Nanofibrous Polymer Systems for Elimination of Estrogenic Hormones from Wastewater

Muhammad Yasir, M.Sc., Ph.D.

Doctoral Thesis Summary

Tomas Bata University in Zlín

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Centre of Polymer Systems

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Nanovlákenné polymerní systémy pro eliminaci estrogenních hormonů z odpadních vod

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Key words in English: *estrogenic hormones, nanofibers, electrospinning, adsorption kinetics, wastewater treatment, polyurethane, polyamide, polysulfone, polylactide, polyvinylidene fluoride, cellulose acetate, polyacryl amide*

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Dedication

This Ph.D. thesis is dedicated to my adorable and beloved parents (late): ***Mrs. Tabassum Zahida***, M.A., my mother, and ***Mr. Ashiq Hussain***, M.A. LL.B., my father.

ABSTRACT

Residual estrogenic hormones represent emerging pollutants in the environment. One of the most important aspects of their effective removal is the design and fabrication of an adsorption system with appropriate properties. This thesis reports on the complex research activities aimed at the development, optimized preparation, and characterization of various electrospun nanofibrous polymer systems for simultaneous removal of estrogenic hormones such as estrone, estradiol, ethinylestradiol, and estriol from wastewater. A wide scale of polymers covering polyurethanes, polyamide, cellulose acetate, polysulfone, polyether sulfone, polylactic acid, polyacrylonitrile, and polyvinylidene fluoride was studied as a matrix for nanofibrous sorption materials. A facile method was developed for the simultaneous determination of tested hormones by using a high-performance liquid chromatography technique coupled with a UV-Vis detector. Sorption kinetics modeling and description of the material vs. hormones interaction mechanisms were an integral part of this study.

Key words: *estrogenic hormones, nanofibers, electrospinning, adsorption kinetics, wastewater treatment, polyurethane, polyamide, polysulfone, polylactide, polyvinylidene fluoride, cellulose acetate, polyacryl amide*

ABSTRAKT

Residua estrogenních hormonů představují aktuální problém pro životní prostředí. Návrh, vývoj a produkce absorpčních systémů schopných jejich efektivního záchytu z environmentu jsou důležitými aspekty při řešení této problematiky. Tato práce se věnuje komplexnímu výzkumu cíleného na vývoj, charakterizaci a optimalizaci přípravy nanovlákenných systémů, připravených pomocí metody elektrozvlákňování polymerních roztoků, pro odstraňování estrogenních hormonů estronu, estradiolu, ethinyestradiolu a estriolu z odpadních vod. Široká škála polymerů zahrnujících polyuretan, polyamid, acetát celulózy, polysulfon, polyetersulfon, polylaktid, polyakrylonitril a polyvinilidenfluorid byla studována jako matrice pro přípravy nanovlákenných sorpčních materiálů, V rámci práce byla vyvinuta metoda pro současné stanovení všech použitých hormonů pomocí metody vysoce účinné kapalinové chromatografie se spektrometrickou detekcí v ultrafialové a viditelné oblasti. Modelování sorpčních kinetik a popis interakce mezi estrogenními hormony a připranými materiály jsou nedílnou součástí práce.

Klíčová slova: *estrogenní hormony, nanovlákna, elektrozvlákňování, sorpční kinetika, čištění odpadních vod, polyuretan, polyamid, polysulfon, polylaktid, polyvinilidenfluorid, acetát celuylózy, polyakrylamid*

ACKNOWLEDGEMENTS

All praise to almighty Allah, the most merciful and compassionate, the creator of the universe, Who enabled me to complete this research work successfully. I feel privileged to have the honor to acknowledge my research supervisor ***Prof. Vladimir Sedlarik,*** to whom I owe my indescribable special indebtedness, who was very affectionate and cooperative during this research work. I am thankful to my doctoral study consultant, ***Ing. Dusan Kimmer,*** for the inspiration throughout my study. Without his kind and sincere efforts, it might not have been possible for me to end this task in time.

Furthermore, I would like to extend my gratitude to ***Tomas Bata University in Zlín*** for providing me with the necessary infrastructure and financial support in the form of a ***Ph.D. extraordinary scholarship (2019-2022)*** and ***IGA project fund (IGA-2019-2022)*** for my research, attending different international scientific conferences and my living in the Czech Republic.

The successful accomplishment of this doctoral thesis has become possible with the sustained support of the dearest ones. I offer my special and sincere thanks to my friends in the dormitory and colleagues in the ***Centre of Polymer Systems*** who guided me through the rough patches in conducting research. Furthermore, I wish to offer my humble gratitude to my deceased parents for their support in the early phase of my life that paved the way for me to reach this destination. I have realized that my whole life, I have been blessed because of them. Finally, I dedicate my success to my beloved wife, son, sister, sister-in-law, and father-in-law; they are a complete inspiration to me throughout my Engineering Career. Their affection, love, prayers, and true guidance have led me to consistent success.

Moreover, I would also thank ***Dr. Agnes Schulze***, head of Surfaces and porous membrane filters at Leibniz institute of Surface Engineering (IOM), Leipzig, Germany, for providing me training opportunity and ***Dr. Daniel Breite*** for helping me participate in learning electron-beam irradiation technique for the development of adsorptive membrane surfaces for the selective removal of hormones from water.

LIST OF PUBLISHED PAPERS

The doctoral work of Mr. Muhammad Yasir, entitled "***Nanofibrous polymer systems for elimination of estrogenic hormones from wastewater,"*** involves the following articles:

Article I

M. Yasir (70%), T. Sopik, L. Lovecka, D. Kimmer, V. Sedlarik, The adsorption, kinetics, and interaction mechanisms of various types of estrogen on electrospun polymeric nanofiber membranes, Nanotechnology 33 (2021) 75702, https://doi.org/10.1088/1361-6528/ac357b.

Article II

M. Yasir (80%), T. Sopik, R. Patwa, D. Kimmer, V. Sedlarik, Adsorption of estrogenic hormones in aqueous solution using electrospun nanofibers from waste cigarette butts: Kinetics, mechanism, and reusability, Express Polymer Letters 16 (2022) 624–648, https://doi.org/10.3144/expresspolymlett.2022.46.

Article III

M. Yasir (50%), F. A. Ngwabebhoh, T. Sopík, H. Ali, V. Sedlarik, Electrospun polyurethane nanofibers coated with polyaniline/polyvinyl alcohol as ultrafiltration membranes for the removal of ethinylestradiol hormone micropollutant from aqueous phase, Journal of Environmental Chemical Engineering 10 (2022) 107811, https://doi.org/10.1016/j.jece.2022.107811.

Article IV

M. Yasir (50%), F. A. Ngwabebhoh, T. Sopik, L. Lovecka, D. Kimmer, V. Sedlarik, The adsorptive behaviour of electrospun hydrophobic polymers for optimized uptake of estrogenic sex hormones from aqueous media: Kinetics, thermodynamics and reusability study, Journal of Chemical Technology and Biotechnology (2022), https://doi.org/10.1002/jctb.7191.

TABLE OF CONTENT

1. INTRODUCTION

Water is the most important and limited resource available on earth, which has been contaminated by toxic metals, pathogens, pharmaceutical chemicals, dust, dyes, pesticides, fertilizers, and organic and inorganic materials. Various methods have been implemented for the remediation of water quality and cleaning, but most of them are expensive, less effective, and time-consuming. In this domain, several solutions related to nanotechnology have been successfully deployed in recent times. In this regard, membranes based on nanofibers produced from different polymeric materials for water treatment applications are promising owing to their benefits, such as affordability, sustainability, efficient performance, durability, high surface area, high aspect ratio, and nanoporous structure. Furthermore, the nanofiber membrane functions precisely in different aquatic conditions without the accumulation of chemicals [1].

Estrogenic hormones (EH) at significant levels are a serious cause of fish femininity and breast and ovarian cancer because of hormonal imbalance. Furthermore, environmental effluents that are being constantly discharged, especially synthetic hormones, are difficult to contain and pose a severe risk to the environment and various forms of life. So far, several techniques have been employed to eliminate such hazardous hormones, such as ozonation, membrane bioreactors, advanced oxidation, membrane filtration, coagulation, and flocculation. These commonly used techniques also result in secondary pollution, which demands secondary water treatment. In this regard, removing synthetic hormones by adsorption via electrospun nanofibers offers a sustainable and relatively environmentally friendly solution for eliminating synthetic hormones with high efficiency and effectiveness of reusability for several adsorption-desorption cycles after regeneration. This brings a practical approach to large-scale production.

The thesis presented here is devoted to fabricating electrospun polymeric nanofibrous membranes that are porous and most suitable for capturing EH, owing to their specific surface area and functional groups on the surfaces involved. The surface treatment of nanofibers further enhances the simultaneous adsorption of EH due to the involvement of several types of interaction mechanisms, such as physical adsorption, hydrophobic interactions, hydrogen bonding, and π–π stacking interaction. This surface modification of the most promising nanofiber is used to evaluate enhanced adsorption in an optimization study with the optimized experimental parameters via the response surface

methodology using a central composite design model and validation of operating parameters by the Design-Expert software. The study also contains devising a facile HPLC method for simultaneous detection and quantification of EH. The core part is devoted to optimized preparation, characterization of the electrospun membranes, testing of adsorption activity under different conditions, optimization of experimental parameters for determination of suitable kinetic models, Isotherms, thermodynamics, and ensuring the effectiveness by reusability of membranes over several adsorption-desorption cycles.

