antibiotics regularly tend to adjust and improve their characteristics that oppose and disable antibiotics. Generally, an increasing number of infections are not responding to antibiotics treatment like gonorrhea and urinary tract infections [105].

Moreover, exposure to pharmaceuticals from the anti-neoplastic category can possibly cause cancer at any level of exposure, as there is no threshold dose for its carcinogenic effects. In addition, the hormonal compound estrogene 17α-ethinylestradiol can cause harmful effects to aquatic life, as it causes feminization of male fish and can alter the

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DNA identity and immune cell number [80]. Likewise, pharmaceutical compounds can cause fish's nephridial tissue necrosis, influence the growth of algae and duckweed, and enhance the microbial resistance to antibiotics [106]. Hence, the U.S. Environmental Protection Agency and European Union added pharmaceuticals to their watch list for water quality [2].

Despite all that, the studies on human exposure to pharmaceuticals from drinking water are very limited due to the lack of monitoring programs or thorough investigations in that area. In addition, there are few scientific risk assessment studies regarding the exposure to low concentrations of pharmaceuticals in drinking water. However, some approaches were suggested in literature to estimate the dangers of exposure and to develop a margin of safety. These approaches include applying the minimum therapeutic dose, lowest clinically effective dose, and the acceptable daily intake along with safety factors [107],[96]. Nonetheless, WHO concluded that considerable adverse effects on humans' health due to low concentrations exposure of pharmaceuticals from drinking-water are very unlikely. As to this day, the scarce data available from research shows that the low concentrations detected are so much lower than the minimum therapeutic dose [107],[96].

However, this conclusion is not quite accurate as there is a knowledge gap due to the limited data available and lack of monitoring. As these concentrations in water are not something stable and can be easily influenced by many factors. For example, the continuous growth of pharmaceuticals consumption by societies can weaken this assumption. In addition to the lack of sufficient information regarding the effects of the metabolites and mixtures of pharmaceuticals that humans can be exposed to [107]. Furthermore, this issue should not be ignored and considerations should always be mandatory regarding the long term effects of these compounds [108].

Consequently, water suppliers must implement comprehensive risk assessments and risk management approaches that ensures water safety due to the uncertainties around these long-term effects of trace levels [96]. Besides, water quality tests and monitoring of effluents discharged to the environment must be done to protect animals and aquatic organisms. Finally, looking into advanced technologies for water treatment that would eliminate the traces of these compounds is the most practical solution that this research is aiming to achieve.

Conventional treatment techniques

The pharmaceutical industries uses the conventional term "active pharmaceutical ingredients" to define substances that are pharmacologically active, resilient to degradation, highly persistent in water, capable of causing serious effects on water organisms, and have an adverse impact on human's health [85]. They have special characteristics that differentiate them from other contaminants such as having molecular masses less than 500 Da mostly, and they can be produced by large and complex molecules that have different molecular weights, functionality, structure, and shape. Moreover, they are polar molecules having more than one ionizable group. This degree of ionization and its characteristics depend on the pH of the medium. Also, they are lipophilic, modestly soluble in water, and most pharmaceutical compounds are photoactive as they absorb luminous radiations [85].

In wastewater treatment plants, mixtures of pharmaceuticals with diverse chemical structures exist simultaneously with different removal rates based on their physiochemical properties [109]. Mostly, many substances discharged to the environment due to the inefficient removal in WWTPs. Conventional wastewater treatment facilities usually use biological degradation using the activated sludge process, while more advanced facilities have tertiary treatment processes like reverse osmosis, ozonation and advanced oxidation technologies. Yet, the treatment efficiency varies with the physical and chemical properties of these substances like hydrophobicity, reactivity towards different treatment processes, retention time, and temperature [96]. This can cause variations in the elimination rates from plant to another [110], which can limit the prediction of removal rate of different substances at different facilities.

Conventionally, pharmaceutical contaminants used to be removed from water using physico-chemical treatments with a secondary system in wastewater treatments plants that contains a biological reactor formed with activated sludge. This process can remove paracetamol, acetylsalicylic acid, and ibuprofen. However, these processes have a limited capacity as most of the compounds do not get metabolized by microorganisms as a source of carbon and can hinder the activity of these microorganisms. Sludge material that ends up in soil usually carry the less polar or nonpolar substances, while the polar substances stays in the aqueous phase. Many pharmaceutical compounds are

polar and neither volatile nor biodegradable, hence can escape sedimentation and biological treatment. Also, some are characterized with low solubility by which they can bypass the removal due to colloid-facilitated transport [100], and many are relatively hydrophilic and their sorption to sludge is limited [110]. Nonetheless, this method was studied extensively in many countries like Australia where it removed β-lactam and ultimately mineralised to CO_2 and water [111], and in France where some estrogens were removed with 90% efficiency [112]. However, the instability of the efficiencies for various pharmaceutical types makes this method incompletely reliable for the use of all the diverse categories removal.

Additionally, the removal rates of pharmaceutical compounds can vary even if the same method is used. For instance, anti-hypertensive drugs like atenolol can be removed by conventional activated-sludge process that can vary from less than 10% to 83% efficiency, while other drugs like propranolol the rates can vary between 28% and 96%. These variations between substances can be due to their relatively low biodegradation rates. As a result, it is suggested that for more effective removal rates, advanced wastewater treatment technologies such as photocatalysis can be used. Nonetheless, even though the removal can be enhanced by such techniques, they will still not be removed completely. In addition, treatment time is a major element in improving the biodegradability [84]. Moreover, high degree of persistence can be a factor of the presence of some pharmaceutical compounds in surface water[84]. This is basically related to the transportation of the chemical substance from the point of emission or source across soil layers, aquifers, riverbanks, and other natural or even synthetic barriers. As the time required for transport can vary according to persistency and mobility in the environment. This property is a main reason of impeding the filtration of such substances in water treatment facilities, as they can circulate in the water cycle and contaminate it [113].

Moving on, Adsorption is one of the most common approaches used where different adsorbents were used to remove different types of pharmaceuticals. Adsorption generally depends on sorption of solutes by solid or liquid surfaces by physical or chemical means [114]. The removal of pharmaceuticals can be achieved by adding a tertiary treatment before discharge mostly done by an adsorptive process. This method is commonly researched and suggested due to the convenience of implementing it in

treatment plants. Yet, many of the studies performed are done in a small scale and not in reality due to the latest attention given to this type of pollutants [115]. Examples of such adsorbents studied include activated carbon from lotus stalks, olive-waste cake, coal, wood, plastic waste, cork powder waste, peach stones, coconut shell, and rice husk. But, these have shown drawbacks like the uncertainties in the interactions, mechanisms, and kinetics which impedes such application on the industrial scale [85]. Other adsorptive materials include: CNTs especially multi-walled carbon nanotubes (MWCNTs), natural clay materials such as bentonite, and ion exchange materials that were also reviewed for antibiotic removal [116].

Another limitation for this conventional method includes high cost, and the difficulty associated with regenerating the adsorbent material like in the case of using activated carbon. Although showing high removal efficiencies for some compounds like nitroimidazoles (antibiotic) that reached to 90%. This was also the case for using MWCNT. Whereas using Clay minerals like bentonite (an adsorbent of aluminium phyllosilicate with has high surface area and pore volume), resulted in a reasonable removal efficiency for Ciprofloxacin of 88%. However, this incomplete removal is constrained by the sorption competition from other substances in the wastewater. In addition, ion exchange resins were also tested in which the cations or anions in the liquid are exchanged with the cations or anions on a solid sorbent to sustain electroneutrality in both phases. This has shown good results for antibiotics removal from wastewater, yet the major drawbacks were backwashing, regeneration, fouling, and irreversible accumulation [116].

Nanoparticles can also be used as adsorbent materials such as zero-valent iron that can efficiently remove pharmaceuticals like Ciprofloxacin yet was not efficient and expensive for other compounds [2]. To sum up, implementing adsorptive removal for pharmaceutical compounds in a large scale can be somehow efficient, nonetheless it has major drawbacks and limitations that can impede the practicality of the removal.

Furthermore, another physico-chemical method includes flocculation and coagulation which is a process by which the soluble or colloidal compounds are removed or suspended as a floc by using chemical flocculants or coagulants and gets settled. For instance, polyferric sulphate an inorganic polymeric flocculant was used for the removal of pharmaceuticals from wastewater. This was used for the removal of

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cefpirome, latomoxef, aztreonam, and cefoperazone where it showed an efficiency of 70% that was significantly affected by the pH of the medium. On the other hand, using this conventional method is characterized by no specificity for pharmaceuticals removal, as other pollutants will be competing in the process which can decrease the efficiency. In addition, the treatment conditions also play a major role in affecting the efficiency so the effective removal happens under specific treatment conditions, with the possibility of forming toxic by-products [2].

Other methods that have been used that are characterized as advanced methods include: ozonation, reverse osmosis, and UV irradiation. The few research done on ozonation showed effectiveness for complete disappearance of most analgesics and anti-inflammatories in secondary clarification effluent [117]. Ozonation depends on oxidation of compounds by reaction with ozone and the hydroxyl formed due to decomposition of ozone in water. However, this is a complex process as it can lead to producing oxidation products with unknown biochemical behavior [118]. Another limitation is that the reactivity of pharmaceuticals with ozone depends on the functional groups in their structure and the operating conditions. As the presence of –OH assist the ozone in degrading phenolic pharmaceuticals. This is also the case of using UV irradiation which is a disinfection process that can be used for some pharmaceuticals transformations, However, this process has shown inefficiency in the removal rates [117].

Furthermore, other processes that were studied includes reverse osmosis and sand filtration for the removal of estrogens and beta blockers (Endocrine disruptors) from raw wastewater. However, the removal efficiency using filtration was found to be less than 30%. The treatments that are based on precipitation or adsorption on suspended solid does not work on beta blockers with relatively low hydrophobicity. While for using reverse osmosis high removal rates were achieved, yet pharmaceutical traces in ng/L were detected in final effluents [112].

To conclude, there are many methods that were studied and proposed for the removal of pharmaceutical compounds from wastewater. However, all these methods have shown limitations or drawbacks that obstruct applying them in an industrial scale. In addition, some methods have shown effectiveness for some specific category of pharmaceuticals and not for others. Therefore, the need for exploring an advanced

technique becomes necessary like the use of adsorptive membranes that will be studied in the research.

Use of adsorptive membranes for removal of pharmaceuticals

The use of adsorptive membranes appears as a promising technology for the removal of pharmaceuticals from wastewater. As this technique, encompasses the advantages of using adsorption and membrane technologies with eliminating their drawbacks. Some studies have explored this technology, which this section will be reviewing. Cellulose acetate/Mg-Al layered double hydroxide nanocomposite adsorptive membranes were used to eliminate pharmaceutical compounds from wastewater [8]. It was applied to remove diclofenac sodium and tetracycline. This showed excellent adsorption capacity and better permeability than using the polymer membrane alone. Tetracycline is an antibiotic and diclofenac sodium (DS) is an anti- inflammatory drug. The use of cellulose acetate porous membrane alone showed such drawbacks as low water permeability, inadequate mechanical strength, and weakness to chemical and microbial attacks [8]. Therefore, blending or adding nanofillers have helped in overcoming these issues, since layered double hydroxides are active adsorbents with large surface areas, extraordinary thermal stability, and porosity which was incorporated by phase inversion as Mg-Al LDH inserted with sodium dodecyl sulfate (SDS) within the polymer matrix [8]. These nanocomposite adsorptive membranes proved to be more hydrophilic according to contact angle measurements with ten times increase in adsorption capacity for diclofenac sodium with respect to the original membrane. This improvement resulted from the electrostatic interactivity between the negatively charged drug molecule and the positive charged Mg-Al LDH layers, yet it was different for tetracycline as the increase was smaller due to hydrogen bonding interactions [8]. This study was inspired by the research done via layered double hydroxides being efficient adsorbents for antibiotics from wastewater. In addition to being easily synthesized in the laboratory by simple and economic techniques [119].

An adsorption hybrid membrane composed of powdered activated carbon PES membrane was used for removing pharmaceuticals that reached to a rejection of 99.8% [9]. Also, alternative adsorbent materials were studied such as biochar, clays, chitosan, agro-industrial wastes, and metal–organic frameworks (MOFs), however the removal effectiveness of pharmaceuticals depends on various factors like pH, temperature, and

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the affinity between adsorbent and pollutant [120]. Another research investigated the removal of xenobiotics which is a general classification that include numerous compound types employed in the chemical and materials industry like pharmaceuticals [121]. A polysulfone membrane was used with polyvinylpyrrolidone additives and different organic acids that increased water flux and rejection [122].

Other studies included the technology of combined adsorption and ultrafiltration membranes [123]. Combined metal organic frameworks and ultrafiltration hybrid systems were used to treat pharmaceutically active substances such as ibuprofen and 17α-ethinyl estradiol, and natural organic matter [123]. Ibuprofen is a well-known pain killer, and 17 α-ethinyl estradiol (EE2) is a synthetic hormone. Metal organic frameworks have high tunable porosity, excellent capability for pollutants removal, and decreasing fouling in adsorbent ultrafiltration hybrid membranes. Although these pharmaceutically active compounds are found at low concentrations in ground, surface, and wastewater, they are very hazardous as they reach the aquatic environments and water supplies through the water cycle and pose threatening physiological effects. Moreover, this study compared the results obtained from their MOF-UF systems with having ultrafiltration membranes only, and with using powdered activated carbon as an adsorbent with UF membranes. It was noticed that better retention rate than UF only under pH of 3, 7, and 11 with no serious fouling because the MOFs adsorbed the selected pharmaceuticals effectively. Additionally, it showed superior results to using powdered activated carbon regarding water flux, retention, and anti-fouling performance as well [123].

Carbon nanotubes (CNT) have been widely researched previously as promising materials for water treatment due to their structure and excellent adsorption capacity [10]. The use of adsorptive membrane filtration for pharmaceuticals removal including Triclosan and ibuprofen have been studied [10]. However, many uncertainties were addressed concerning the toxic effects of ingested CNT when directly dosing it to the polluted water. Consequently, they have to be accompanied with other practices to avoid contaminating the treated water. Membranes consisting of a functional CNT layer on top of a substrate membrane was used. The substrate membrane which is a flat sheet polyvinylidene fluoride (PVDF) membrane acting as a mechanical support to the CNT layer, and as a barrier to avoid CNT leaking into clean water. This study indicated that

using multi walled carbon nanotubes layers above a PVDF membrane substantially improved PPCP removal. This proved the promising potential of this technology for water treatment applications. Also, the process was affected by different PPCP–CNT interactions, as the efficiency was excellent with PPCP having aromatic rings like triclosan. Also, CNT that has a larger specific surface area favors PPCP molecules [10].