2. Theoretical background

2.1 The global challenge of water filtration

In the last few decades, rapid industrialization and human population growth have raised serious environmental concerns due to the high demand for various synthetic chemicals, which are being released into the environment without proper treatment. Today, the freshwater available on earth is less than 1% for the use of human beings. This freshwater has comprised the form of snow-capped peaks, glaciers, and ice mountains. The earth's water includes freshwater (2.6%) and saltwater (97.4%), which is primarily oceans (Figure 2.1). Of the freshwater, 70% is utilized for the purpose of irrigation, 10% for domestic use, and 20% for industrial work [2]. About 1.3 billion population worldwide cannot acquire safe water for drinking [3]. Approximately 1.8 million people consume unsafe and unclean water and die yearly because of diseases such as diarrhea. The world's population is massively growing, with an expected number to reach 3 billion in the next 30 years. There are almost 2.7 billion people exposed to devastating use of poor water quality due to an economic crisis in the developing world [4]. According to reports, around 5500–6200 children die worldwide per day using contaminated water. Globally, 0.8 million humans have unavailability of safe drinking water because of several reasons such as climatic effects of the growing population, increasing demand for energy, food crisis, ground and surface water pollution, improper use of resources, sanitation problems, soil erosion, excessive use of pesticides and fertilizers, contamination by heavy toxic metals, industrial effluent waste, oils spillage, pharmaceutical chemicals, and steroid hormones which are a significant contributor to contaminated water. These continuously spreading bioactive contaminants have severe consequences on the health of humans and marine life, uptaking water from sources leading to fatal diseases, among them being different kinds of cancer. Thus, micro-pollutants in water are needed to be immediately abolished and eradicated by strict control policies at wastewater treatment plants before consumption. The fabrication of high-performance and sustainable fibrous membranes is a necessity for all environmental applications areas, such as the removal of effluents waste from industries, textiles, dyes, heavy metals in water, nitrates, per- and polyfluoroalkyl substances, bacteria, pharmaceutical chemicals, EH, viruses, desalination and filtration of water for drinking purposes [5].

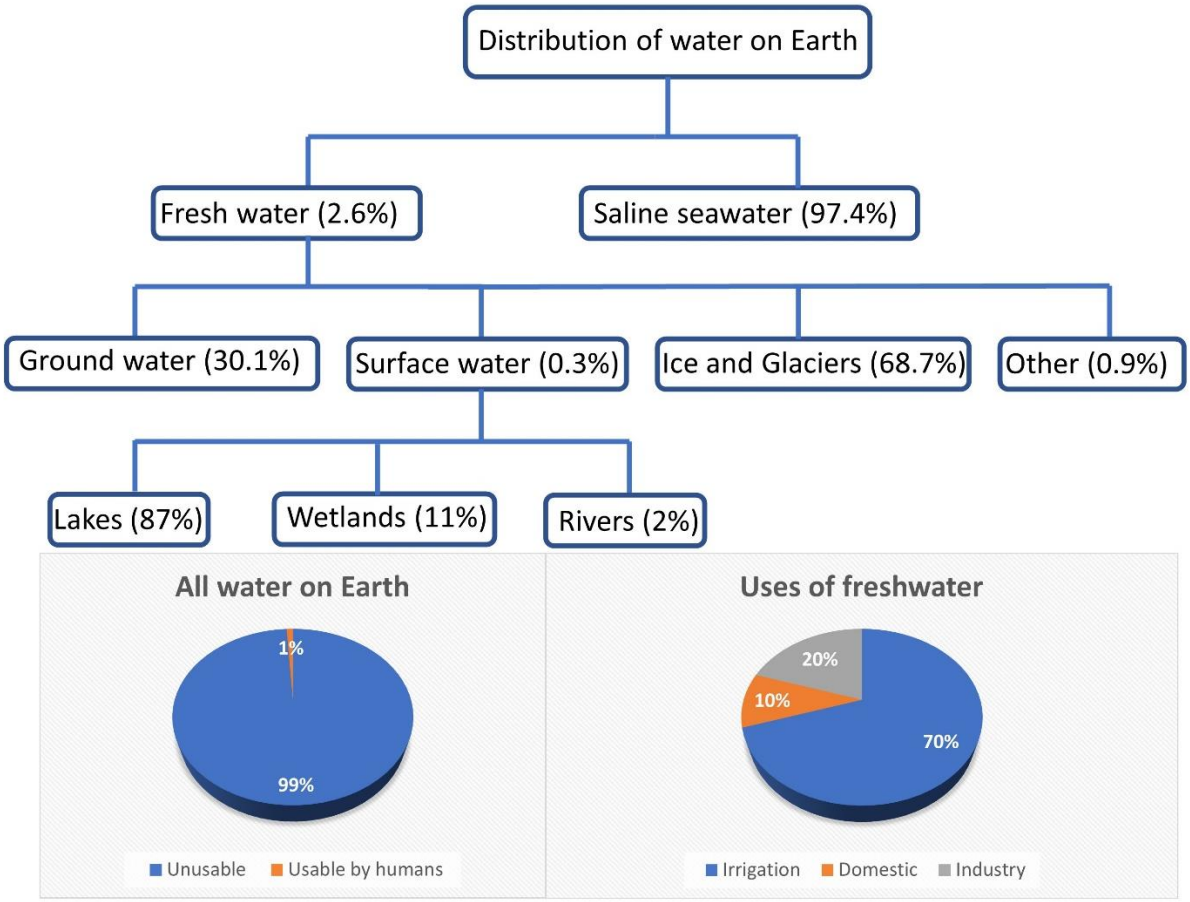


Figure 2.1: Distribution of Earth's water and its uses (Self-representation by the author).

2.2 Methods of removing contaminants from water

The equilibrium between sewage and freshwater resources is achieved by wastewater treatment. Therefore, the efficiency of wastewater treatment has a significant impact on water neutralization and reduces the depletion of precious water resources. Therefore, the most crucial needs of the modern period are technological advancements for wastewater treatment. The traditional and cutting-edge methods of water purification are described in detail here.

i) Conventionally applied methods

The removal of a wide range of hazardous compounds, bacteria, and chemicals contained in wastewater is limited by traditional methods of water filtration [6]. Conventional methods are displayed in Figure 2.2.

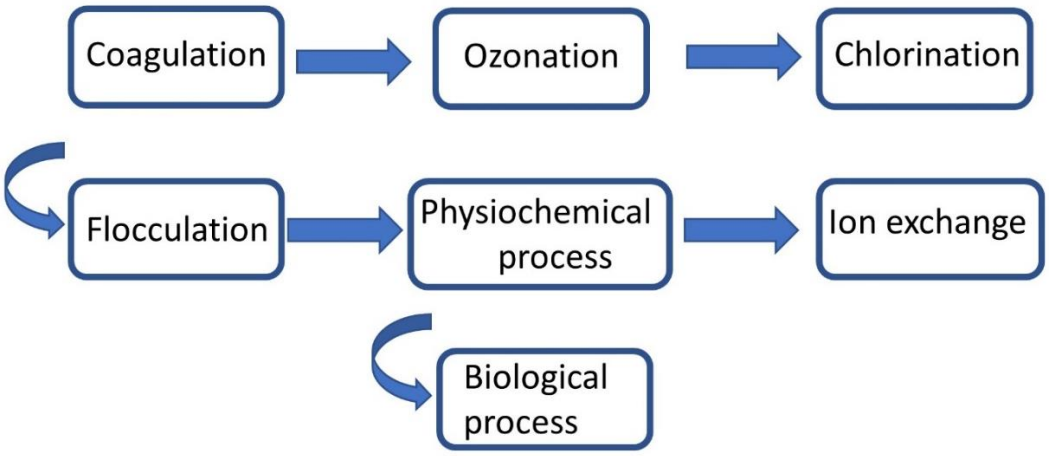


Figure 2.2: Conventional techniques of water filtration (Self-representation by the author).

Coagulation process

Before filtration and sedimentation, the technique of coagulation is used to clean wastewater. In this method, charged coagulants are employed to remove the wastewater's suspended solids and neutralize them. The flocs, which are invisible to the human eye, are formed when neutralized particles clump together. Additionally, the wastewater can be stirred to create micro flocs, as illustrated in Figure 2.3; however, this method is quite endothermic. Numerous academics have been studying the coagulation method for the treatment of wastewater [7,8]. While coagulation is widely used, new pilot plants and fully functional industrial units have also used the ozonation process to purify water.

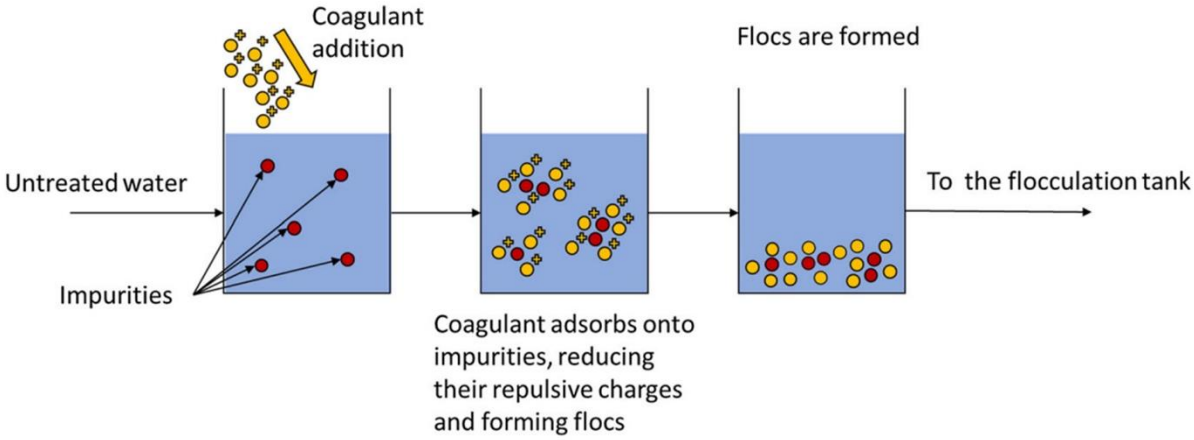


Figure 2.3: The Coagulation Process [9].

Ozonation process

wastewater effluents are taken out using this method, and drinking water is cleaned. By reducing the amount of organic and inorganic compounds in water, ozonation purifies it. Many studies have also reported using the ozonation technique to purify water and eliminate impurities such as effluents, dyes, and particles. Figure 2.4 displays a schematic representation of the procedure. This approach for purifying water is less effective due to its high cost and limited lifespan [10,11]. These ozonation difficulties are handled in the chlorination process, which is one of the most basic methods for purifying water.

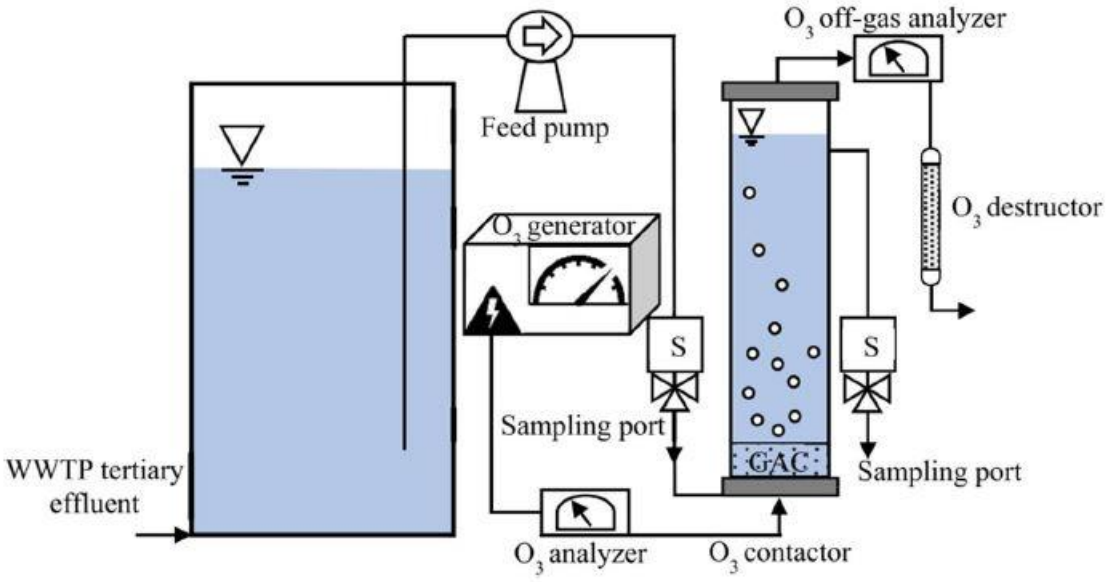


Figure 2.4: The Ozonation Process [1].

Chlorination process

This method is frequently employed to eliminate bacteria, pathogens, and other germs in wastewater because its mechanism offers a residual defense against bacteria and other organisms. Pathogens cause unwanted odor and taste in water. Various scientists have utilized this procedure to purify wastewater [12,13]. Chlorination may alter the taste and aroma of water, which is much less likely to occur in coagulation and flocculation.

Flocculation process

This procedure involves gentle mixing to agglomerate and settles the particles, as seen in Figure 2.5. The settled particles are subsequently removed from the wastewater using a filter. As the molecules are slowly mixed together, a bond is formed that makes the agglomerated particles visible. In order to improve floc density and settling speed, the coagulant can also be used to create a bridge

between the flocs. Once the floc reaches its maximum size, filtering is used to remove it from the media. Several researchers have reported that flocculation can remove pollutants [14].

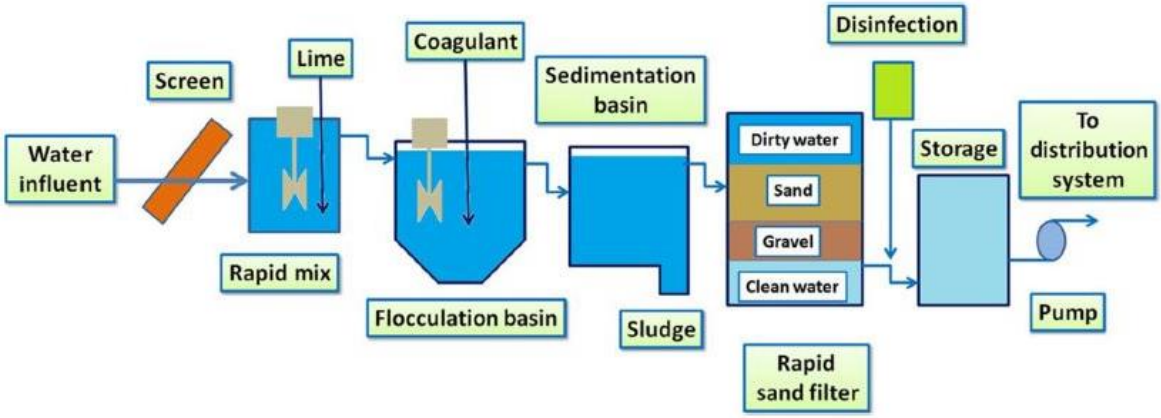


Figure 2.5: The Flocculation Process [1].

Physiochemical process of treatment

This method comprises the softening, coagulation, and flocculation of lime, and it is effective at removing a wide range of endocrine-disrupting compounds (ECDs). Numerous scholars have described a physiochemical method for wastewater cleaning [15,16].

Ion exchange and photolysis technique

Various treatment plants currently utilize ion exchange and photolysis to purify water; however, these methods have drawbacks that limit their utilization. The major downside of this approach is that it cannot be utilized to eliminate water pollutants at the microscale [17,18]. One of the biological processes used in the traditional category of water purification can be used to remove microscale particles.

The biological process of treatment

Due to the biological trickling filter and sludge, which the filtering and purification operations could not remove, several contaminants are still soluble in wastewater. Therefore, the biological process, also known as the cellular method, is employed by bacteria and microorganisms to break down organic waste and remove water contamination. Figure 2.6 depicts a procedure to remove microorganisms and other impurities from wastewater [19,20]. Both domestically and industrially, these traditional techniques are still in use. However, a few

cutting-edge water filtration methods have also been developed that are more effective and offer several benefits.

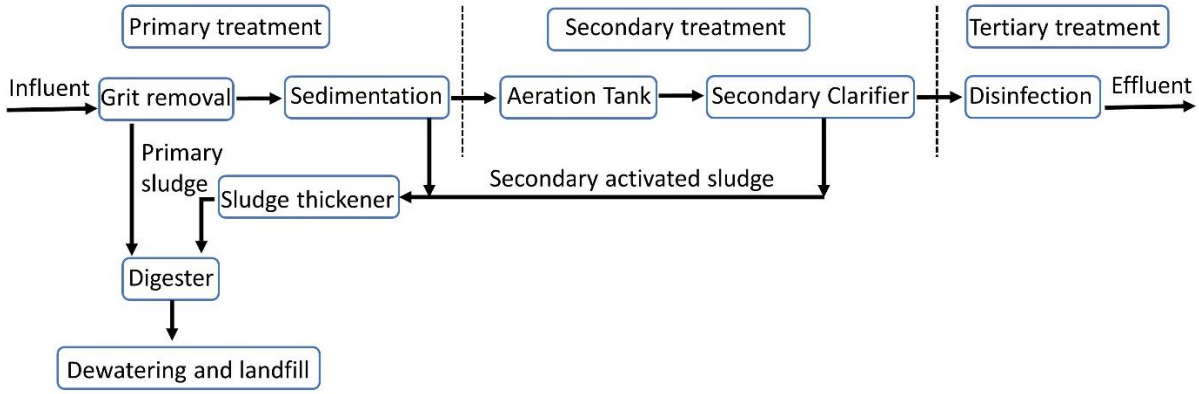


Figure 2.6: Biological treatment of wastewater (Self-representation by the author) [21].

ii) Advance adsorption methods for wastewater treatment

Membrane filtration of water and wastewater is frequently employed to uphold water quality standards. The pressure mechanism in the membrane purification process serves as a barrier between beneficial water and contaminants [22]. These membranes have a variety of advantages, including the fact that they are sturdy, effective, take less time, take up less space, and use fewer chemicals. Additionally, barrier membranes are sufficiently flexible. The type of material from which it is made and the kind of nanomaterials incorporated into it significantly impact how well membrane technology works [23]. According to the porosity of the membranes, there are four types of advanced methods or membrane filtering processes, as depicted in Figure 2.7.

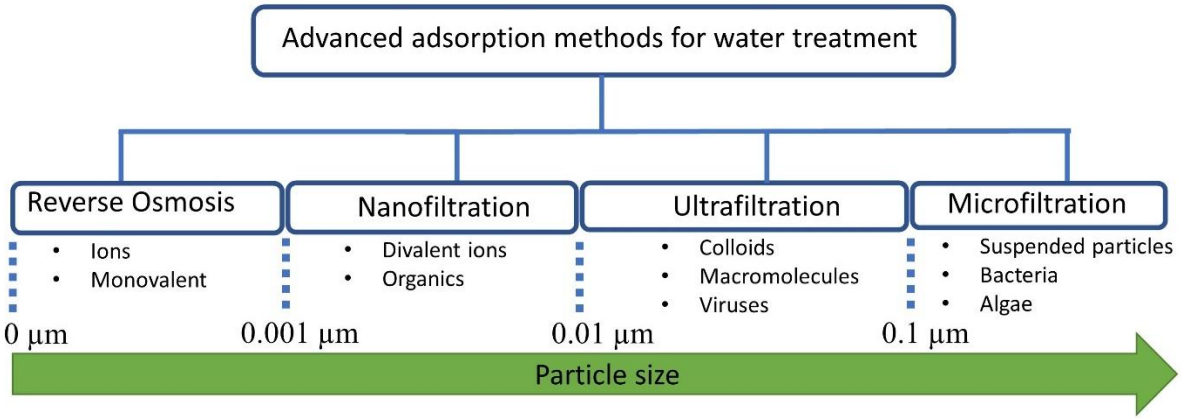


Figure 2.7: Advanced adsorption methods for water treatment (Self-representation by the author) [24].

Ultrafiltration technique

Microorganisms and large molecules can be retained by filters employed in the ultrafiltration process, which operate in the pressure range of 1 to 10 bars and have pores between 5 and 2 nm [25]. The method is displayed in Figure 2.8.

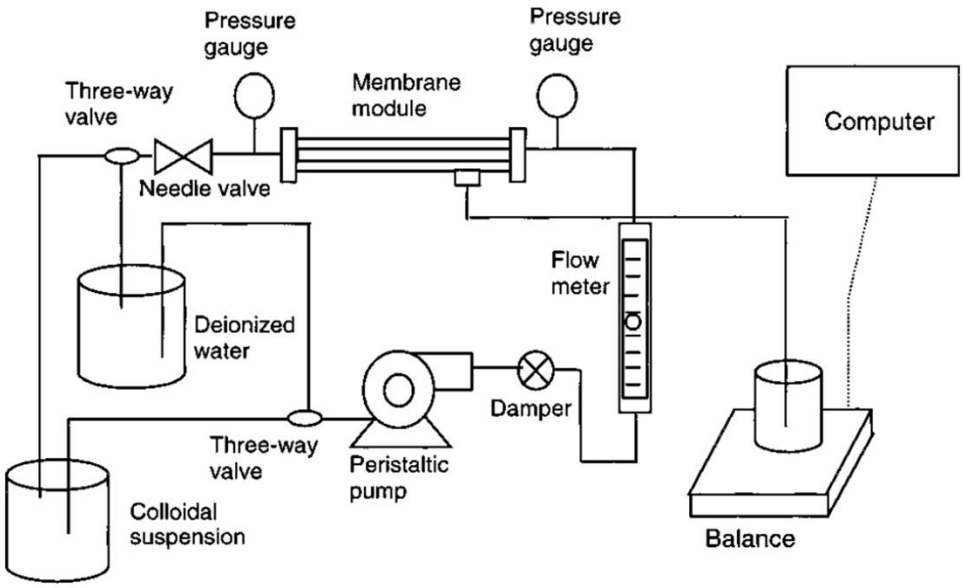


Figure 2.8: Schematic diagram of the cross-flow ultrafiltration technique [26].