On the other hand, a novel nanocomposite ceramic ultrafiltration membrane with CuO and TiO_2 nanoparticles was used for the removal of Ciprofloxacin, a frequently used antibiotic. This nanocomposite membrane was fabricated by inclusion of nanomaterials in a ceramic matrix via coating on surface or membrane casting. The main observations were achieving high permeability, more stable flux, and excellent rejection rate when using such membrane. This was evidenced by the maximum adsorption of 99% obtained with minor fouling and longer usage time without requiring regular cleaning [124].

Despite the promising potential of applying adsorptive membranes for the removal of pharmaceuticals from contaminated water, there are limited studied and this has not been extensively researched. Hence, this is the idea of this research since there is promising potential.

2.5. Fabrication Methods of Adsorptive Membranes

- **Summary of major findings for fabrication techniques**

Table 2-1 displays summary of the different fabrications' techniques with description and examples.

Table 2-1: Summary of fabrication techniques details

Technique	Definition	Uses	Description	Examples
Blending and Coating	Physical adsorption of blended polymer onto the surface and depositing the hydrophilic layers[125].	Used commonly in fabricating mixed matrix membranes especially chitosan membranes[125].	Done by dispersing the filler into the solvent using ultrasonic bath or with stirring where the polymer is added. Then the cast solution is cast on a flat surface and dried by evaporation of solvent [39].	1) N,O–carboxymethyl chitosan blended with cellulose acetate to fabricate nanofiltration membranes [126]. 2) Flat sheet MMM with chitosan beads in Ethylene vinyl alcohol polymer matrix[127]. 3) Fe_3O_4 blended PES membrane[6].
Grafting	Fixing organic adsorbents on the polymeric membrane surface [4].	Used to prepare chelating microfiltration membranes[4].	Grafting on surfaces methods include: plasma treatment, UV irradiation and ozone [4].	1) Polypropylene hollow fiber membrane grafted with polyacrylamide polymer brush by surface-initiated atom transfer radical polymerization [128]. 2) Hyperbranched poly(amidoamine)-grafted poly(tetrafluoroethylene) microfiltration membranes [129].

				3) Sulfobetaine methacrylate grafted on polyamide membrane [130].
Assembling	Assembling layer by layer of cationic and anionic polyelectrolyte [61].	Fabricating mixed matrix membranes with improved permeability due to the increase in hydrophilic property, mean pore size, and overall porosity [131].	At normal conditions, the polymeric membrane is a negative porous support that adsorbs cationic polyelectrolyte by electrostatic attraction [61].	1) Ultrathin layer on a modified Torlons hollow fiber support was utilized with the layer-by-layer assembly to get the composite membrane used in removing Pb, Ni, and Zn ions [132].
Composite Membrane	A composite is a mixture of immiscible additives with polymeric components [133].	Used to produce membranes with high adsorption capacity, fast kinetics, reduced fouling, promising reactivity, and flexibility [134].	Adding micro or nanomaterial in membrane's structure on the surface or dispersed in the matrix [133].	1) A hybrid membrane fabricated by coating activated carbon fibers/chitosan/TiO$_2$ solution on a terylene fiber via a multi-step chemical grafting technique [134]. 2) A bio-composite membrane adsorbent synthesized by cellulose nanocrystals

			(CNCs) as functional sites in a chitosan matrix by freeze-drying technique [11]. 3) Microporous chitosan membranes produced by leaching [135].
Phase inversion and solution Casting	Membranes synthesis using polymer-solvent mixture to form a homogeneous solution at specific conditions of temperature and composition which separates if these conditions change [41].	Better dispersion of fillers, excellent interaction between the matrix and the filler, and uniform merging of polymer and adsorbent [136].	It can be done by evaporating a volatile solvent from the homogenous solution or via cooling a casting solution [41]. Phase inversion can entrap nanomaterials within the matrix where they get blended and dispersed in a polymer dope solution [137].	1) Chitosan–Montmorillonite nanosheets prepared by phase inversion with better antifouling nature and higher flux recovery ratio [53].
Electro-spinning	A high voltage-driven process which creates an electric field that induces the electrostatic	Used to synthesize Nanofibrous membranes with improved efficiency, and excellent removal	Electrospinning is a high voltage-driven process which uses a pump equipped with a nozzle-fitted syringe, a spinneret, an electric	1) Different fiber diameters for pure chitosan nanofibrous membranes were

repulsion forces which shatters the polymer surface tension and stretches its droplets to form solid continuous nanofibers [138].	capacity for heavy metals and organic pollutants [139].	current source, and a counter electrode or grounded target. Applying high voltage creates the electric field and the droplet at the nozzle takes a cone-shaped deformation. When the charged jet accelerates toward the collector, the solvent evaporates and the nanofibers [138].	prepared to absorb acid blue-113 dye [139]. 2) Citosan/cellulose acetate blend hollow fiber adsorptive membranes were prepared by wet spinning [16].

2.6. Common Analytical Techniques Used with Adsorptive Membranes

While conducting the experiments, some analysing tests are used to understand the behavior of the adsorptive membrane and be able to evaluate its performance. For instance, SEM and BET techniques are widely used to investigate the membrane morphology and pore structure. SEM is "scanning electron microscope" which scans an electron beam over a surface to generate an image by electrons interaction with the sample to get surface topography and composition [140]. It is the most common approach to examine the structure of the membrane and evaluate the bulk and surface morphology to compare modified and unmodified membranes [141]. While the BET analysis evaluates the specific surface area of materials and the pore area using nitrogen multilayer adsorption computed as a function of relative pressure. This is done by applying an automated analyser [142]. Moreover, X-ray diffraction (XRD) is a method used to define the atomic and molecular structure of a material through irradiating it with incident X-rays, then determining the intensities and scattering angles of the X-rays scattered by the substance [143]. As for example, it was used to study the locations of nanoclay particles in chitosan matrix of TFC membranes [141].

2.7. Challenges Associated with Adsorptive Membranes

The use of adsorptive membranes' technology has some issues and challenges that needs attention from the research community. These may include, but not limited:

- Fouling has been a serious problem in the membrane industry for so long. Solutions to overcome this issue include incorporation of antifouling nanoparticles, surface modification, and processing (post or pre-treatment). As blending with nanoparticles, improves the anti-fouling properties significantly [144]. However, future research should focus on preventing the regeneration of microbial colonies on membrane surface and reducing the leaching of the filler. In addition, backwashing is used to reduce fouling issues during operations.

- Identifying and developing new filler materials is a challenge in adsorptive membranes industry. As the advancements in this field reached a high level and many filler materials are found and studied yet accompanying problems with that occur. For instance, their availability, usage practicality, cost, stability, agglomeration, and interfacial contact are always a great concern when putting these materials in application [44].

- Ensuring the safety and nontoxicity of the adsorptive material added to the membrane is a challenge. Some fillers have a toxic nature or applying them in water purifications results in toxic water. Therefore, any water treatment applications should be free from any great risk to humans or the environment. This can be done by multiple tests and experiments.

- Developing novel materials for mixed matrix membranes is a big challenge, as many materials so far have been only tested on a laboratory scale and need further investigation. As many novel materials could not get widespread due to their high prices or expensive synthesis processes, so looking for cheaper materials could be a potential research area.

- Finding new processes for membranes fabrication: As many materials are being discovered and investigated, the limitation associated with fabricating the material is restricting the usage of many promising adsorptive membranes. As current processes are not capable of producing defect-free membranes even on laboratory scales, therefore new techniques to can be developed to attain the required interface and binding between the adsorptive material and the membrane without affecting the performance. In addition, to finding the required processes that enables the scaling up of novel membranes [145].

- Developing models for the new adsorptive membranes, as thorough research is required to determine the morphology and unique characteristics of the filling adsorptive material in the membrane. Since such models need to be developed to predict the membrane performance [146].

Research should be focused in overcoming these challenges to be able to utilize adsorptive membranes in the water treatment fields efficiently. In addition, most researches are using polymers-based membranes. Furthermore, the issue of having pharmaceuticals in water as the emerging contaminant is a serious problem that need to be getting more attention. As the details regarding their harmful effects and impact on human's health and living organisms is very limited. As more environmental risk assessment investigations are necessary for various pharmacologically active compounds and their metabolites [85].

Chapter 3.   Materials and Research Methodology

3.1. Introduction

This thesis aims to study the use of adsorptive membrane technology for the removal of pharmaceuticals from wastewater in a laboratory scale. In addition to studying the elimination of antibiotics such as ciprofloxacin as a model of pharmaceutical materials. Antibiotics are emerging contaminants that have attracted the attention of researchers due to the increased global concern about their presence in water. One major issue is the antibiotic resistant genes which are capable of causing superbugs which are antibiotic resistant bacteria that can result from the continuous exposure. This issue has increased recently, due to the increased consumption of antibiotics as there are more than 250 different antibiotic entities for humans and veterinary medicines [116]. Therefore, it is highly important to remove these traces before discharge to the environment.

This research seeks to remove Ciprofloxacin which is an antibiotic used to treat many bacterial infections such as pneumonia, infectious diarrhea, infections of the skin, bone, joint, abdomen, prostate, sinus, kidney, urinary tract, and bronchitis. It has some side effects such as vomiting, nausea, or sleepiness [147]. The chemical structure of Ciprofloxacin ($C_{17}H_{18}FN_3O_3$) is shown in Figure 3-1 [148]. It is an abundant pharmaceutical compound that is widely used for many medical purposes. In 2018, the estimated number of prescriptions for ciprofloxacin in the United States was 6,736,471 [149]. This has triggered the interest of its removal from wastewater containing ciprofloxacin.
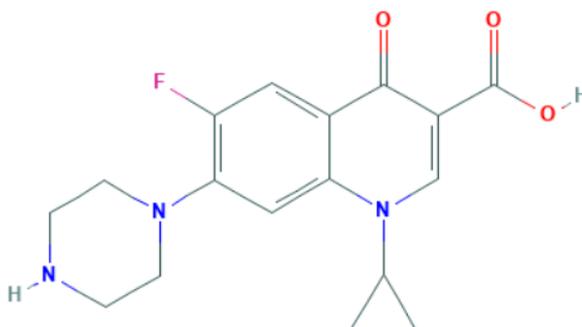

Figure 3-1: Chemical Structure of Ciprofloxacin [148]

Some Ciprofloxacin's properties are shown in Table 3.1:

Table 3-1: Ciprofloxacin properties

Molecular weight	331.34 g/mol
Physical description	Faint to light yellow crystalline solid powder
Melting point	255-257 °C
Water affinity	Hydrophilic
Metabolites	Oxociprofloxacin, sulociprofloxacin, desethyleneciprofloxacin, and N-formylciprofloxacin

Initially Polyetherrsulfone membrane and α-zirconium phosphate (ZrP) will be tested individually for their ability to remove Ciprofloxacin from aqueous solutions. After that, Polyethersulfone incorporated into α-zirconium phosphate (PES/ZrP) will be tested in a flat-sheet composite membrane for the removal of ciprofloxacin from wastewater. Polyethersulfone membrane has shown good efficiency in the removal of heavy metal ions due to the improved electrostatic attraction forces. It is one of the most used polymeric membranes for such purposes due to its outstanding properties. Also, the addition of ZrP particles to the membrane would enhance many of its properties including mechanical strength, porosity, thermal stability, and mitigate fouling. Zirconium phosphate is widely used for ion exchange purposes because of their unique chemical properties in the crystalline and amorphous forms. It is an effective cation exchanger that has been widely used for adsorption of heavy metals from wastewater [150][151]. Also, it is characterized with high biocompatibility, outstanding thermal stability, and the ability to trap many types of molecules with various sizes. Therefore, incorporating this inorganic acidic material with unique layered structure and hydrophilicity into the membrane is highly recommended for wastewater treatment applications [152].

Incorporation of zirconium phosphate into PES membrane by phase inversion was previously investigated where the adsorptive membrane was utilized for the removal of such heavy metal ions as Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+}. This showed substantial enhancement in removal efficiency, membrane hydrophilicity, water flux, porosity, and

anti-fouling [152]. Therefore, this research will investigate the applicability of PES membrane with ZrP adsorptive membranes for the removal of pharmaceuticals from wastewater, Ciprofloxacin in specific to a low final concentration in the parts per billion range.

3.2. Materials

Ciprofloxacin removal was tested using Ciprolon I.V. infusion solution from HIKMA pharmaceuticals (Jordan). The adsorbent used Zirconium (IV) hydrogen phosphate Zr $(HPO_4)_2$ or ZrP and the Zirconyl chloride octahydrate $(ZrOCl_2)$ reagent used for the membrane fabrication reaction were bought from SIGMA-ALDRICH (Germany), and the Polyethersulfone membrane sheets from Sterlitech. Ortho-Phosphoric acid H_3PO_4 (85%) from EMSURE, 0.1M NaCl and 0.1M HCl for pH adjustments, and deionized water were used for all experiments.

3.3. Instrumentations

Several instrumentations and apparatuses were used in the experiments. For sample filtration after the adsorption process, 0.45 µm syringe filters (MCE Membrane, Membrane Solutions) were used. In addition to the XIEYING 50 mm membrane filter holder and 20 mL syringe. Furthermore, Orbital shaker, magnatic stirrer, Carbolite furnace, and Radwag weighing balance were used throughout the work.

3.3.1 Feed and permeate analysis

E-1000UV Peak Instruments UV-VIS spectrophotometer was used to analyze the samples' concentrations. The ciprofloxacin concentration in the feed and permeate were determined by measuring the absorbance at a wavelength of 275 nm.

3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis (Tescan VEGA XMU, LaB6 filament, Oxford Instruments X-Max 50 SSD detector) were used to visualize the morphology and analyse the elemental composition of the membrane, respectively.

3.3.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was performed using PerkinElmer machine, Spectrum One FT-IR Spectrometer over a wavelength range of 350 up to 7800 cm-^{1}. It is used to detect the functional groups and understand the surface chemistry of the membrane.

3.3.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) assists in understanding the structure of the membrane and studying its nature. The analysis was carried out using Bruker D8 Advance, scintillation point detector, with a 1-D detector. The scanning diffraction angle range was set at 2–60◦ and scan with the Cu Kα ray source ($\lambda = 1.54 \times 10^{-10}$ m (1.54 ˚A)).

3.3.5 Brunauer-Emmett-Teller (BET)

In order to calculate the sample specific surface area and pore volume, the Brunauer-Emmett-Teller (BET) technique was used. It was performed via NOVA touch LX2 instrument with nitrogen adsorption-desorption isotherms analysis. This was operated along with Quantachrome TouchWin^{TM} software.