Microfiltration technique

Contrary to regular filtering techniques, microfiltration often eliminates colloids and tiny particles with coarse pore sizes of 1–2 μm and works by the driving force. Figure 2.9 illustrates the schematic diagram.

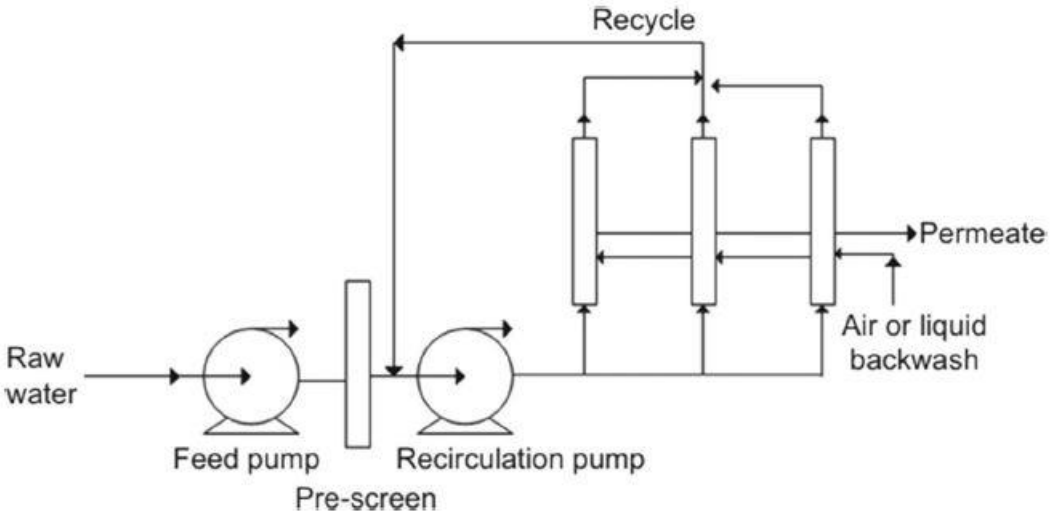


Figure 2.9: Schematic diagram of the microfiltration technique [27].

Reverse osmosis technique

Reverse osmosis is a method that uses a semi-permeable membrane at the highest pressure of 20 to 100 bars. The membrane stops salts and must withstand high pressures, as shown in Figure 2.10.

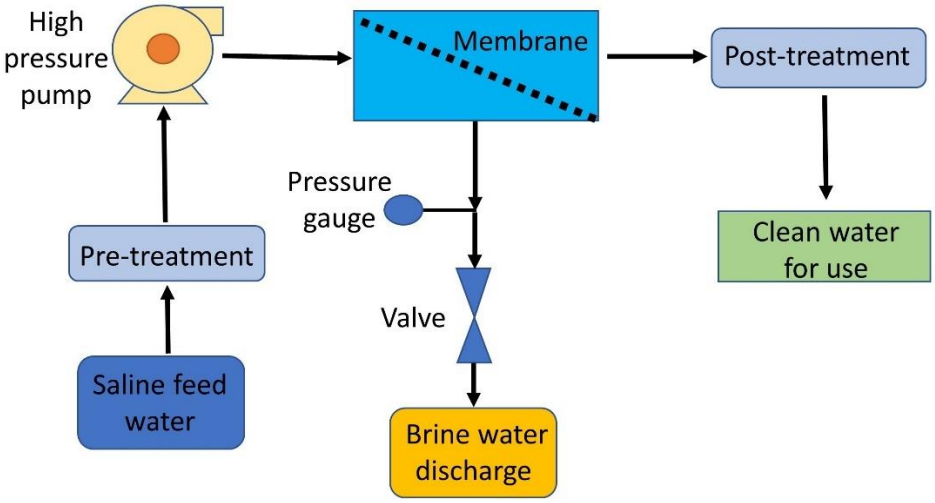


Figure 2.10: Schematic diagram of the reverse osmosis technique (Self-representation by the author) [28].

Nanofiltration technique

The most cutting-edge pressure-obsessed membrane method for molten-stage separation is called nanofiltration (NF), which operates at pressures of 7 to 30 bars and has pores of 1–5 nm that can hold ions and organic contaminants with low molecular weight. Because NF uses less energy but produces more fluidity, it has replaced chiefly reverse osmosis (RO). This method is believed to be more effective where size exclusion is crucial. By combining ions' dimensions, electrical properties, and contact tools like RO, NF allowed ions to be separated. Additionally, the NF's nanoporous shape makes it very effective in excluding tiny amounts of uncharged colloids. At the same time, the exterior electrostatic characteristics document monovalent ions to get conveyed while recalling the multivalent ions. In recent years, NF has developed into a workable technique, which has encouraged its usage in various industries for operations like the treatment of bleaching wastes from textile manufacturing, the separation of pharmaceuticals from fermentation batches, and the removal of viruses. It works pretty well in treating organic and inorganic pollutants in water [29]. Recently, new techniques for purifying water have been introduced. Compared to traditional water purification techniques, these technologies are more effective. The use of nanofiltration, ultrafiltration and microfiltration membranes for water and

wastewater purification has increased because the nanofibrous membranes have a high surface area to volume ratio, higher efficiency, very fine and small pore size, good product quality, easy handling, high selectivity, ease of manufacturing, no use of harsh chemicals, environmentally friendly, and low-cost technology [30]. Figure 2.11 shows a schematic diagram of nanofiltration.

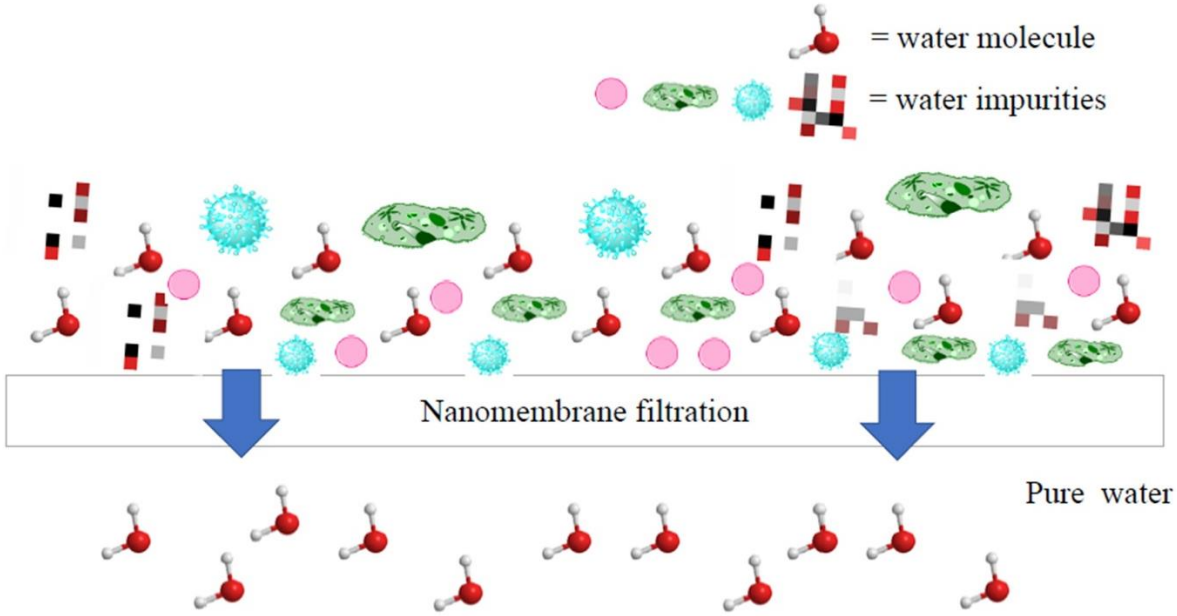


Figure 2.11: Nanofiltration technique as applied in water treatment [31].

2.3 Emerging micropollutants in water

Synthetic EH, also called endocrine-disrupting chemicals (EDCs), have an adverse effect on both human beings and animals [32,33]. Residual micropollutants of this type are observed in low concentrations - at the level of micro-and nanograms - in cleaning reservoirs at wastewater treatment plants [32]. This problem has aroused serious concerns among the scientific community since synthetic hormones are known to interfere with the functional groups of natural hormones by blocking endogenous and mimic ability, which makes it much more dangerous [34–38]. The presence of a minuscule level of hormones represents a severe threat to human and aquatic life through exposure to food sources or drinking water [38,39]. Recently, the European Union directive 2020/2184 concerning drinking water quality recommended a threshold limit of 1 ng/L as a benchmark for assessing the occurrence and treatment of EDCs [40]. The primary sources of hormones and fatal effects are displayed in Figure 2.12.