3.4. Experimental Setup

The experimental work will be divided into two main stages:

1. Studying the potential of Zirconium phosphate powder (ZrP) toward adsorption of Ciprofloxacin using batch adsorption experiments.

2. Developing adsorptive membranes based on batch adsorption experiments and test them using the replaceable membrane syringe filter set-up. Ciprofloxacin's concentration in the feed solutions and permeate will be determined using UV-VIS spectroscopy at wavelength 275 nm.

3.4.1 Batch adsorption tests

Ion exchange is one of the most important methods for pollutants removal from wastewater, especially after the developments related to preparing novel organic and inorganic ion exchangers. zirconium phosphate $Zr(HPO_4)_2$ known as ZrP is one of the important inorganic ion exchangers [153]. Hence, ZrP will be examined in this work in batch adsorption tests using the procedure described below:

A stock solution of 200 ppm was prepared to obtain different samples' concentrations by dilution. For all the tests, seven initial concentrations of Ciprofloxacin were tested

(1, 5, 10, 20, 30, 40, and 50 ppm) and the absorbance was measured using UV-VIS spectrophotometer. The batch adsorption tests were carried out based on one factor at a time method (OFAT) which includes varying one condition at a time and keeping the other constant to determine the optimum conditions and study the effect of several parameters such as: adsorbent dosage, contact time, initial concentration, pH, and temperature. The 50 mL samples' solutions were prepared in Erlenmeyer flasks, and then a known mass of adsorbent in the range of 0.05 g to 0.6 g was added. The solutions were placed in an orbital shaker at 160 rpm speed for several contact times for adsorption until reaching equilibrium. Samples were taken at different time intervals to determine adsorption kinetics. The orbital shaker with the samples is shown in Figure 3-2.

Figure 3-2: Batch adsorption experiment

After that, the solutions get filtered by 0.45 µm syringe filter to remove all the ZrP adsorbent solids, and the absorbance of the filtrate was measured by the UV-VIS spectrophotometer. This was done to determine the final ciprofloxacin concentration using the calibration curve. Also, the ciprofloxacin uptake was calculated by a mass balance before and after the test. All the parameters studied were optimized to obtain the highest pharmaceutical removal efficiency.

3.4.2 Preparation of Calibration Curve

The calibration curve was constructed by measuring the absorbance of samples of known concentrations by UV visible spectroscopy to determine the concentration of the ciprofloxacin pharmaceutical in the treated water samples before and after adsorption

tests. The wavelength at which maximum absorbance of ciprofloxacin occurred was 275 nm [154].

3.4.3 Adsorptive Membrane Synthesis

Following the successful removal of ciprofloxacin pharmaceutical from the samples of water solution by ZrP, it was added to Polyethersulfone membrane to its removal using the produced adsorptive membrane. The following procedure was followed to synthesize the PES/ZrP composite membrane.

1- Wetting step: $ZrOCl_2 \cdot 8H_2O$ as a source of zirconium, and o-phosphoric acid as a source of phosphorous for obtaining ZrP were used. A suspension containing $ZrOCl_2 \cdot 8H_2O$ salt having a liquid phase that can wet the surface of the porous PES film was prepared. The suspension can be prepared by using isopropanol which has lower surface tension than water; thus, can wet the PES surface. The alcohol can penetrate through the membrane, while salt particles can be suspended in alcohol. A mixture of alcohol and water was prepared, as the water can dissolve much of $ZrOCl_2 \cdot 8H_2O$ and the liquid mixture can we wet the film. The quantity of $ZrOCl_2 \cdot 8H_2O$ to be used was calculated using stoichiometry. Next, the suspension was added into the pores of the PES film by weighing a piece of porous PES and placing it between two Teflon hoops that are then fixed to an SCK 300P spin coater, (purchased from INSTRAS) as shown in Figure 3-3.
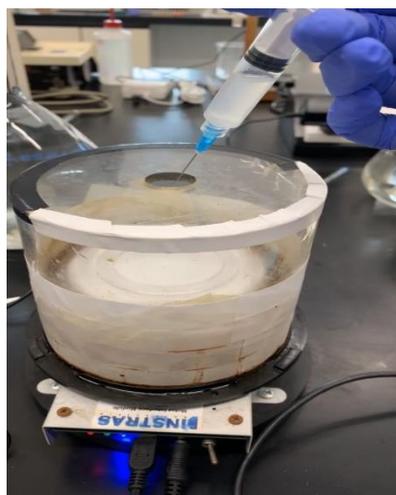
Figure 3-3: Spin coater with the fixed Teflon hoops in wetting process

The spin coating technique is a procedure under solution coating membrane preparation technique. It is used to synthesize composite membranes by adding a thin dense film, known as skin layer or selective layer on top of a porous support. The thinness of the layer increases the transport rate through the membrane with mechanical stability provided by the support. It is considered an easy and practical technique [155]. A 20 mL wetting solution was gradually added to the PES surface using a syringe, while the spin coater was operated at 255 rpm for 45 s and progressively increased to 3600 rpm for uniform and proper solution distribution.

2- Reaction step: this step involves immersing the $ZrOCl_2 \cdot 8H_2O$ membrane into H_3PO_4 for 24 hrs where the following reaction occurs:

$$ZrOCl_2 \cdot 8H_2O + 2H_3PO_4 \rightarrow Zr(HPO_4)_2 \cdot H_2O + 2HCl + 8H_2O \tag{1}$$
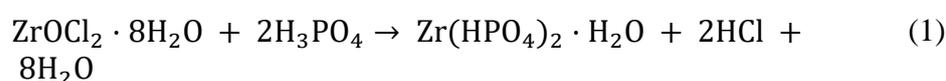
3- Drying step: the membrane was rinsed with deionized water, then oven dried for 2 hrs at 90°C to be used for further examinations [156]. The resulting synthesized membrane is shown in Figure 3-4.

Figure 3-4: The membrane sheet fixed between Teflon hoops

3.4.4 Adsorptive Membrane Tests

The synthesized membrane was then tested to remove ciprofloxacin from the prepared samples of water solutions by placing the membrane in a membrane filter holder connected to a syringe. The flowrate was controlled by pushing a specific solution

volume over a fixed period of time monitored with a stopwatch. This setup is shown in Figure 3-5.

Figure 3-5: Membrane filtration setup

Then, the permeate concentration was determined using UV-VIS spectrophotometer via the prepared calibration curve. Several membranes were prepared with different ZrP loading and their removal efficiencies were determined to select the optimum loading. This is followed by characterising the prepared membrane with the best efficiency by different analyses to study its surface, composition, and structure. In addition to comparing between the pure PES membrane, adsorptive membrane, and the used membrane after ciprofloxacin filtration.

Chapter 4. Results and Analysis

This section presents the results obtained from experimental work and discuss the various outcomes of the studies done to draw the appropriate conclusion.

4.1. Batch adsorption analysis

4.1.1 Preparation of calibration curve

The main purpose of the calibration curve is to determine the final concentration of ciprofloxacin pharmaceutical in the treated water samples. The light absorbance spectra of solutions of known ciprofloxacin concentrations were measured using UV-Vis spectrophotometer. The wavelength that showed the maximum absorbance (λmax) is 275 nm which agrees with literature [154]. The constructed calibration curve is shown in Figure 4-1.
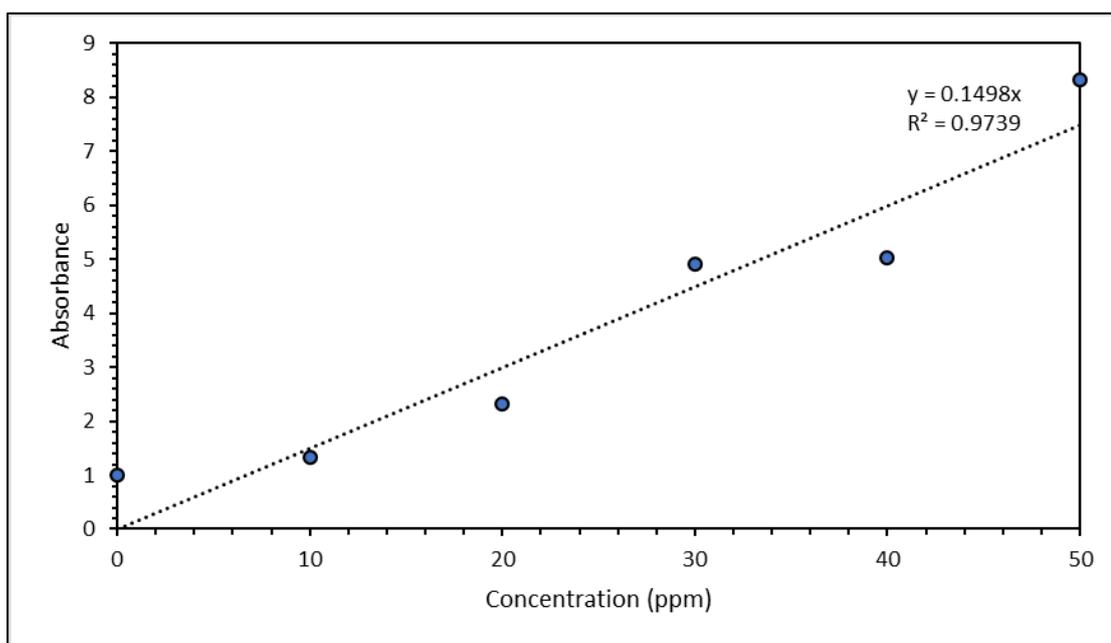
Figure 4-1: Calibration Curve

This enables calculating the removal efficiencies by comparing the initial and final concentration of the pharmaceutical in the water sample using Equation 2.

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where C_0 and C_e are initial and equilibrium final concentrations (ppm) of the pharmaceutical solutions, respectively.

4.1.2 Effect of adsorbent dosage

The amount of adsorbent used is an important parameter that can decide the practicality of application on an industrial scale. The removal is determined by the number of available sites on the adsorbent's surface. Five different dosages of ZrP were tested: 0.05, 0.1, 0.2 g, 0.4 g, and 0.6 g and the removal efficiencies were compared to determine the optimum amount. The contact time was held constant at 2 hours. Taking a fixed initial concentration of ciprofloxacin solution at 30 ppm and comparing the removal efficiencies of the different ZrP dosages it appears from Figure 4-2 that the highest removal efficiency was obtained at 0.2 g adsorbent dosage of 99.24%. However, it can be observed that increasing the ZrP amount did not affect the removal efficiency significantly, in fact the difference observed was only few decimals.

Table 4-1: Removal efficiencies with different adsorbent dosage

ZrP Adsorbent Dosage (g)	Removal Efficiency (%)
0.05	53.33
0.1	66.66
0.2	99.24
0.4	98.82
0.6	98.64
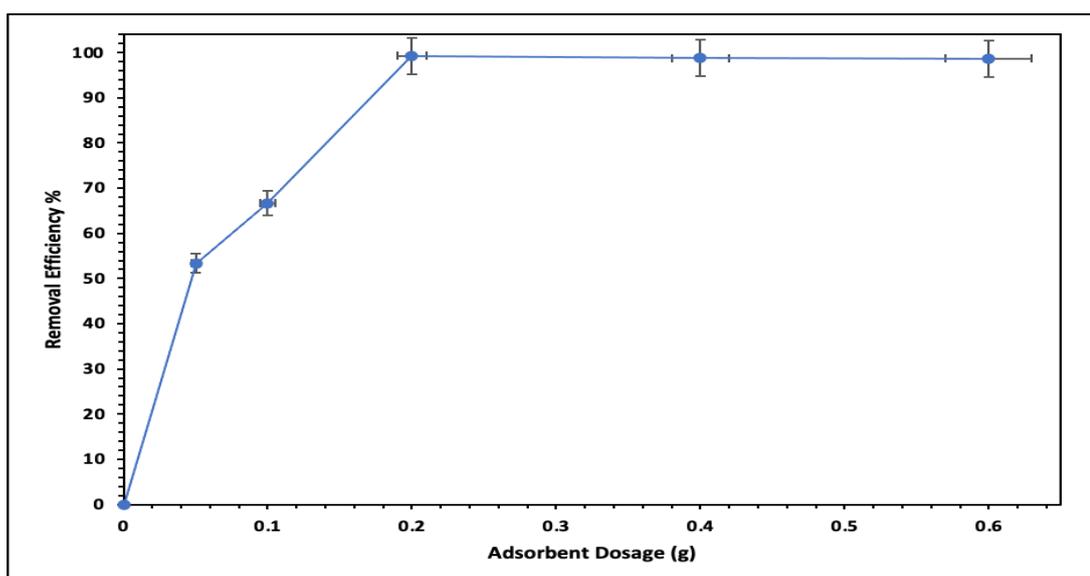
Figure 4-2: ZrP dosage Vs Removal Efficiency

The results show that the optimum dosage is 0.2 g of ZrP as it is able to remove 99.24% of ciprofloxacin pharmaceutical, therefore any extra adsorbent added is just an excess that doesn't contribute to the adsorption process. As increasing the adsorbent dosage, increases the number of available sites thus increases the removal efficiency until it becomes constant. This was noticed when increasing the ZrP dosage from 0.05 g to 0.2 g, as the removal efficiency increased reaching an optimum value. While after the 0.2 g the adsorption efficiency is nearly constant due to the saturation of the adsorbent with the pharmaceutical as all surface sites get occupied, or adsorption is thermodynamically limited due to the unavailability of driving forces as a result of the sufficient removal [157]. The slight decrease can be attributed to the excess of adsorbent dosage that can hinder the process.

4.1.3 Effect of contact time

The effect of contact time between the adsorbent and the material to be removed differs from one system to another. The tests were performed at distinct contact times: 15 mins, 30 mins, 75 mins, 1 hour 15 mins, 2 hours, 4 hours, and 6 hours to ensure reaching equilibrium. With fixing the optimum adsorbent dosage of 0.2 g and initial concentration of CPFX to 30 ppm, the removal efficiencies were compared and presented in Table 4-2.