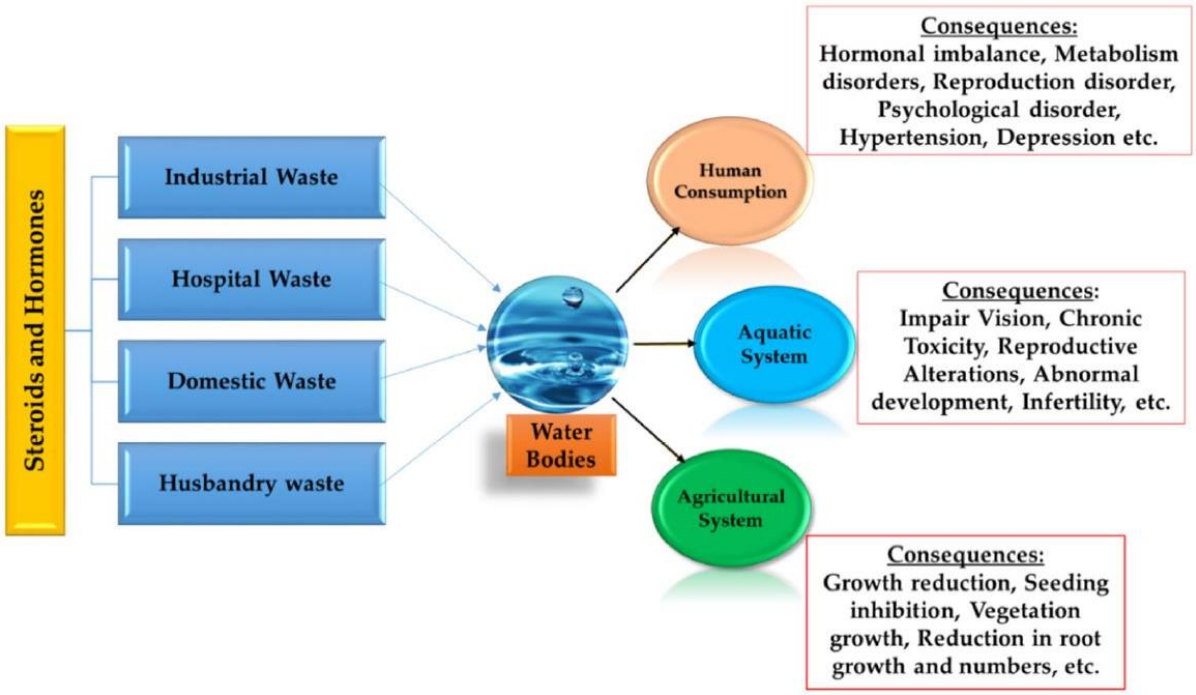


Figure 2.12: Schematic diagram of the primary sources of hormones in the environment and their fatal consequences [41].

The types of natural and steroid hormones found in wastewater can be classified in Figure 2.13 as follows:

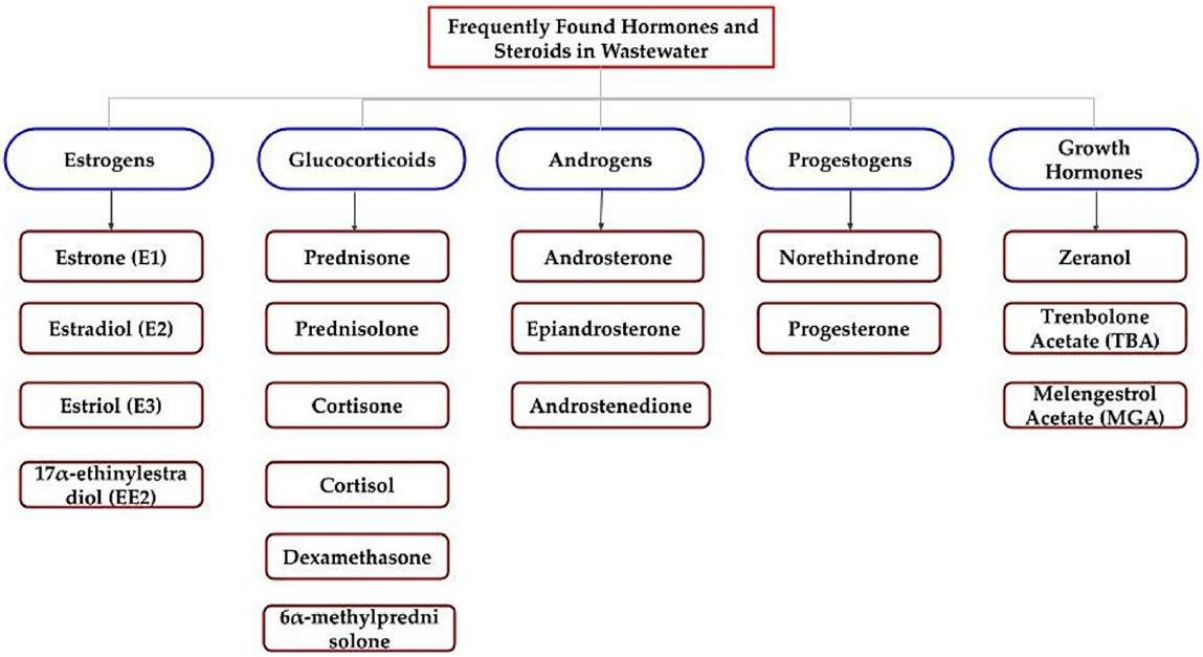


Figure 2.13: Classification of hormones potentially found in the natural environment [41].

EH include estrone (E1), estradiol (E2), ethinylestradiol (EE2), and estriol (E3), which disrupt the reproduction of aquatic species and the function of natural

hormones in the human body [39]. Studies have proven that a rise in femininity occurs in fish, weight loss affects the testicles of quails, and alligators experience issues with fertility [42]. Meanwhile, reports show that humans demonstrate a decline in the sperm counts of males, and the risk of breast and ovarian cancer is heightened in females [43]. Quantities of these EH have been observed downstream of the treatment plants [44–46], with lower limits having been reported of 3.4-41 ng/L at constructed wetlands in the Czech Republic [47]. Of the aforementioned estrogens, EE2 is a modern, formulated, synthetic EH used in oral contraceptive pills in the treatment of prostate cancer and menstrual problems in females [48]. It is considered the most fatal among all the EH as it only degrades partially at wastewater treatment plants and is challenging to be removed [49]. Consequently, the natural environment deconjugates the metabolites of EE2 and makes them active again under a suitable environment [50]. EE2 is the most potent EDC and is considered to have high estrogenicity [51–53]; In general, these EH (natural and synthetic) are majorly from anthropogenic sources, antibiotics, contraceptive pills, chemotherapy drugs and are present in excreting of humans and animals (feces and urine). These EH are released into the environment (e.g., reservoirs, rivers, and lakes) via insufficiently treated effluents. Hence, proper disposal of these EH is immediately required. Figure 2.14 shows the appearance and surface morphology of each hormone; it was captured at 8 kV applied potential and at a magnification of 10000x except for E1, which was 1000x due to the large size of particles. The structure and properties of EH are stated below in Figure 2.15 and Table 2.1.

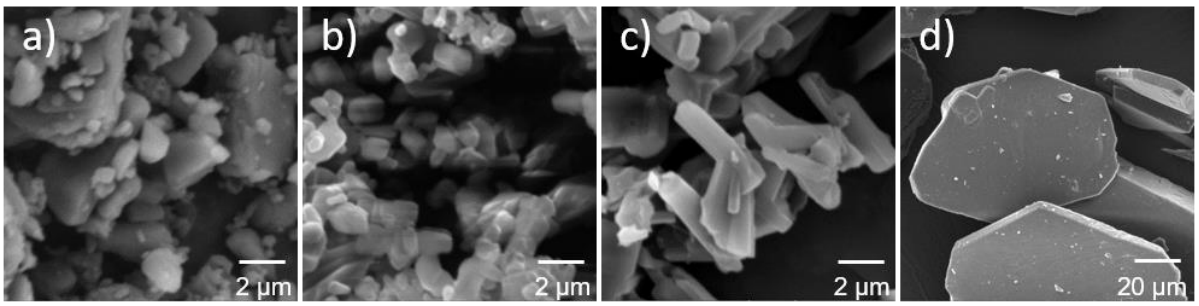
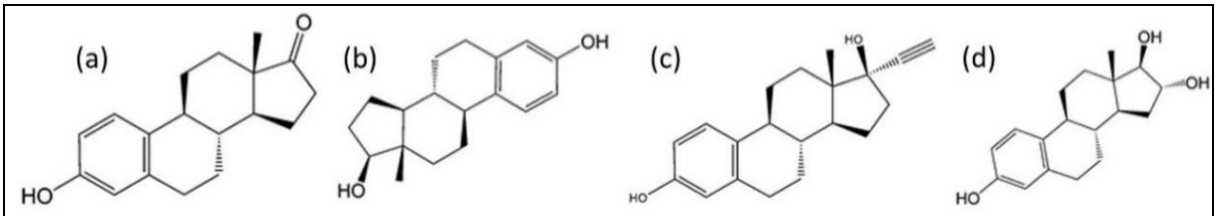


Figure 2.14: SEM of a) E3, b) E2, c) EE2 and d) E1 hormones, respectively (Self-representation by the author).



log K_{ow}	3.43	3.94	4.15	2.45
pK_a	10.34	10.46	10.40	10.38

Figure 2.15: Steroid estrogenic hormones a) E1, b) E2, c) EE2, d) E3 (self-representation by the author).

Table 2.1: Specific properties of hormones

Estrogenic Hormone	**Molecular formula**	**Molecular weight (g/mol)**	**Melting point (°C)**	**Solubility in water (mg/l)**
Estrone	$C_{18}H_{22}O_2$	270.37	258.0-260.0	12.42
B-Estradiol	$C_{18}H_{24}O_2$	272.38	178.5	12.96
17α-Ethinyl-Estradiol	$C_{20}H_{24}O_2$	296.40	182.0-183.0	4.83
Estriol	$C_{18}H_{24}O_3$	288.38	282.0	13.25

2.3.1 Solution preparation and sampling

Hormone solution was prepared in three different mediums viz. ethanol, ethanol: water (20:80), and water. For the ethanol, 5 mg/L stock solution was prepared after stirring the solution for 1 h, and it was seen that hormones dissolved immediately. For the ethanol: water system, the concentration of 20 mg/L in solvent 10:90, 10 mg/L 10:90, 20 mg/L 20:80, and 10 mg/l 20:80 was prepared but didn't dissolve completely and stayed as a suspension. However, at a higher volume ratio of ethanol: water 20: 80, solubility was better, as can be seen in Figure 2.16 below.

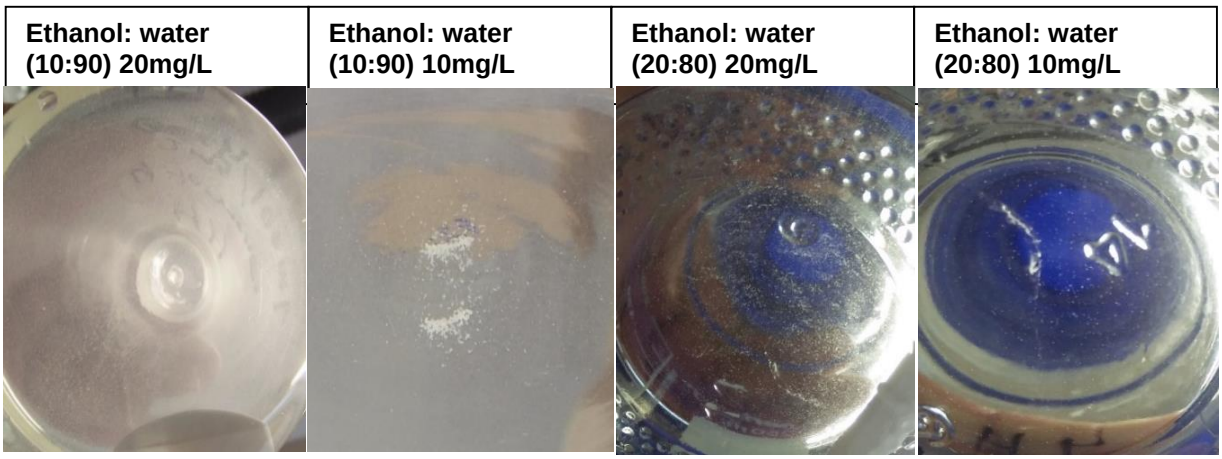


Figure 2.16: Solubility of all four hormones together in a solution at different concentrations (Self-representation by the author).