Table 4-2: Contact time vs removal efficiency

Contact time (mins)	Removal Efficiency (%)
15	90.88
30	95.33
60	97.77
75	98.44
120	99.24
240	99.13
360	99.13
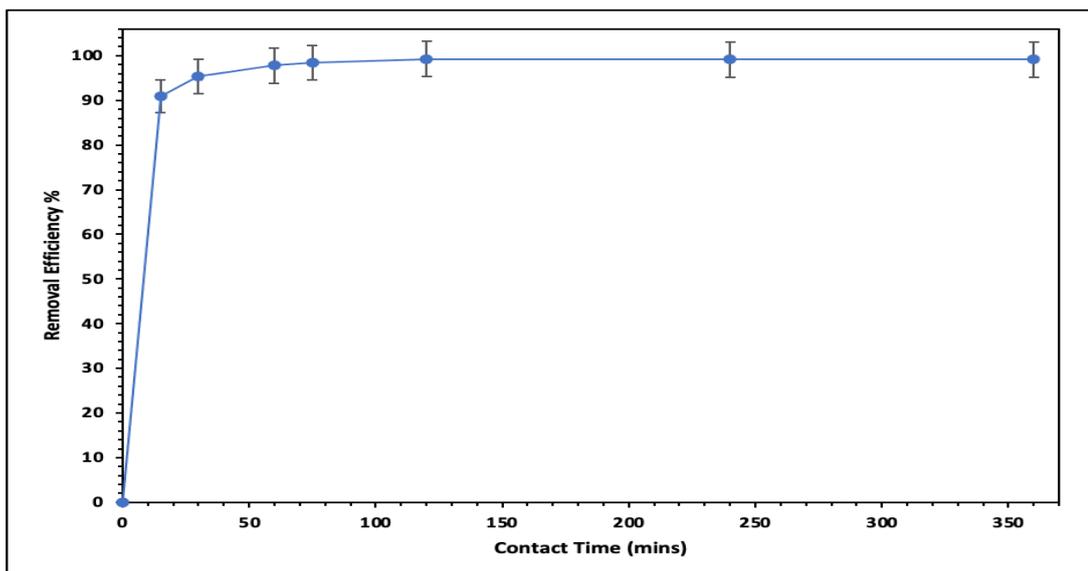
Figure 4-3: Contact time Vs removal efficiency

As it can be noticed from Figure 4-3, the highest removal efficiency of 99.24% was obtained after 2 hours of contact time. As it continuously increased with increasing the contact time until reaching equilibrium after 2 hours. The contact time did not affect the removal efficiency after that as it decreased slightly and stayed constant thereafter. This can be explained by the reduction of available active sites as time increases and attaining equilibrium when the adsorbent and sorbate are in contact for sufficient time owing to the continuous drop in the driving force (concentration)[158]. In addition to the rapid diffusion of ciprofloxacin to the external surface of ZrP where adsorption on the active sites occur [159].

4.1.4 Effect of pH

The effect of pH is an essential parameter that determines the efficiency of adsorption. To begin with, the natural pH of ZrP in ciprofloxacin solution was measured using pH meter to be 7. Tests in the acidic and basic pH were conducted to observe the effects of pH alteration on the removal efficiency. 0.1 M HCl was added to the samples dropwise to adjust the pH to 3 and 5 using the 30 ppm sample with 0.2 g ZrP and 2 hours contact time. It can be noticed from Figure 4.4 that decreasing the pH from 7 to 5 then 3 resulted in a decrease in the removal efficiency from 99.24% to 98.26% to 94.15%. On the other hand, adding 0.1 M NaOH to the same sample to attain a basic pH of 8 and 9 affected the removal efficiency significantly, as it declined to reach 64.84% and 40.58%,

respectively. This lower adsorption in alkaline medium is due to the competition from excess hydroxide ions (OH)$^-$ with the drug molecules for the adsorption sites [159].

Moreover, these results imply testing the removal at neutral pH in the membrane stage to obtain optimum results. This can be explained by focusing on the zeta potential which is a property associated with the surface charge of the membrane. Increasing the pH values results in a decrease in the ζ value, since PES membrane surface is negatively charged over a wide range of pH due to the large density of $- SO_3H$ [160]. In addition, at pH 7 high surface negativity occurs in ZrP due to the presence of $-OH$ groups which improves the adsorptive membrane surface negativity with reinforcing it with functional groups [161]. Thus, leads to enhancing the removal efficiency using ZrP.

Table 4-3: pH vs removal efficiency

pH	Removal efficiency (%)
3	94.15
5	98.26
7	99.24
8	64.84
9	40.58
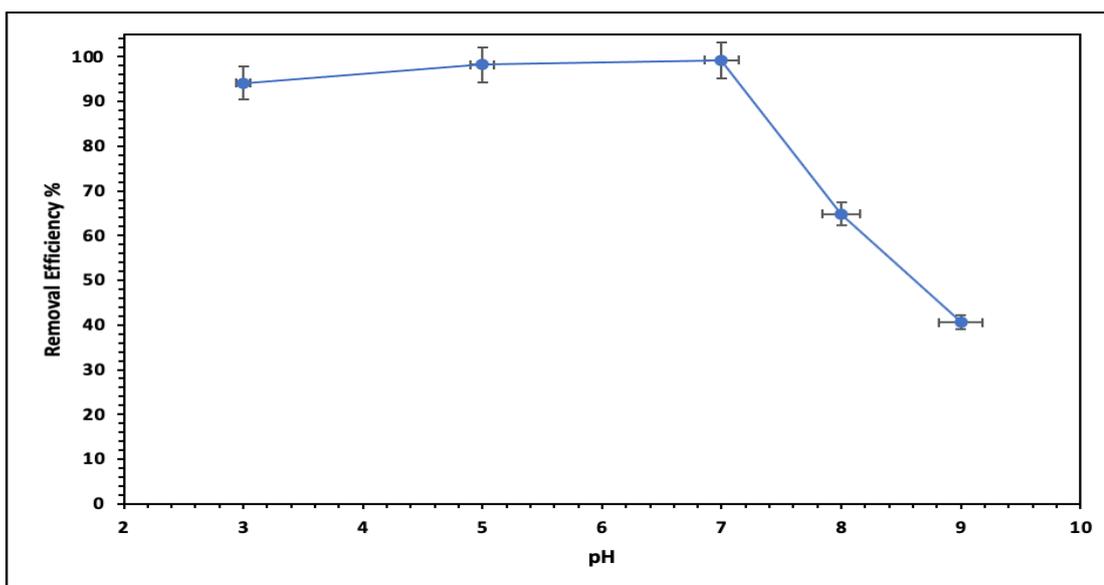
Figure 4-4: pH vs removal efficiency

4.1.5 Effect of drug initial concentration

Pharmaceuticals in wastewater are found in traces and concentrations usually in the ppm range. Also, these concentrations vary depending on the wastewater type and source in industries. Therefore, the initial concentrations of ciprofloxacin studied in the experiments are in ppm and they are varied to study the effect of initial concentration on the process efficiency. The concentrations tested are 1, 5, 10, 20, 30, 40, and 50 ppm. Using 0.2 g ZrP for 2 hours at room temperature and pH of 7, the highest removal efficiency was found to be 99.24% for an initial CPFX concentration of 30 ppm. As shown in Figure 4-5, the efficiency increased to reach a maximum then started decreasing slightly. As the concentration increases, the driving force for the removal increases, thus assists in overcoming the mass transfer resistance between the aqueous and solid phases [159]. This is until reaching a maximum where the adsorbent available sites become saturated or poisoned with CPFX and the removal efficiency decreases. Despite that, the removal efficiency is not much affected by the initial concentration as it can be noticed that it did not change significantly.

Table 4-4: Initial concentration and removal efficiency

Initial Concentration of CPFX (ppm)	Removal Efficiency (%)
1	97.33
5	97.79
10	98.26
20	99.03
30	99.24
40	99.17
50	99.11
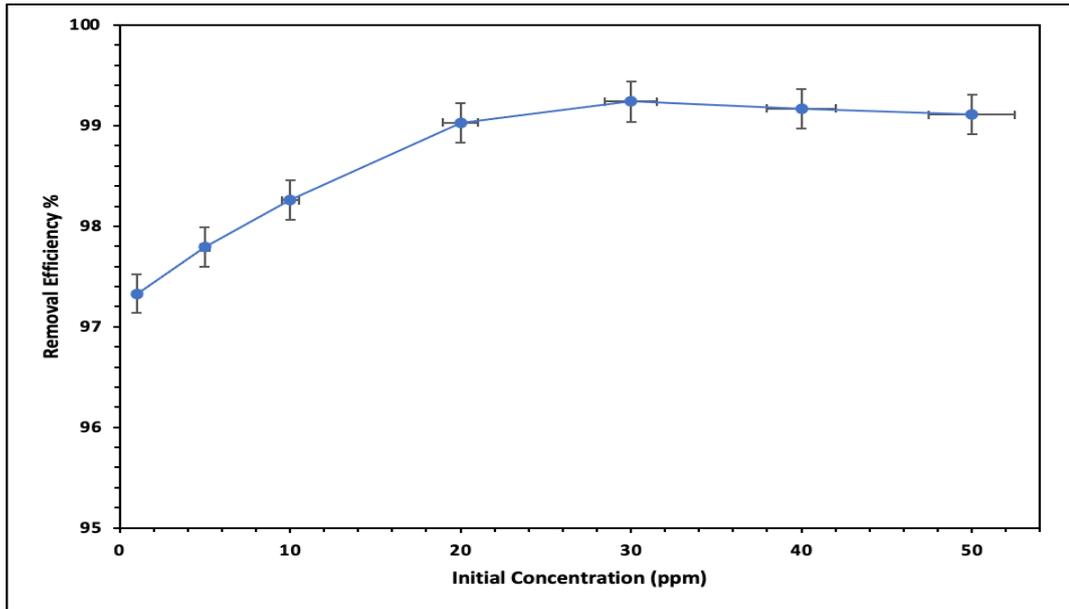
Figure 4-5: Initial concentration vs removal efficiency

4.1.6 Effect of temperature

The previous tests were carried out at room temperature around 25℃, therefore the effect of temperature is important to be observed. As temperature requirement plays an important role in energy requirement and consumption, thus affects cost and financial burdens on an industrial level. The adsorption was tested at different temperatures including 4℃, 25℃, 50℃, and 75℃ to observe its effect on the removal efficiency and the results are shown in Table 4-5 and Figure 4-6.

Table 4-5: Temperature vs Removal efficiency

Temperature (℃)	Removal Efficiency (%)
4	99.01
25	99.24
50	97.95
75	97.62
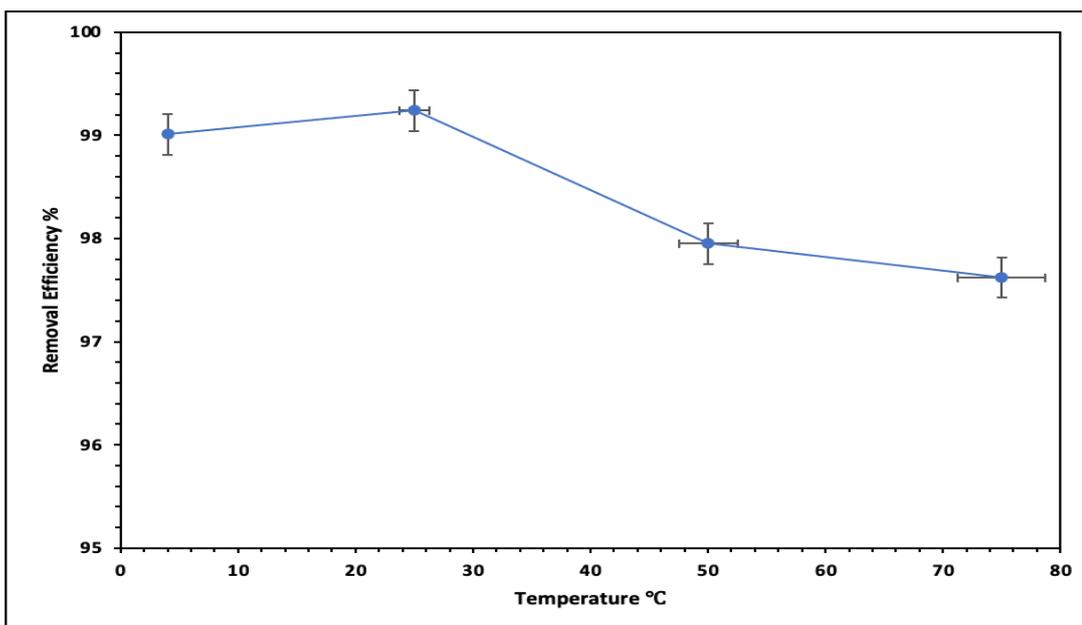
Figure 4-6: Temperature vs Removal Efficiency

It can be noticed from (Figure 4-6) that the removal efficiency wasn't significantly affected by increasing the temperature from 4℃ to room temperature which is the storage temperature of ciprofloxacin. However, the removal decreased with increasing the temperature further while keeping other conditions optimum. This can be explained by the fact that adsorption is an exothermic process, therefore increasing the temperature reduces adsorption and its efficiency. As adsorption occurs spontaneously, the change in Gibbs free energy, ΔG, is negative, hence the enthalpy change, ΔH, associated with physisorption is always negative (exothermic). As a result, temperature rise decreases the uptake [162]. This is beneficial since water treatment processes are usually conducted at ambient temperature.

4.2. Adsorption isotherm

Adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature [163], or simply the expression of adsorbate loading on adsorbent as a function of concentration at constant temperature. There are numerous adsorption isotherm models such as Langmuir, Freundlich, Temkin, and Doubinin–Radushkevich [164]. The experimental data were fitted using the different isotherms to determine the best model for adsorption representation.

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4.2.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm assumes that there is no interaction among molecules adsorbed on the neighbouring adsorption sites [164]. It is basically used for homogeneous surfaces and contains only one type of binding sites (monolayer), so the energy of adsorption is constant [165]. Experimental data can be fit in a Langmuir isotherm model expressed as [166]:

$$q = \frac{Kq_mC_e}{1 + KC_e}$$ (3)

where q is the amount of the adsorbed substance on the surface at equilibrium in (mg/g), and K is the adsorption equilibrium constant (L/mg). Moreover, qm is the maximum monolayer adsorption capacity (mg/g) and Ce is the equilibrium concentration of the adsorbate (mg/L) in the solution [166]. This equation can be linearized to the following form:

$$\frac{1}{q} = \frac{1}{Kq_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m}$$ (4)

A graph of 1/q against 1/Ce gives a straight line of slope (1/Kqm) and an intercept of (1/qm). This enables obtaining the adsorption capacity of the adsorbent as well as the adsorption equilibrium constant. In order to get q which is the amount of CPFX adsorbed onto ZrP i.e. the uptake, the following mass balance equation is used:

$$q = \frac{(C_o - C_e)V}{m}$$ (5)

where qe is the equilibrium adsorption capacity (mg absorbate/g absorbent), V is the sample volume (in L), Co is the initial concentration of the solute (in mg/L), Ce the equilibrium concentration of the solute after adsorption (in mg/L), and m is the weight of the adsorbent used (in g).