Hence, using ethanol: water 20:80, 5 mg of each hormone was dissolved in a total of 1000 mL by initially dissolving in 200 mL ethanol, followed by 800 mL of water properly stirred at 800 rpm for 24 hours to make sure complete homogenous mixing and solubility. It was also observed that if hormones are first dissolved in water followed by ethanol, then hormones are only partially dissolved. The descending order of solubility using HPLC is EE2>E3>E2>E1. In the case of water, solubility was a problem because individual solubility of each hormone is available in literature but considering all 4 hormones together in a single solution was challenging, especially for distilled and deionized water. Solubility was lower than the values available in the data, and it was seen that preparing a solution of 1mg/L concentration of each hormone, even after stirring for 1 whole day, there were still some particles at the bottom of the container which could be referred to as E1 because of its least solubility [39]. It was also checked by separately dissolving each hormone in 1 L of water. When the solution was sonicated for 30 mins, there was an increase in peak for E1, proving that its solubility improved. Therefore, finally, a concentration of 0.2 mg/L of each hormone was prepared by adding 1 mg of the given hormone into 5 L of HPLC grade water; magnetic stirring was maintained at 800 rpm for 24 h to prepare 0.8 mg/L of solution and stored in the dark. Samples of concentrations 0.2, 0.15, 0.1, 0.05, 0.03, and 0.02 mg/L were collected by a micropipette and dosed into 1.5 mL screw neck vials after passing through a glass microfiber (GMF) filter of pore size 0.45 μm and 25 mm diameter. HPLC was performed on triplicated samples, resulting in mean concentrations plotted on a calibration curve.

2.3.2 Devised method of High-Performance Liquid Chromatography (HPLC)

Several methods have been devised in the literature using various instruments to quantify EH. However, they are limited to a single or two hormones at a time. Herein, using this procedure, we have devised a facile HPLC method for concurrent detection and quantifying of four EH in a single run. The hormone samples (E1, E2, EE2, E3) were analyzed, and their calibration standards were discerned on an HPLC DionexUltiMate 3000 Series unit (Thermo Fisher Scientific, Germany). Separation took place on a reversed-phase column (Kinetex 2.6 µm C18 100 A, 150x4.6mm; Phenomenex, USA) equipped with an ULTRA precolumn guard, UHPLC C18 (Phenomenex, USA) at 30 °C. A mixture of HPLC grade acetonitrile and water constituted the mobile phase (45:55, vol/vol) applied at the flow rate of 0.8 mL/min over a total isocratic run time of 12 min. The autosampler chamber was set to 5 °C, and a volume of 20 µL was injected each time into the column. Eluates were detected at the wavelengths 200 and 205 nm, and the concentration of hormones was calculated from the findings of the 200 nm tests. A calibration vial with a concentration of 0.02 mg/L was employed to determine the detection limit for each hormone in water; the limit of detection and quantification were found to be 0.560 and 1.867, 1.189 and 3.963, 0.920 and 3.067, and 1.883 and 6.280 µg/L for E3, E2, EE2, and E1, respectively. Values for concentration were quantified by external calibration in software Chromeleon version 7.2 (Thermo Fisher Scientific, USA), as demonstrated in Figure 2.17.

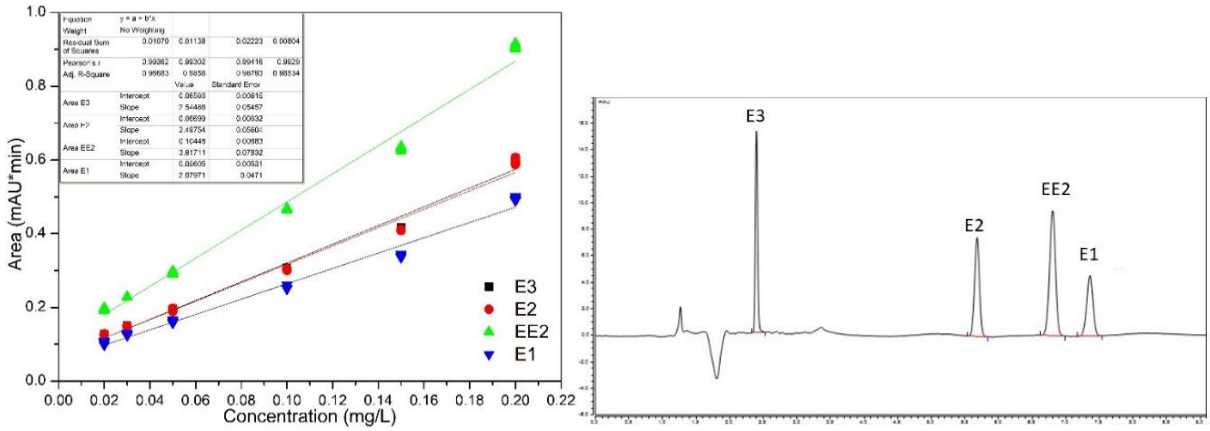


Figure 2.17: Calibration curve and chromatogram of stock solution concentration of 0.8 mg/L containing 0.2 mg/L concentration of each hormone (E1, E2, EE2, E3) in the mixture (Self-representation from experimental data).

2.3.3 Detection and quantification

To identify the peak of hormones, firstly, each hormone solution was tested to detect and identify the retention time (r.t), and then a combined solution of hormones was tested. Also, the limit of detection (LOD) and limit of quantification (LOQ) were calculated from 0.01 mg/L standard as given in the formulas below:

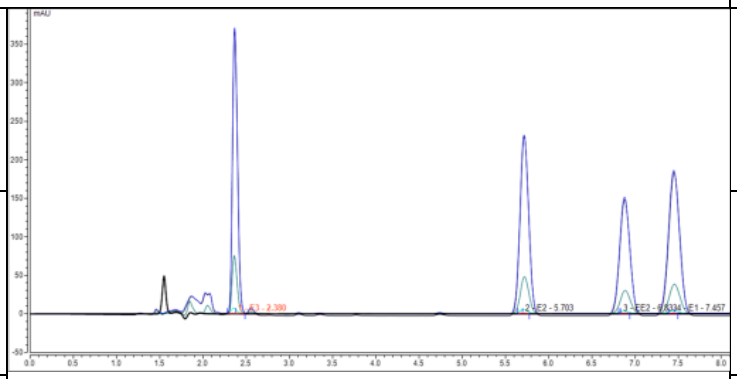
$$LOD = ((\frac{c}{S/N}) \times 3) \quad (2.1)$$

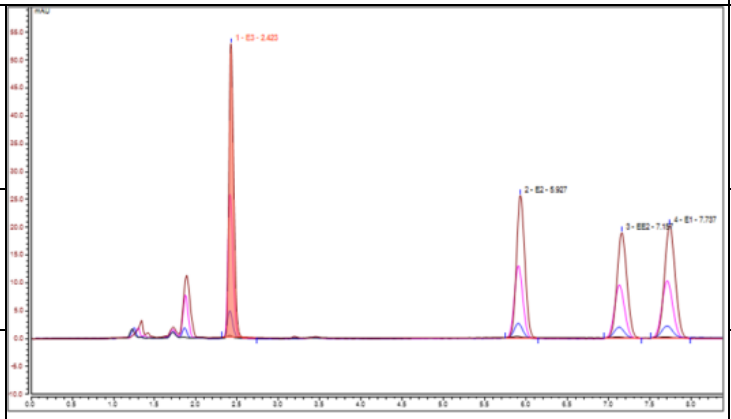
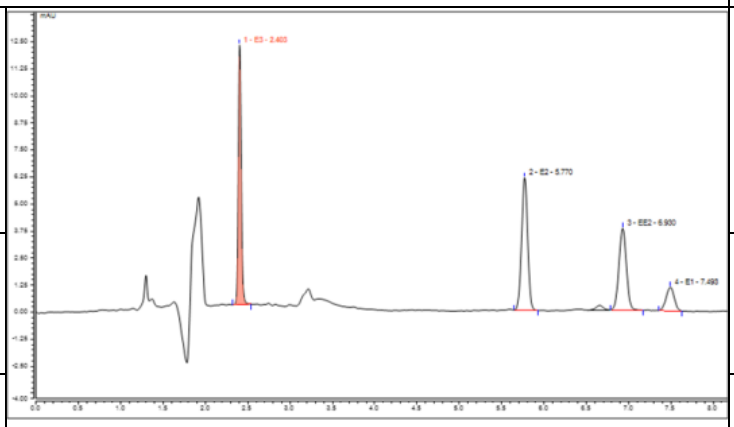
$$LOQ = ((\frac{c}{S/N}) \times 10) \quad (2.2)$$

Where *c* is the concentration (mg/L) of each hormone and *S/N* is the signal-to-noise ratio.

Table 2.2 represents intensity peaks, calibration equations along with LOD (mg/L) and LOQ (mg/L) of each hormone at their particular retention time in the ascending order of time of E3, E2, EE2, and E1, respectively, in a given medium.

Table 2.2: Intensity peak, calibration equation, and limits of each hormone when mixed in a specific solution medium (a) ethanol, (b) ethanol: water 20: 80, and (c) water

Ethanol		Equation	Limits
E3		y = 5.11x + 0.02 (R^2 = 1)	LOD: 0.001 LOQ: 0.004
E2		y = 5.52x + 0.04 (R^2 = 1)	LOD: 0.002 LOQ: 0.006
EE 2		y = 4.2557x – 0.0004 (R^2 = 1)	LOD: 0.003 LOQ: 0.009
E1		y = 5.64x + 0.04 (R^2 = 1)	LOD: 0.002 LOQ: 0.007

Ethanol: water 20: 80		Equation	LOQ/LOD
E3		y = 3.44x + 0.07 (R^2 = 1)	LOD: 0.002 LOQ: 0.006
E2		y=2.92x + 0.06 (R^2=0.9999)	LOD: 0.003 LOQ: 0.011
EE 2		y=2.58x +0.05 (R^2=0.9999)	LOD: 0.005 LOQ: 0.015
E1		y = 2.99x + 0.06 (R^2 = 1)	LOD: 0.004 LOQ: 0.014
Water		Equation	LOQ/LOD
E3		y=2.00x +0.04 (R^2= 0.9885)	LOD: 0.0005 LOQ: 0.002
E2		y=2.06x +0.05 (R^2= 0.9918)	LOD: 0.001 LOQ: 0.004
EE 2		y=1.60x +0.04 (R^2=0.9939)	LOD: 0.002 LOQ: 0.005
E1		y= 0.61x +0.02 (R^2=0.9901)	LOD: 0.005 LOQ: 0.017

2.4 Method of membrane preparation (Electrospinning)

Although a variety of approaches have been used in the literature to remove water pollutants, some of them are appropriate and effective, but they all have drawbacks [54,55]. Conventional treatment plants cannot eliminate EDCs efficiently owing to their properties of low molecular weight and slow biodegradability [56]. This has led to the widespread occurrence of the same

quantity in reservoirs, rivers, and lakes since they are released from treatment plants alongside treated effluents [57,58]. In this regard, various strategies have been applied to capture, eliminate or completely degrade the EDCs and other common toxic chemical effluents, such as ozonation, membrane bioreactors, advanced oxidation, membrane filtration, coagulation, flocculation, and photocatalysis [59–61]. Each technique has certain limitations, such as low efficiency, and any resulting by-products demand further purification and sophisticated methods for processing them. Nano-filtration and reverse osmosis have proven to be interesting, but the extent of energy consumption makes them unfavorable for treatment at a large scale [62,63].

Sorbents based on nanofibers have garnered much attention due to a number of favorable characteristics reported for them, such as large aspect ratio, high surface area, and small pore size [64]. For this purpose, electrospinning is a versatile technique for generating continuous nanofibers, which gives rise to a material's diameter ranging from tens to hundreds of nanometers for adsorption and water filtration processes [65,66]. The large aspect ratio of nanofibers gives significant rise to the filtration efficiency since the pore size is reduced; moreover, the large surface area allows greater contact between the solution and filtration-sorption adsorbent [67]. The apparatus requires an applied voltage between the cathode and anode to allow the electrostatic forces to overcome the tension on the surface of the polymer, thereby ejecting the polymeric solution and solidifying non-woven nanofibers on a collecting electrode covered in a textile substrate [65,68–71]. The quality of nanofibers can be improved by utilizing binary polymers with additives such as acetone and polyethylene oxide (PEO) to obtain beadless nanostructures [67]. The schematic diagram of electrospinning is displayed in Figure 2.18.

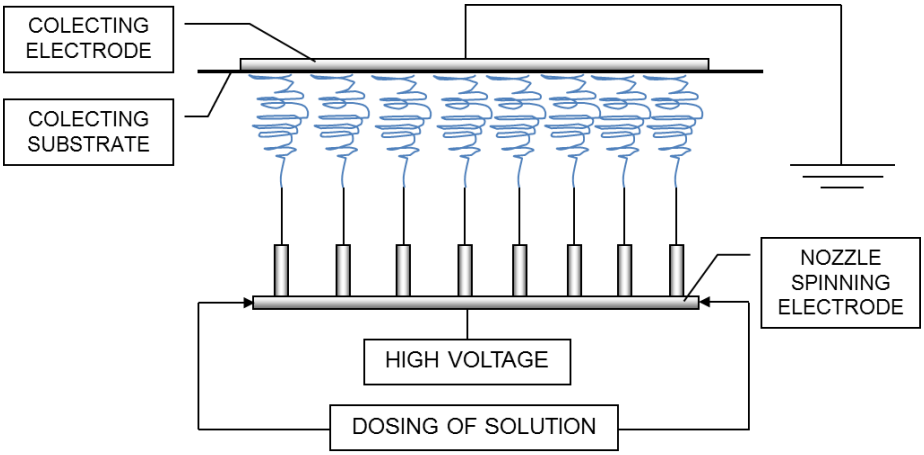


Figure 2.18: Illustration of a needle electrospinning system for the fabrication of nanofiber sheets (Self-representation by the author).

The other types of electrospinning are needleless electrospinning, two-layer fluid electrospinning, rotating roller electrospinning, bubble electrospinning, and conical wire electrospinning.

2.4.1 Influence of parameters for electrospinning

Numerous factors involved in the solution preparation process can be divided into various categories and have a major impact on the morphology of nanofibers are discussed here in detail [72].

Effect of molecular weight and polymer concentration

The molecular weight of the polymer and concentration of the polymer solution directly impact the viscosity of the polymer solution. The entangled molecule chains at the desired molecular weight and concentration prevent the solution jet from breaking during stretching as it advances toward the collector. Similar to the situation of high concentration, a greater number of molecular chains in a polymer solution will result in more entanglements and viscosity. As chain length rises, molecular chains get more entangled, and eventually, viscosity increases with increasing molecular weight. The drawback of high concentration is caused by the nanofibers' small surface area of deposition. To create continuous nanofibers without flaws, sufficient molecular weight and concentration are needed. Increasing the concentration of the solution, which prevents the solvent from moving freely and forming the beads, can remove the beads in nanofibers. Smooth nanofibers that are appropriate for filtering nanoscale particles will form as the molecular weight is further increased while the concentration is held constant. The creation of microribbons, which are appropriate for filtering microsize particles, is caused by raising the molecular weight to a greater level [73].

Additionally, maintaining a lower solution concentration before electrospinning enables the production of nanofibers with the smallest fiber diameter at the given constant molecular weight.

Influence of intrinsic viscosity

Viscosity is a crucial factor in the formation of continuous, bead-free nanofibers. When the viscosity of the polymer solution is extremely low or extremely high, electrospinning is not feasible. It will be challenging to push the fluid through the syringe at greater viscosities. Second, the solvent may evaporate at the needle's tip before the solution can be ejected. Numerous researchers have looked at the beads along the length of nanofibers at low viscosities. They have also looked at how a progressive increase in viscosity causes the shape of the beads to change from spherical to elliptical until smooth fibers are produced. After the creation of smooth fibers, a further rise in viscosity may result in the formation of coarser nanofibers. The main jet may not create secondary jets due to the increased viscosity, which causes the nanofibers' diameter to expand. Similar to this, helix-shaped microribbons that are appropriate for micro-size particles are seen at very high concentrations. Additionally, the low concentration results in nanofibers with narrow pore sizes [74].

Effect of electrical conductivity

To start the viscoelastic jet, the polymer solution must overcome surface tension, which necessitates the delivery of a crucial amount of electrostatic force. Due to the solution's surface tension, the solution jet may fracture during stretching. At low viscosities, the solvent's surface tension begins to take control and forms beads along the length of the nanofibers. Therefore, it is possible to increase the electrical conductivity of the solution and lower its overall surface tension by adding solvents such as ethanol, borax, and citric acid (BC). The wide surfactant varieties can also be utilized to create continuous and smooth nanofibers. The surface tension of the solution has a direct impact on the filtration abilities of nanofiber. Bead fibers can be transformed into a smooth fiber mesh that is ideal for nanoscale particles at low surface tension [75].

2.4.2 Influence of parameters while electrospinning

Variation of voltage

Voltage is a key factor in the creation of smooth, bead-free nanofibers. Most of the time, stronger electrostatic forces at high voltage (greater stretching) cause the finer fibers to form. To create finer or coarser fibers at a certain voltage, flight

duration is also important. By reducing flight time and raising voltage, the solution jet has less time to stretch, resulting in the formation of coarser fibers. Below the minimum voltage necessary to create a Taylor cone at the needle tip, the solution cannot erupt from the needle. Therefore, producing fine and smooth fibers is only possible at a certain voltage level. The smaller pores in the finer fibers make them appropriate for nanoscale particles and other agents [76].

Variation of flow rate

The amount of solution that is accessible for electrospinning at the needle tip depends on the feed rate. A crucial feed rate value should match the applied voltage for a stable Taylor cone. More solution is available at the needle tip at high feed rates, which causes the formation of coarser or beaded nanofibers. The solvent may be fused together and create web-like structures when fed at a greater rate since it doesn't have enough time to dissipate. Lower flow rates are preferred for the production of finer fibers. In comparison to coarser fiber filters, finer fiber nano filters offer more filtration capacity.

Effect of distance between needle and collector

The distance between the needle and the collector has a direct impact on the electric field's strength and flight time. The strength of the electric field increases at very close ranges, causing the solution jet to accelerate and, ultimately, shorten flight time. The flight duration shortens, preventing solvent from evaporating and leading to the formation of an interconnected mesh. Beaded fibers occur because a low distance has the same effect as a high voltage. However, at a higher distance, the stretching of the solution jet is increased due to an increase in flight time; a longer distance produces finer fibers. As a result, finer fibers are favored for removing tiny particulates from water [77].

Type of needle

The process is directly impacted by the needle's interior diameter. Because less solution is exposed to the environment when utilizing smaller inner diameter needles, the likelihood of needle clogging is significantly decreased. The nanofibers' diameter is also decreased due to the smaller inner diameter. Various materials can be electrospun using different types of needle spinnerets depending on their physiochemical needs for the intended usage. The type of needle can be altered based on the level of filtration necessary. Tiny diameter needles are preferred for removing the finer fiber and small particulates. Similar to this, a bigger diameter needle is preferred for prefilter application and the removal of large particles from water [78].

3. MOTIVATION FOR THE DOCTORAL STUDY

3.1 Conclusions and bridging the gap

Today, there is a vast awareness of the growing water challenges due to the growing population, use of synthetic chemicals, newly developed pharmaceutical products, industrial waste, pesticides, and especially the use of contraceptive pills that leads to hormonal imbalance, which ultimately ends up in fatal diseases such as breast, ovarian and prostate cancer. Therefore, considering smart, functionalized, and high-performance polymeric materials are highly desired to overcome this nuisance.