The graph obtained from using the linearized model is shown in Figure 4-7. By plotting 1/q versus 1/Ce, the best linear curve fitting shows an R^2 of 0.7129 with a slope of 0.0759 that represents (1/Kqm). Other adsorption isotherms will be studied as this low R^2 value indicates that Langmuir model is not the best representation of the adsorption happening in this experiment.
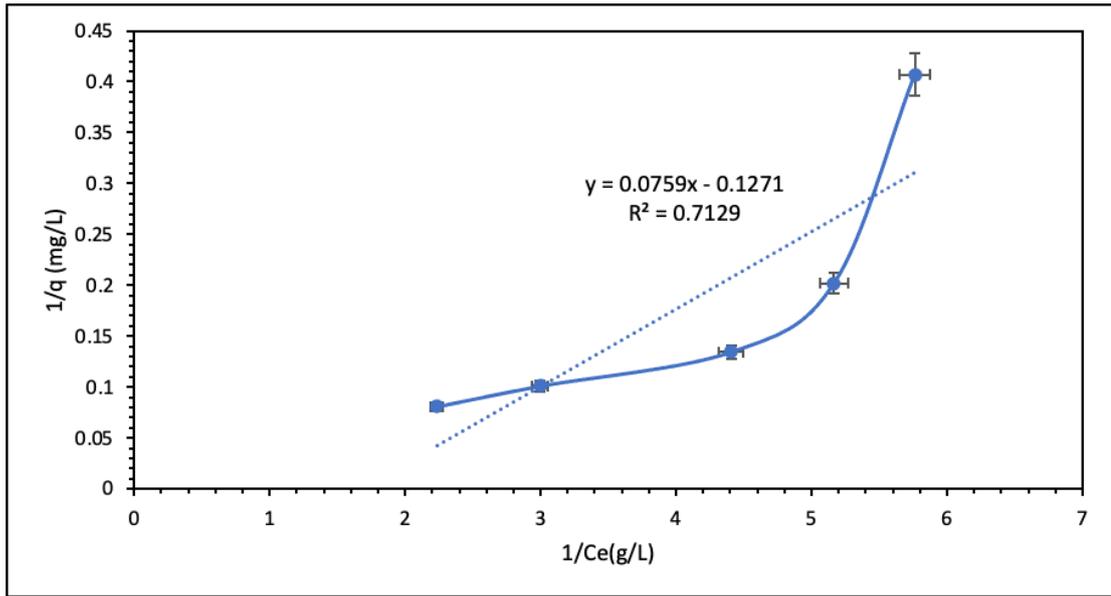
Figure 4-7: Langmuir Model fitting for the experimental data

4.2.2 Freundlich adsorption isotherm

The Freundlich isotherm is an empirical equation that can be used to describe heterogeneous systems for multilayer adsorption, in which it is characterised by the heterogeneity factor 1/n [68]. It assumes that stronger binding sites are occupied first, and the strength of adsorption decreases with the degree of occupation [164]. The Freundlich equation can be written as follows:

$$qe = K_f C_e^{1/n} \tag{6}$$

where qe is the solid phase sorbate equilibrium concentration (mg/g), Ce is the equilibrium concentration of adsorbate (mg/L), K_f is Freundlich isotherm constant (L/g) and 1/n is the intensity factor [68]. The intensity factor value can give important information regarding the degree of non-linearity or intensity of adsorption between solution concentration and adsorbed phase as follows: if it is equal to unity then the adsorption is linear, while if the value is below unity, the adsorption is chemical, and the surface is comparatively homogeneous. However, if the value is above unity, the adsorption process is physical process, and is considered heterogeneous [167].

The linearized form of the equation can be expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

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This linearized equation was used to plot the experimental data in a graph of ln (qe) versus ln (Ce) shown in Figure 4-8. It can be observed that the R^2 obtained from linear curve fitting (0.8113) is higher than the Langmuir model. The line equations show a slope of 1.456 which is the heterogeneity factor 1/n that is a greater than unity. Therefore, according to this model the adsorption is physical adsorption, and the surface of the adsorbent is heterogenous. Moreover, the Freundlich isotherm constant K_f is found from the intercept to be 46.39 L/g.

y = 1.456x + 3.8371
R^2 = 0.8113
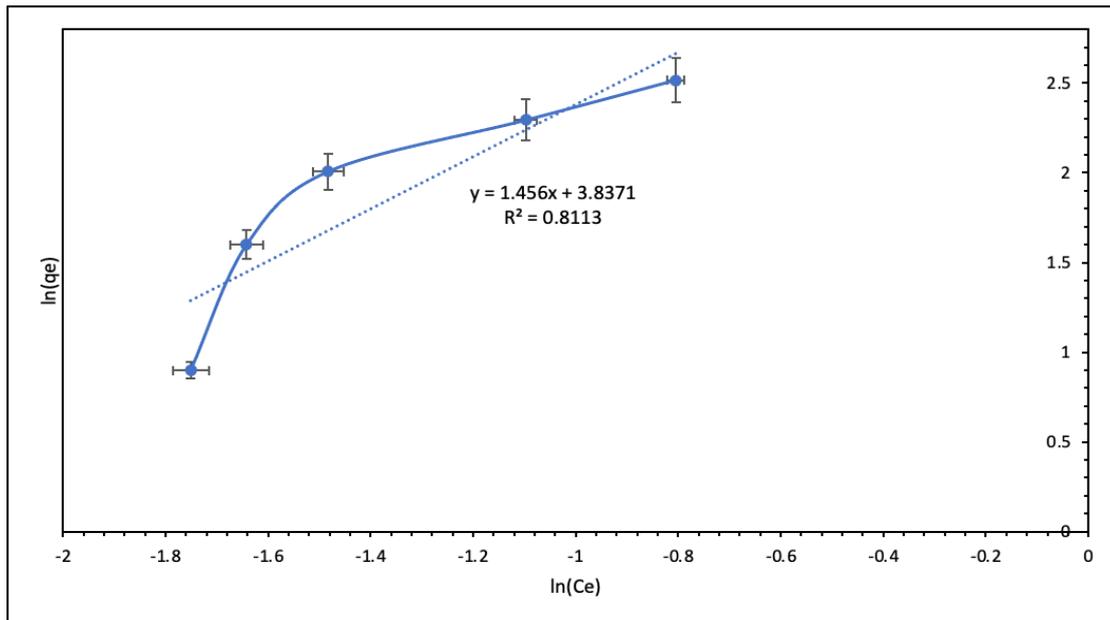
Figure 4-8: Freundlich model fitting for the experimental data

4.2.3 Temkin adsorption isotherm

The Temkin isotherm model proposes that there is an equal distribution of binding energies over the number of the exchanging sites on the surface [168]. In addition to considering the adsorbent–adsorbate interactions unlike the Langmuir and Freundlich isotherm models with the effects of adsorption heat as it decreases linearly with coverage of the interactions [169],[163]. The linear form of Temkin isotherm can be written as[169]:

$$q_e = (B \ln A) + B \ln C_e$$

where B=RT/b, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant in (L/g) and b is the Temkin constant related to the heat of sorption in (J/mol) [163]. This model is checked

by plotting the quantity adsorbed q_e versus $\ln C_e$ and the constants are determined from the slope and intercept [169].

The Temkin model was tested by plotting a curve of qe versus ln(Ce) and resulted in the best fit of the data shown in Figure 4-9. This model has shown the highest R^2 value (0.9499) compared to the previous two models. The line equation has a slope of 9.6788 representing the B value which yields a value of 255.97 J/mol for the constant related to the heat of adsorption (b). The intercept was found to be 20.552 related to (B ln(A)). Therefore, the equilibrium binding constant is equal to $A = e^{\left(\frac{20.552}{9.6788}\right)} = 8.359$ L/g. The positive value of b indicates that the adsorption is exothermic [170]. Moreover, this value indicates that the type of adsorption happening is a physical process since it is less than 1.0 kcal/mol [171][172][167] which agrees with the results from Freundlich model.
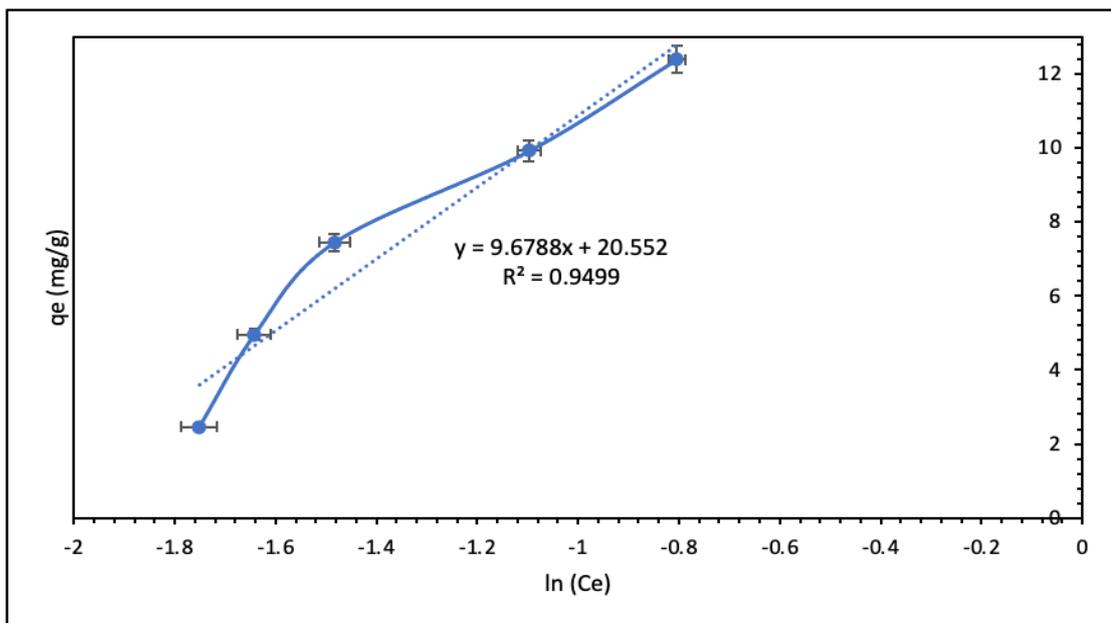
Figure 4-9: Temkin model fitting for the experimental data

4.2.4 Doubinin–Radushkevich (D–R) isotherm

Doubinin–Radushkevich model is a more general model compared to the Langmuir isotherm, as it assumes no homogeneous surface or constant adsorption potential. In addition, it gives valuable information regarding the type of adsorption. The linear form of the model is as follows [168]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{8}$$

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where q_e is the amount adsorbed at equilibrium (mg/g), q_m is the theoretical isotherm saturation capacity (mg/g), K is the isotherm constant (mol^2/kJ^2), ε the Polanyi potential calculated using the equation below:

$$\varepsilon = RT \ln \left(1 + \frac{1}{Ce}\right)$$

(9)

where R (kJ mol^{-1} K−1) is the gas constant and T (K) is the absolute temperature. E which is the mean free energy of adsorption is calculated from the K value by the following relation [168]:

$$E = 1/(2K)^{1/2}$$

(10)

The Doubinin–Radushkevich model was tested by plotting ln(qe) versus ε^2 as shown in Figure 4-10. The R^2 value obtained is the second highest value obtained compared to other models. According to the linear equation, the isotherm constant K is deduced from the slope to be 0.1015 mol^2/kJ^2, while the qm is found to be 32.999 mg/g which represent the maximum adsorption capacity. This adsorption capacity is considerably a competitive value compared to other investigated ciprofloxacin adsorbents [159]. Moreover, the value of E is calculated to be 2.219 kJ/mol which also solidifies that the adsorption happening is by physisorption and not ion exchange since it is out of the ion exchange reaction range i.e., 8–16 kJ/mol [173].

Figure 4-10: Doubinin–Radushkevich model fitting for the experimental data

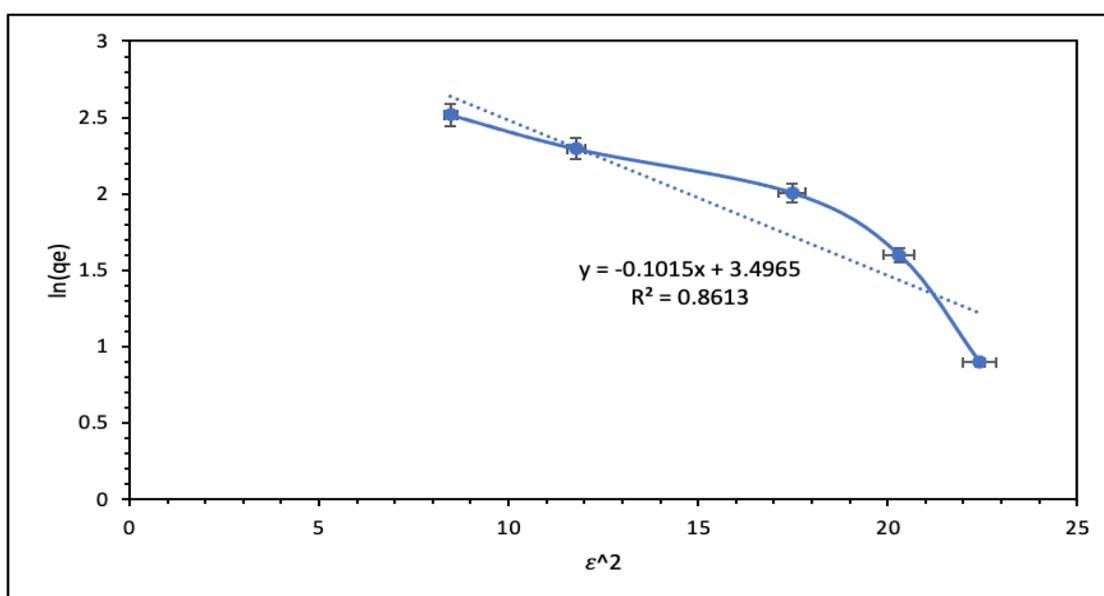After testing the four adsorption models, the model that gave the least error and best fit was the Temkin isotherm model. This result indicates that the adsorbent surface is mostly homogenous in nature and have equal distribution of binding energies on the available sites [168], and the heat of sorption of all molecules in the layer decrease linearly with surface coverage as a result of sorbate/sorbent interactions [174]. Furthermore, three models have confirmed that the adsorption type in this experiment is physisorption and not ion exchange reaction. This physisorption can be due to hydrogen bonding between ZrP and ciprofloxacin, since the adsorption caused by hydrogen bonding is under the category of physical adsorption [175].

4.3. Membrane Analysis

Based on the batch test results, the adsorptive membrane PES/ZrP was synthesized and tested for the removal of ciprofloxacin from water solutions. Several tests were conducted on the membrane to study its performance and characteristics.

4.3.1 Effect of loading

The adsorptive membrane was synthesized in the laboratory using the method explained previously. Three membranes were prepared with different loadings to study the effect of ZrP loading on the removal efficiency and permeability based on the porosity and pore volume of the membrane namely 0.097 g, 0.129 g, and 0.195 g. The highest removal efficiency found was 99.67% for a loading of 0.097 g and initial ciprofloxacin concentration of 20 ppm. This adsorbent loading proved to be efficient since it did not block or clog the pores of the membrane and can achieve high removal simultaneously. As it can be noticed from Figure 4-11, the ciprofloxacin removal efficiency decreased with increasing the loading, since overloading the adsorptive membrane can have counteract results which compromise the performance. Table 4-6 presents the removal efficiencies achieved for the different initial concentration of ciprofloxacin. It is also worth noting that this removal efficiency increased from 68% by using the pure PES membrane which proves that the adsorptive membrane significantly enhances the filtration process. Moreover, it can be noticed that for a lower ZrP amount the adsorptive membrane was able to obtain a higher removal efficiency compared to the batch adsorption test at 20 ppm which makes this technology advantageous.

With the optimum ZrP loading of 0.097 g, the removal efficiency of the adsorptive membrane using different initial concentration of ciprofloxacin were tested. The results obtained in Table 4-7 and Figure 4-12 show that the removal efficiency reached a maximum at 20 ppm and then decreased. This is due to the deposition of ciprofloxacin on the surfaces of the adsorbent and the membrane which leads to covering and reducing the number of available active sites, in addition to fouling the membrane faster thus reducing the rejection and the efficiency of the membrane.

Table 4-6: Removal efficiencies for different ZrP loadings

ZrP loading (g)	Removal Efficiency (%)
0.097	99.67
0.129	94.09
0.195	81.31
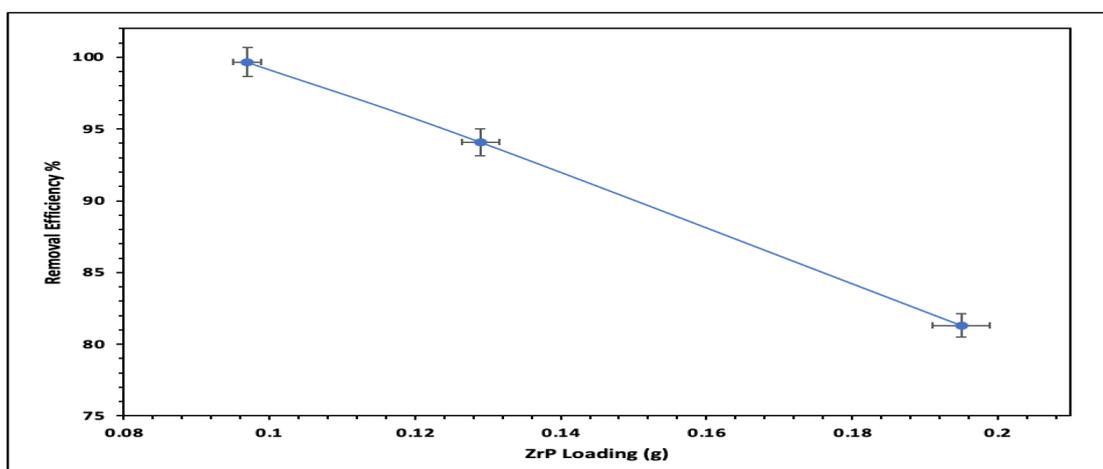
Figure 4-11: ZrP membrane loading vs removal efficiency of Ciprofloxacin

Table 4-7: Removal efficiencies for different CPFX initial concentrations

Initial Concentration (ppm)	Removal Efficiency (%)
10	95.99
20	99.67
30	92.66
40	91.32
50	90.89
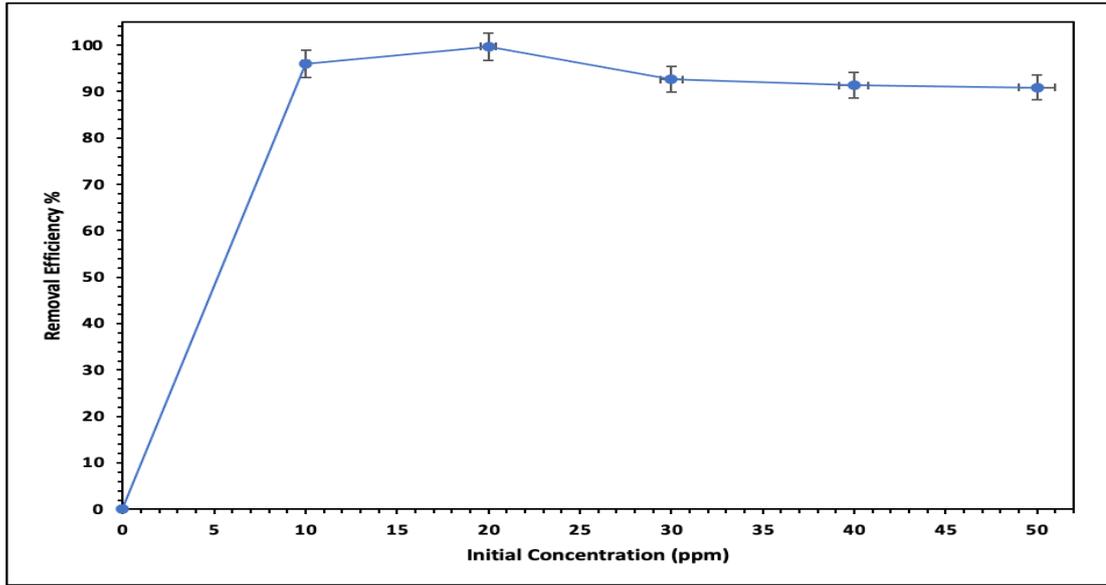
Figure 4-12: PES/ZrP Removal Efficiency vs Initial Concentration

4.3.2 Swelling and porosity tests

Membrane swelling is a phenomenon caused by slow diffusion of solvents into polymer chains which leads to a swollen polymeric membrane [176], or the process of dissolution of a polymer in a certain solvent. The solvent molecules gradually diffuse into the polymer to produce a swollen gel and cause an expansion of the polymer network in the case of strong polymer–polymer intermolecular forces. However, if the polymer-solvent forces are stronger, dissolution of the membrane occurs. This can be avoided by crosslinking, crystallinity, or strong hydrogen bonding [177].

PES/ZrP adsorptive membrane swelling was tested by immersing the membrane in distilled water for 24 hrs at room temperature. Following that, the membrane's wet weight was measured, then dried in an oven at 99°C until till the weight is constant [178]. The swelling behavior (Ws) or the degree of swelling was calculated using the following equation:

$$W_s = \frac{W_{wet} - W_{dry}}{W_{dry}} \qquad (11)$$

where W_{wet} and W_{dry} are the weights of the wet and dried membrane, respectively.

In addition, the water content (Wc) can be calculated using this following equation [179]:

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$$W_c = (\frac{W_1 - W_o}{W_1}) \times 100 \qquad (12)$$

where W_1 and W_o are the weights of the swelled and dried membrane, respectively.

Table 4-8 presents the swelling behaviour and water content for the PES/ZrP membrane. The results have shown that the membrane has low water content of 11% and a low swelling degree of 0.12 thus proving the fact that Polyethersulfone and polysulfone-based membranes generally contain only small amounts of water [180]. On the other hand, increasing the ZrP content within the PES membrane matrix increases both the water content and swelling degree since there is a direct relationship between them due to the hydrophilic character associated with the presence of hydroxyl groups in Zirconium phosphate. Therefore, this also agrees with the fact that the chosen ZrP content is the optimum to avoid membrane dissolution in water purification applications which makes it a safe applicant.

Table 4-8: Swelling behaviour and water content for the PES/ZrP membrane

Water Content (%)	Swelling Degree	Porosity
11	0.12	0.13

The porosity of PES/ZrP adsorptive membrane was estimated using the dry–wet weight's technique. In this method, the membrane was immersed in distilled water overnight to make sure that all the pores of the membrane were filled with water then weighed as wet weight after cleaning any excess water. Then, it is dried in an oven at 90 °C for 2 hrs to evaporate the water from the pores and weighed again to find the dry weight [181]. The membrane's porosity is calculated using the following equation:

$$\varepsilon = \frac{W_{wet} - W_{dry}}{\rho \times A \times H} \qquad (13)$$

where ε is the membrane porosity, ρ is the water density (0.998 g/ cm^3), A is the membranes area (cm^2) and H is the membranes thickness (cm) [178].

The laboratory membrane having an area of 19.635 cm^2 and a thickness of 0.012 cm. The adsorptive membrane porosity was found to be 0.13 which is the void volume fraction of the membrane and specified as the volume of the pores divided by the total

volume of the membrane [182]. Further information regarding porosity and pores volume will be investigated in the characterization by the BET analysis.

4.3.3 Regeneration Study

The regeneration study for the adsorptive membrane was carried out using 0.1 N NaOH. A basic solution was used due to the acidic nature of Zirconium phosphate. After adsorption of ciprofloxacin, the membrane was soaked in 0.1 N NaOH for 1 h as a desorption process to regenerate the membrane's adsorption capacity, followed by washing with distilled water various times util the pH reached neutrality [178]. The adsorption and regeneration process were repeated 6 cycles.

It was found that the adsorptive membrane developed in this work is capable of removing ciprofloxacin efficiently up to 5 cycles. The removal efficiency decreased with each regeneration cycle and reached to 62.35% in the fifth one, which is reasonably acceptable. This decrease in uptake with each regeneration cycle can be attributed to the acidic nature of ZrP which reacts with NaOH and lead to consumption of the active sites.

Moreover, one-way filtration using NaOH was done, and the desorption of ciprofloxacin was found to be around 91% of the adsorbed particles. This indicates that most of ciprofloxacin was easily adsorbed on the easily accessible adsorption sites in the membrane, thus easily desorbed and recovered in the NaOH solution [183]. This proves that PES/ZrP adsorptive membrane is easily recovered and reused.

4.3.4 Membrane Permeate Flux

An important parameter in evaluating the performance of the membrane is its flux (Jw). It can be determined by collecting the permeate at intermittent times [33], and using the following equation:

$$J_w = \frac{Q}{\Delta t \times A} \tag{14}$$

where Q is the collected permeate water volume, Δt is the filtration time or the time of permeate collection, and A is the membrane area [32].

The permeate flux was calculated to be 100.84 L/m^2.h which is a higher flux considerably with respect to the pure PES membrane of 81.48 L/m^2.h. This could be

due to the increase in the hydrophilicity of the PES membrane and the change in the membrane's surface and sub-layer morphology caused by the incorporation of ZrP in the membrane's matrix. Enhancing the membrane's hydrophilicity results in increasing the water molecules attraction into the membrane's matrix, promoting their passage across the membrane, and thus increase the membrane's water flux [71].

The permeate flux has decreased with every cycle used during the regeneration test as shown in Figure 4-13. However, it is less significant compared to the pure PES membrane as presented. This is an indication that less fouling is happening in the adsorptive membrane since membrane fouling causes a decline in the permeate flux with time. This is a result of the deposition of ciprofloxacin on/in the membrane pores which reduces the effective membrane area [184]. Fouling generally leads to irreversible fouling formation that cause high permeate flux reduction rates and makes the recovery of the permeability challenging [185]. Moreover, as mentioned before increasing the hydrophilicity of the membrane is one of the important factors in enhancing its anti-fouling property [186], [71]. Hydrophobic membranes have no hydrogen-bond interaction with water, thus hydrophobic solutes will spontaneously get adsorbed on the surface. This leads to blocking the membrane pores, cause fouling, hinder the performance, and reduce the membrane's life span [187].
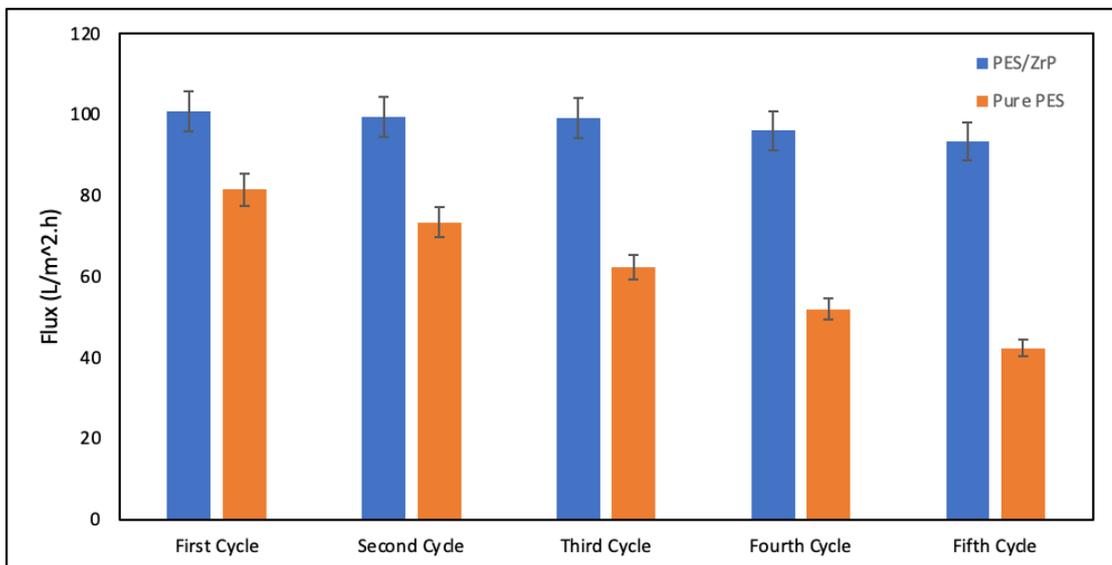

Figure 4-13: Permeate flux comparison between PES/ZrP and PES membranes

To assess the fouling resistance ability of the membrane, flux recovery ratio (FRR) is calculated using the following equation [71]:

$$FRR = (\frac{J_{w,2}}{J_{w,1}}) \times 100 \tag{15}$$

where $J_{w,1}$ and $J_{w,2}$ are the permeate fluxes in the first and last cycle respectively. The flux recovery ratio % was found to be 92.76% which is reasonably indicating excellent anti-fouling properties for the adsorptive membrane [71].

4.3.5 Membrane Permeability

The permeability of the membrane can be calculated from the pure water flux and the applied transmembrane pressure [45]. The corresponding equation is:

$$L_p = \frac{J_w}{\Delta P} \tag{16}$$

After applying a transmembrane pressure of around 1.033 bar, the water permeability of the membrane was found to be 97.62 L/m^2.hr.bar. This value is considered high compared to the general permeability values of membranes reported in literature. The permeability of the modified membrane with ZrP was found to be higher than pure PES membrane permeability of 59.3 L/m^2.hr.bar. This can be attributed to the increase in the hydrophilicity of the membrane after the incorporation of the adsorbent which is one of the advantages of utilizing adsorptive membranes.

4.3.6 Adsorption capacity

The adsorption capacity of the membrane is calculated using the following equation:

$$q = \frac{(C_o - C_e) \times V}{m} \tag{17}$$

where q is the equilibrium adsorption capacity (mg/g), m is the weight of the dried membrane (g), and V is the volume of the adsorbate solution (L)[19].

The highest adsorption capacity of the membrane for ciprofloxacin obtained was 8.896 mg/g as shown in Table 4-9 and Figure 4-14, which is an acceptable value since the mechanism of this adsorptive membrane is not solely dependent on the adsorption process.

Table 4-9: The membrane adsorption capacity

q (mg/g)	Ce (mg/L)
1.88	0.40
3.90	0.07
5.44	2.21
6.92	3.47
8.89	4.56
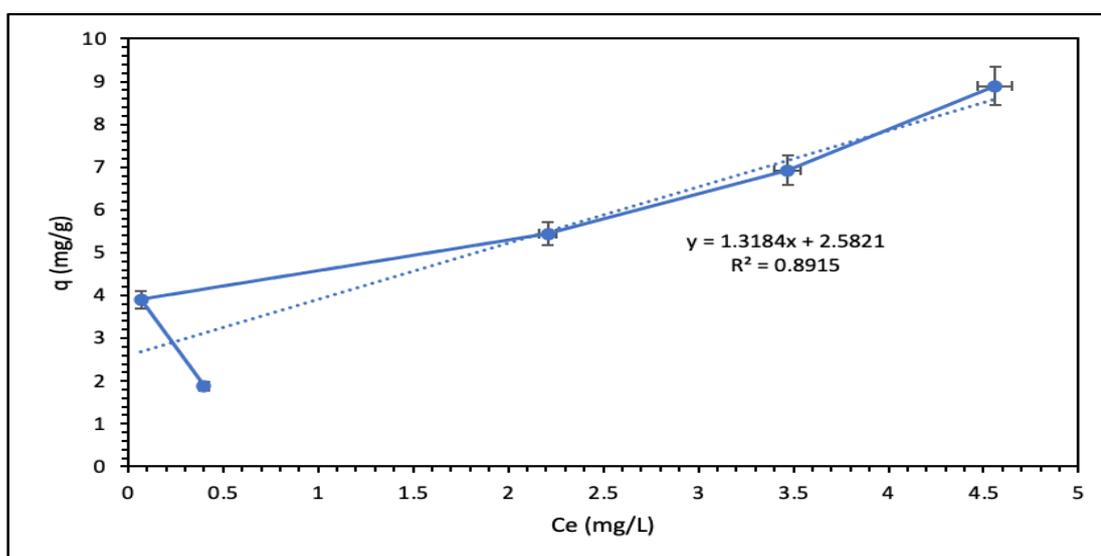
Figure 4-14: Ce vs q for PES/ZrP membrane

4.4. Membrane Characterization

Membrane characterization provides valuable information about the membrane, and it includes chemical and physical characteristics, surface morphology, and properties such as porosity and tendency to fouling [188]. Several tests were done on the adsorptive membrane that will be discussed in this section.

4.4.1 SEM images

Scanning electron microscopy is used to study the morphology of the membranes. This was done to compare the adsorptive membrane's surface before and after ciprofloxacin filtration. Images a,b and c of Figure 4-15 show the SEM images of PES/ZrP membrane at 10, 25, and 50 $\times 10^3$ magnification. The images show the embedded ZrP particles in the membrane's matrix which proves successful immobilization of the adsorbent in the

highly porous asymmetric polyethersulfone support. The zirconium phosphate are mostly spherical shaped particles with sizes ranging between 574 nm and 684 nm diameter. These particles which are in the nanometre range, exhibit outstanding chemical and physical properties that enhances the filtration process. Moreover, it can be observed from these images that ZrP is fixed in the pores of the polyethersulfone membrane in such a way that avoids pores' blockage. This assists in the dual advantage of the adsorptive membrane that facilitates both adsorption and membrane filtration processes, since small particles get adsorbed by ZrP and larger particles get filtered by molecular sieving. Therefore, the adsorbent loading was an important factor to study to ensure membrane's permeability.

The SEM images (d-g) show the PES/ZrP membrane's surface after ciprofloxacin filtration. The small particles are clearly deposited on the adsorbent and membrane's surfaces, which confirms the high removal efficiency obtained. The physiosorption has successfully occurred between ciprofloxacin in the water solution and the adsorptive membrane with thin surface layer, large pores and macrovoids. The highly magnified image (g) shows the rough surface of the ZrP particles and the membrane after the deposition of ciprofloxacin on their surfaces.
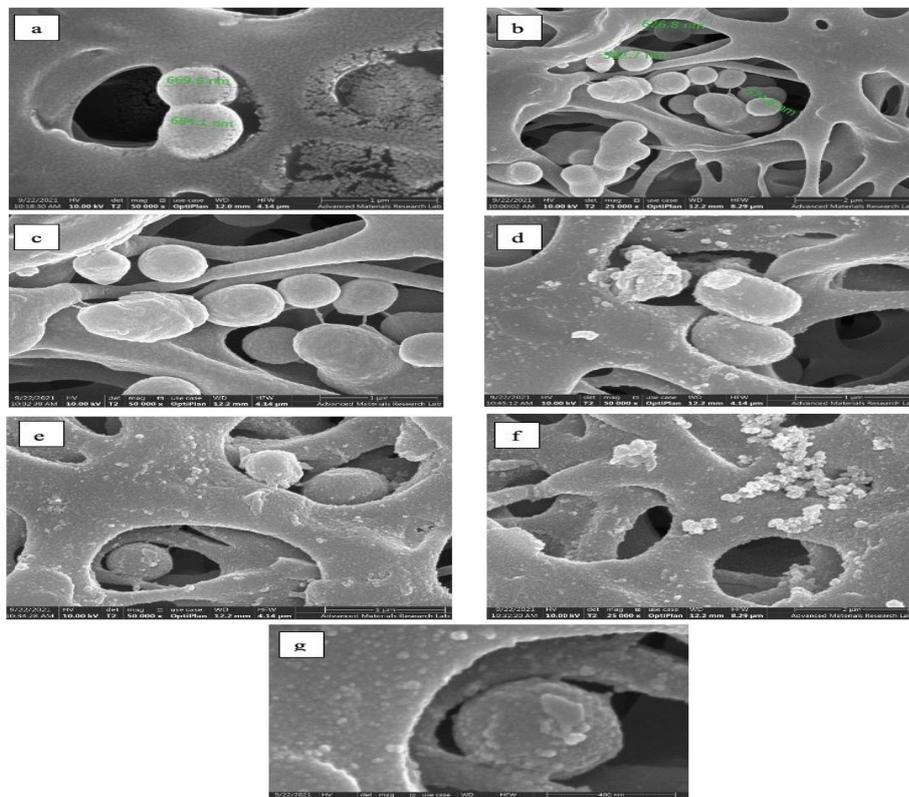
Figure 4-15: SEM images for PES/ZrP membrane before and after filtration

The Energy Dispersive X-Ray Spectroscopy (EDS or EDX) provides the elemental composition of the analyzed samples for the PES/ZrP membrane before and after filtration of ciprofloxacin. Figure 4-16 shows the EDS results of polyethersulfone/ zirconium phosphate membrane revealing the highest wt% of carbon, oxygen, then sulphur which agrees with the chemical formula of polyethersulfone $(C_{12}H_8O_3S)n$ and zirconium phosphate $Zr(HPO_4)_2$. Moreover, the addition of zirconium phosphate to the membrane's matrix have reflected in the chemical composition as phosphor appeared in the analysis. However, the wt% of Zr does not appear in the analysis and this can be attributed to several reasons such as the small amount of ZrP embedded in the membrane, or it is overlapped or covered by other elements.
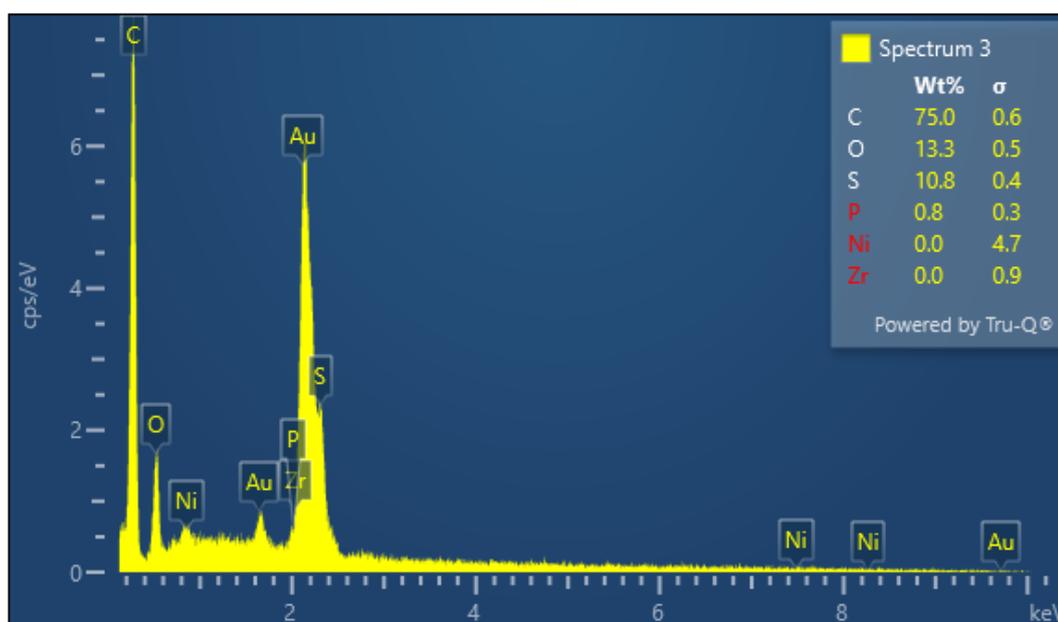
Figure 4-16: EDS results of PES/ZrP membrane

Figure 4-17 shows the EDS results after ciprofloxacin filtration. The analysis indicates an obvious change in the chemical composition of the adsorptive membrane. The wt% of O increased, while N and F appeared in the analysis with considerable amounts. This is an indication of successful ciprofloxacin adsorption as these elements are parts of its molecular structure (Figure 3-1).
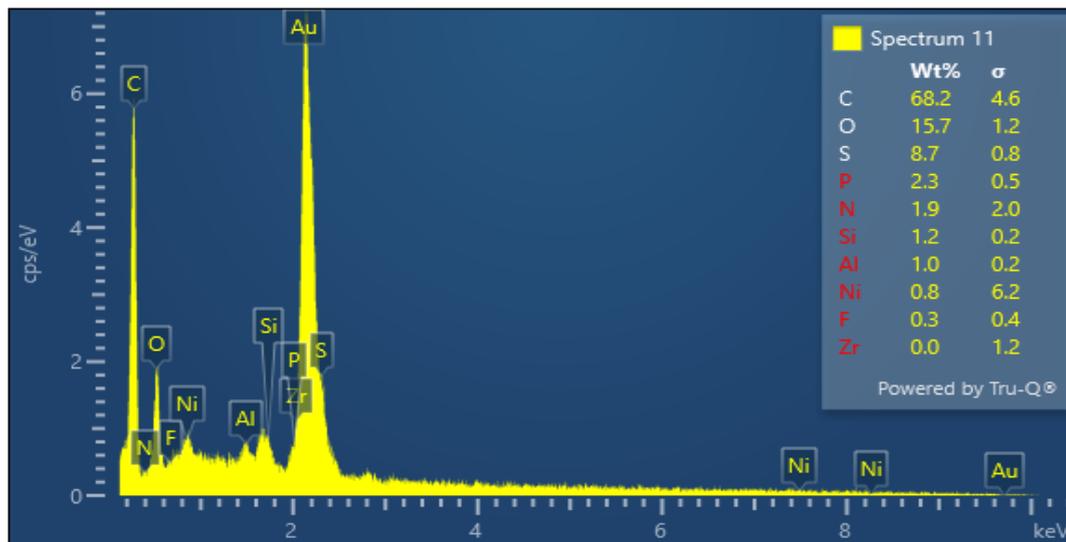
Figure 4-17: EDS results of PES/ZrP membrane after ciprofloxacin filtration

4.4.2 FTIR

Fourier transform infrared (FTIR) spectroscopy is one of the most effective techniques to study and understand the chemical and surface chemistry of membranes. It assists in detecting the functional groups that attributes to the membrane's behavior, properties, and performance [189]. The FTIR spectra of the PES/α-ZrP membrane is shown in Figure 4-18. The weak peak observed at 3100 cm^{-1} represents the symmetric stretching vibration absorption peak of the intercalated water molecules. While the characteristic peak at 1620 cm^{-1} is the absorption peak caused by the deformation vibrations of the O-H bonds of the water molecules and indicates the bending of water molecules, in addition to the O-H stretching occurring at around 2400 cm^{-1}. The strong peak that occurs at around 1000 cm^{-1} is the stretching vibration peak due to P-O in -PO$_4$ group. The Zr-O stretching peak is clear at 560 cm^{-1}, while the absorption band at 730 cm^{-1} corresponds to P-O-P vibration of the diphosphate groups (O$_3$P-OPO$_3$) and the peak near 1250 cm^{-1} is related to the in-plane P-OH deformation modes [190][191][161].

The trend in peaks up to 1600 cm^{-1} were also observed in pure PES membranes in literature attributed to the C=C, C=H, and S=O stretching vibrations [192]. At 1150 cm^{-1}, the vibration of the sulfone group (S=O) occurs, and at 1322 cm^{-1} is the stretching of CSO$_2$C, in addition to the 1244 cm^{-1} peak corresponding to the stretching of CO- group. Moreover, the C$_6$H$_6$ ring stretching vibration peak was detected at 1498 cm^{-1} [161]. The other changes in the trend are clearly caused by the addition of ZrP.

87
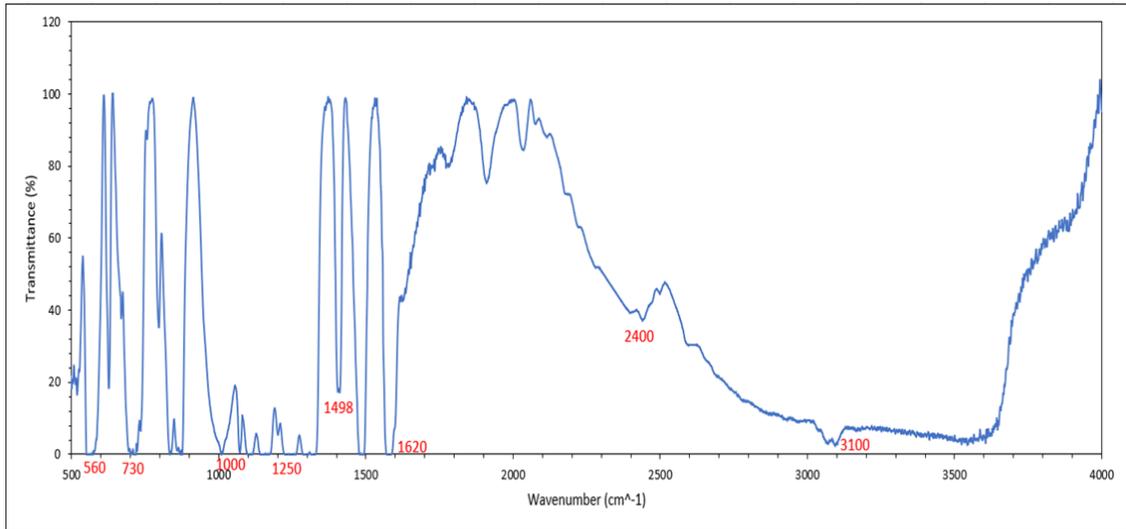
Figure 4-18: FTIR spectra for PES/ZrP adsorptive membrane

Moreover, the FTIR spectra of the adsorptive PES/ZrP membrane was analysed after the filtration of Ciprofloxacin from the water samples and the results are shown in Figure 4-19. Comparing this graph with pre-filtration graph, it can be noticed that there is band shifting and intensity changes due to the coverage of the surface with ciprofloxacin. This observation was also noted in another study with ciprofloxacin adsorption [159]. The modified membrane shows a decrease in transmittance which indicates higher population of bonds, binding of molecules to the surface of the membrane, and the presence of more functional groups in the membrane [119][79][193].
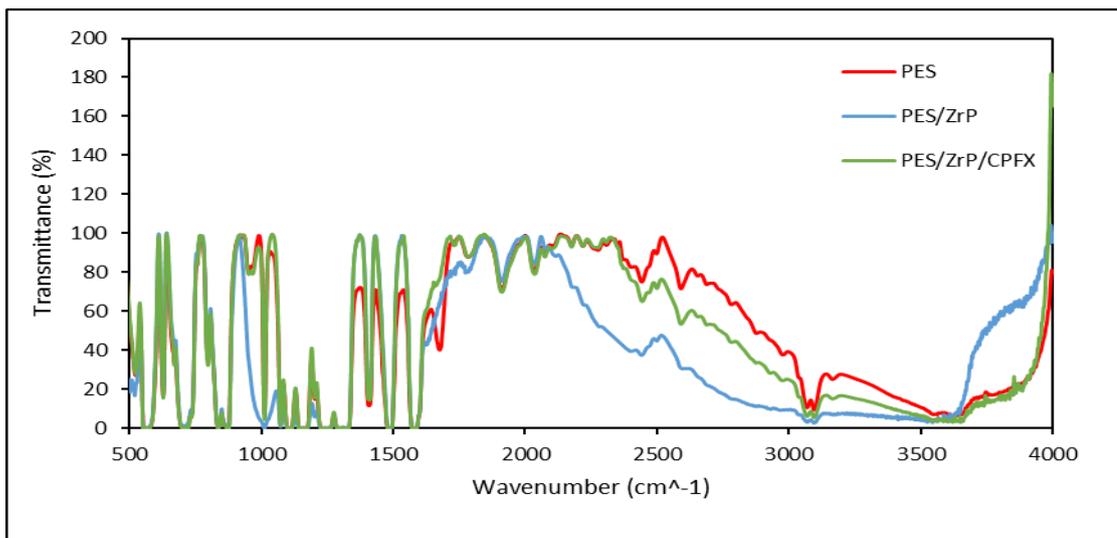
Figure 4-19: FTIR spectra comparison

4.4.3 BET

The Brunauer-Emmett-Teller (BET) method is applied to calculate the sample specific surface area on the basis of nitrogen adsorption isotherm measurements at 77 K [194]. The BET analysis has shown a specific surface area of 115.677 m^2/g for the PES/ZrP adsorptive membrane using the multipoint analysis compared to a specific surface area of 22.510 m^2/g for the pure PES membrane. In addition, the average pore radius and total pore volume that increased from 1.72 nm and 0.03 cm^3/g to 2.14 nm and 0.11 cm^3/g. This increase that led to a higher specific surface area is attributed to the dispersion of zirconium phosphate particles which results in an increase in the contact area between Ciprofloxacin particles and the adsorption active sites. However, increasing the loading more than the optimum value leads to agglomeration and blocking the pores, thus lowering the surface area.

Worth mentioning that the BET results can give valuable information regarding membrane fouling. Since generally, the formation of a fouling layer on the pores and membrane's surface results in an increase in the cumulative pore volumes and pore areas. It was found that after operation, the increase in the average pore radius to 2.80 nm resulted in an increase in the total pore volume to 0.28 cm^3/g. This indicates cake fouling and porous fouling layer formation on the adsorptive membrane's surface [195].

4.4.4 XRD

X-ray diffraction (XRD) was used to analyse the structure of PES/ZrP adsorptive membrane. It is a technique used to determine the nature of the materials as crystalline or amorphous [196], in addition to ensuring the presence of α-ZrP particles. X-ray diffracted intensities were analyzed in the 2θ range of 10°–60° and the results are shown in Figure 4-20, where θ is the angle of deflection of the incident beam. Intensive diffraction peaks indicate the crystalline structure, while the broad peaks represent the amorphous structure. A well-defined intensive peak mainly appears at around $2\theta=16°$ which is a typical peak of polyethersulfone polymer structure at low intensity [197].

The less intense broad peaks appearing are characteristics peaks attributed to the presence of amorphous ZrP happening at about 2θ of 31° and 42° which agrees with values found in another study [198]. This assures the presence of α-ZrP particles in the membrane's matrix.

A shift in the 2θ of the characteristic peak of PES can be observed after ZrP incorporation. It should be mentioned that any changes that occur in the composition would affect the lattice which change the inter-planar spacing (d). This causes a shift in the diffraction pattern to a different 2θ value [199][200]. Moreover, an increase in the intensity occurs after the addition of ZrP and more after the filtration of ciprofloxacin which indicates an increase in the amorphous structure. The pure membrane already has an amorphous structure which is increased by the incorporation of the amorphous ZrP. This increased loss of crystallinity is related to the introduction of more water molecules [201]. However, the changes in PES structure seen not to be significant as no new peaks were formed due to the addition of a small amount of ZrP. This also proves the good compatibility and mixability between PES and ZrP.
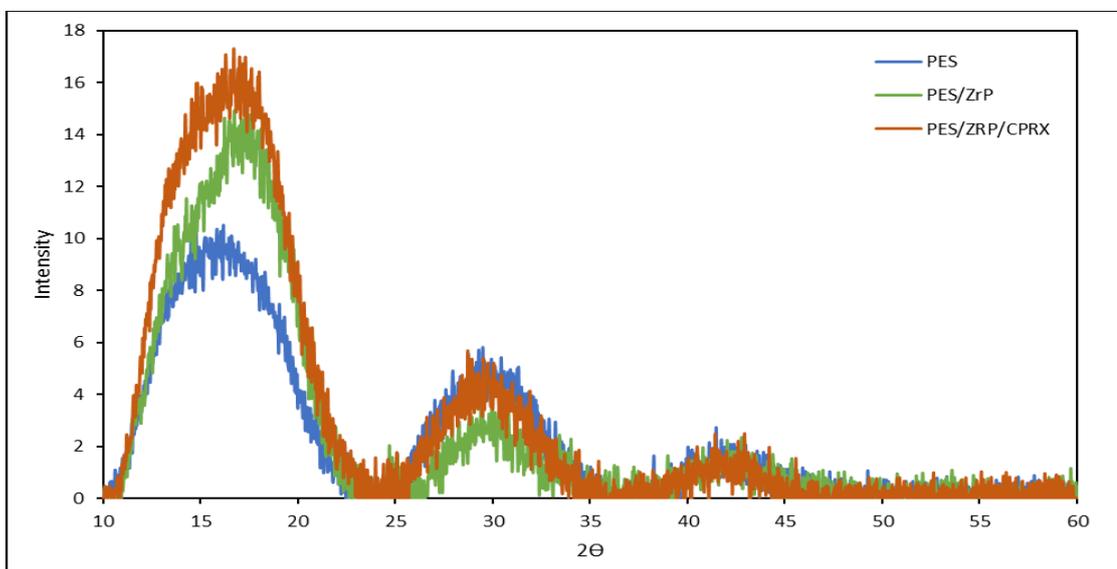
Figure 4-20: XRD analysis of the membrane samples

The XRD is useful in calculating the changes in the lattice or d spacing by implementing Bragg's law which determines the angles of coherent and incoherent scattering from a crystal lattice [202]. Bragg's equation basically justifies the reflection of Xray beams from the faces of crystals at specific angles of incidence θ [202]:

$$n\lambda = 2 \text{ d } \sin\theta \tag{18}$$

where d is the distance between the atomic layers, λ is the wavelength of the incident X-ray beam, and n is an integer respective to the order of the diffraction peak [202].

The values of the lattice d-spacing are calculated and presented in Table 4-10 when n=1 and λ =1.54 Å.

Table 4-10: Values of interlaying spacing for characteristic peaks

Sample	2 θ	Lattice d-spacing (Å)
Pure PES	16°	5.53
PES/ZrP	18°, 31°,42°	4.92, 2.88, 2.15
PES/ZrP/Ciprofloxacin	17°,31°,42°	5.21,2.88, 2.15

The XRD results showed no major structural changes occurring, however some small shifts in the major peaks were noticed. This indicates a change in the interlayer spacing due to the incorporation of ZrP between the PES layers. The results obtained from the FTIR and XRD analysis agrees with the possible interaction between ZrP and PES by hydrogen bond interaction suggested in literature [161] and shown in Figure 4-21.
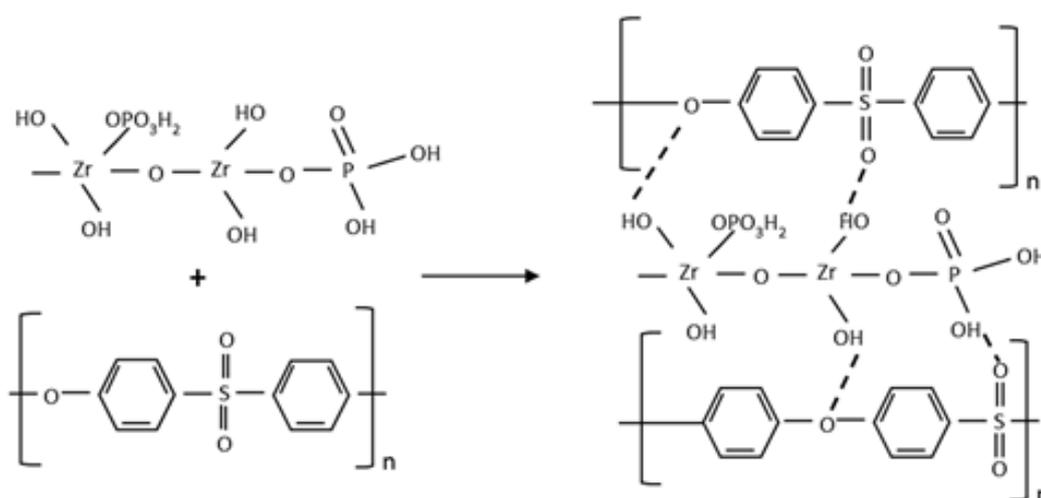
Figure 4-21: Possible interaction of α-ZrP particles with PES polymer [161]

Chapter 5. Conclusions and Future Work

This research tested the use of adsorptive membranes for the removal of pharmaceutical compounds from wastewater. Polyethersulfone porous membrane was used as a polymer support and Zirconium phosphate as an adsorbent embedded in its matrix to remove Ciprofloxacin antibiotic from water solutions. The experiments focused on determining the adsorption capacities, permeability, efficiencies, and flux with analytical techniques and adsorption isotherms.

The results have shown successful removal of ciprofloxacin as the removal efficiency reached to 99.67%. This was a significant enhancement than using the pure PES membrane or ZrP adsorbent alone. Since with lower ZrP amount a higher removal efficiency was obtained, this proves the effectiveness and cost-efficiency of PES/ZrP adsorptive membrane. Moreover, several improvements in the membrane's properties were observed with the aid of characterization techniques after the adsorbent incorporation. These properties include: the pure water flux, permeability, membrane specific area, porosity, and hydrophilicity. This outcome proves the initial claim that adsorptive membranes encompass the advantages of both adsorption and membrane filtration processes and enhance the performance of the membrane.

Moreover, the results confirm that utilizing adsorptive membranes in pharmaceuticals removal is as promising and effective as the removal of metal ions and dyes. However, it has not been researched extensively. Furthermore, the results show that solution coating is a successful membrane fabrication technique, as ZrP was well incorporated in the membrane's pores as shown by the SEM images. In addition to being practical and easy to perform on a lab scale.

On the other hand, applying adsorptive membranes have many challenges associated with ensuring their safety to humans and the environment, scaling them up to industrial applications, and fouling. Therefore, future research can study the possibility of utilizing PES/ZrP membrane on a larger scale by performing a thorough toxicity analysis to ensure no hazardous effects on drinking water. In addition to studying the financial aspects of applying them via feasibility and cost analysis.

Moreover, further investigations need to be done on the membrane to examine its fouling properties like atomic force microscopy (AFM), despite that the initial

conclusions were made in this research regarding the successful capability of regenerating and reusing the membrane. Moreover, the membrane stability can be furtherly examined and confirmed by doing FTIR analysis to the regenerated membrane. Finally, another recommendation for future work would be using synthesised or real wastewater to study the membrane's performance more accurately instead of water aqueous solutions.

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