In this regard, special attention has been given to EH due to their minuscule concentrations in water streams, and the difficulty is complex methods of detection. Limited methods have been devised in the literature that can simultaneously quantify EH at lower limits of micro and nanograms. These four EH: estrone (E1), estradiol (E2), estriol (E3), and ethinylestradiol (EE2), have high potencies measured in wastewater and the existing conventional wastewater treatment plants are inefficient in removal, recovery, and proper disposal of these EH or have high operating costs.

In literature, nanoparticles for adsorption have been used in this application which further requires additional purification and separation steps that raise the cost of work. However, nanofibers prepared from electrospinning have recently gained great attention due to their high aspect ratio, lightweight, and reusability. Still, they have least been used for this application in water treatment. Therefore, few works have been done with electrospun nanofibers for eradicating these EH from wastewater. Some works have been done with PA, nylon, PVDF, and PES membranes but are limited to just removing a single EH. Hence, it creates a gap that needs more comprehensive work to be done in this area to address this issue properly.

To bridge this gap, this application requires the preparation of more optimized polymeric nanofibers with a facile technique and their surface modification to enhance activity, which can be cost-effective and better in simultaneously adsorbing EH. Further, discuss the mechanisms, measure kinetics, isotherms, and thermodynamics with appropriate models, and finally, prove the effectiveness of materials with several adsorption-desorption cycles for the recovery of EH, as

well as test the reusability of materials to be practically applicable over large-scale use.

3.2 Aims of doctoral thesis

The aims of this doctoral research work are defined in the state-of-the-art study and, based on the conclusions made, are classified into four main categories of work which are demonstrated in the schematic diagram in Figure 4.1 below.

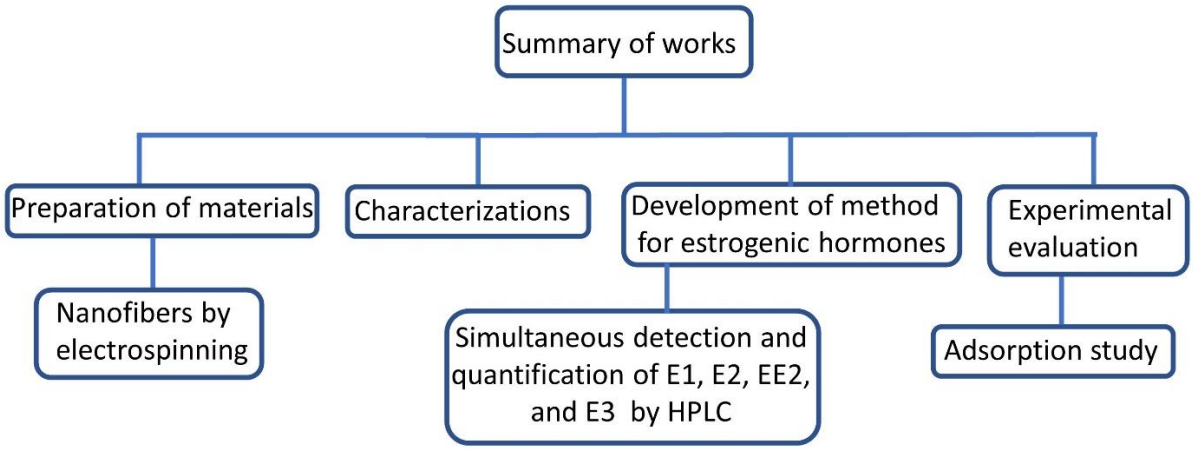


Figure 3.1: Schematic outline of works (Self-representation by the author).

This thesis work includes the preparation of nanofibers based on selective polymers via electrospinning, their characterization, determination of adsorption activity by nanofibers, the study of interactions between polymeric nanofibers and EH, desorption study for the recovery of hormones and reusability of materials. The specifications of these classifications are described in more detail as follows:

- Developing a method for simultaneous detection and quantification of EH (E1, E2, EE2, and E3) via HPLC technique using UV-Vis detector.

- Selection of appropriate polymers for high removal of EH and their optimized synthesis prior to electrospinning. These materials include both hydrophilic and hydrophobic polymers (polyurethanes commercial and lab synthesized (PU Elastollan and PU 918), PA, CA, PSU, PES, PLA, PAN, and PVDF).

- Preparation of solution for each polymer with the desired properties such as solution concentration, intrinsic viscosity, and electrical conductivity of each polymer based on its molecular weight and density.

- The fabrication of nanofibers with the least diameter (ideally < 350 nm) using defined adjusted parameters on electrospinning such as applied

voltage, the distance between electrodes, the rotational speed of collecting PP roll, solution dosage, chamber temperature, and pressure to eliminate and avoid bead defects.

- Determination of adsorption removal efficiency of each EH on the prepared nanofibers via static adsorption test.

- Investigation of adsorption mechanisms (hydrophobic interactions, hydrogen bonding, charge interaction, size exclusion, and π–π stacking interaction) for the promising adsorbent polymers based on their structure and the functional groups of the hormones.

- Determination of contact time study to apply suitable kinetic models (pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion, Elovich, Boyd, and fractional power models), variation in adsorbate concentration for isothermal models (Freundlich and Langmuir) and thermodynamic study.

- Optimization study with variation in experimental condition parameters such as concentration of adsorbate, adsorbent dosage, pH of the solution, the temperature of interaction, and time of contact.

- Testing reusability of high-performance materials for at least six adsorption-desorption cycles.

- A separate study of recycled CBs to prepare CA electrospun nanofibers (WCENFs) to compare their performance with the commercial CA nanofibers and further fabrication of membrane film for possible comparison of hormone uptake with the commercially available syringe filters (CA, regenerated cellulose (RC), polytetrafluoroethylene (PTFE), and PP).

- Surface modification of the best performance polymeric nanofiber by coating it with polyaniline/polyvinyl alcohol to enhance the adsorption activity of hormones owing to stronger hydrogen bonding interactions.

- Determination of optimum experimental conditions by analysis via response surface methodology using a central composite design model and validation of operating parameters by the Design-Expert software.

- Comparative study of prepared materials' performance of capturing EH with the materials reported in the literature.

- Publish all the data from the mentioned works in Q1/Q2 impact factor journals and international scientific conferences within the frame of university policy and the rector's directive.

4. CONCLUDING REMARKS

4.1 Conclusions of work done

This doctoral work focused on developing and characterizing ***electrospun nanofibrous polymeric materials that were tested for the elimination of estrogenic hormones from wastewater by adsorption***. All the mentioned aims were successfully achieved, and the **brief summary** of this doctoral work which was prepared and published in the form of articles, is explained below:

Article I entitled ***"The adsorption, kinetics, and interaction mechanisms of various types of estrogen on electrospun polymeric nanofiber membranes."*** This work comprised of preparation and characterization of six different electrospun polymeric nanofibers: CA, PA, PES, polyurethanes (918 and Elastollan), and PAN to simultaneously adsorbing four EH (E1, E2, EE2, and E3) in a single step process and to compare their performance (adsorption efficiency and adsorption capacity). The nanofibers possessed an average fiber diameter in the range of 174–330 nm, and their specific surface area ranged between 10.2 and 20.9 $m^2\ g^{-1}$. The adsorption-desorption process was investigated in four cycles. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were deployed on experimental data to determine the kinetics. Findings showed that E1, E2, and EE2 best fitted pseudo-second-order kinetics, while E3 followed pseudo-first-order kinetics. It was found that PU Elastollan nanofibers were the best and had maximum adsorption capacities of 0.801, 0.590, 0.736, and 0.382 mg g^{-1} for E1, E2, EE2, and E3, respectively. In addition, the results revealed that PU Elastollan nanofibers had the highest percentage efficiency of estrogens removal at ~58.9% due to its strong hydrogen bonding with EH, which was explained in the mechanism. In comparison, the least removal efficiency was observed for PAN at ~35.1%. These mentioned results were **reported and published in** "*Nanotechnology*" 33, (**2021**), 75702, https://doi.org/10.1088/1361-6528/ac357b (Web of Science Indexed [Materials Science], Q2, J_{imp}: 3.953)

Article II entitled ***"Adsorption of estrogenic hormones in aqueous solution using electrospun nanofibers from waste cigarette butts: Kinetics, mechanism, and reusability."*** This study emphasized recycling waste CBs to produce detect-free electrospun nanofibers (WCENFs) to adsorb EH simultaneously. The WCENFs were characterized by SEM, XRD, FTIR, BET, porosimetry, contact angle by sessile drop technique, TGA, DSC, GPC, and tensile test. Five models (pseudo-first-order, pseudo-second-order, intraparticle diffusion, elovich, and fractional power model) were deployed to determine the kinetics. The strong

affinity of WCENFs was found to be towards all EH due to abundant hydrogen bonding interactions between functional groups (C=O, C–O–C, and C–O–H) of WCENFs and O–H of all EH (additionally, with C=O group of E1). The highest percentage removal efficiencies from the batch adsorption were 64.3, 53.6, 52.7, and 34.6% for EE2, E1, E2, and E3, respectively. Results showed that the total adsorption capacity achieved was 2.14 mg/g, whereas the individual values for E1, E2, EE2, and E3 were 0.551, 0.532, 0.687, and 0.369 mg/g, respectively. To summarize, the WCENFs was further thermally pressed to fabricate PET/WCENFs syringe film. It successfully and better responded to the retention time for these EH compared to the commercial CA syringe film. Therefore, it implies that recycled WCENFs can be considered a promising adsorbent for rapidly remediation wastewater streams to eliminate hormones and possibly replace the commercially available CA syringe film. These results were **reported and published in** "*Express Polymer Letters*" 16, (**2022**), 624–648, https://doi.org/10.3144/expresspolymlett.2022.46 (Web of Science Indexed [Polymer Science], Q2, J_{imp}: 3.952)

Article III entitled ***"Electrospun polyurethane nanofibers coated with polyaniline/polyvinyl alcohol as ultrafiltration membranes for the removal of ethinylestradiol hormone micropollutant from aqueous phase."*** This study reported the fabrication of electrospun polyurethane (PU 918) nanofibers modified by coating with polyaniline/polyvinyl alcohol (PANI/PVA) to form filtration membranes for the enhanced removal of ethinylestradiol (EE2) hormone. Structural and morphological characterization was performed by FTIR, SEM, and optical microscopy, while the detection and quantification of EE2 were analyzed using HPLC. PU-PANI-ES as a modified material demonstrated to be the most efficient with 90.30% removal efficiency of the studied hormone compared to its base form PU-PANI-EB (81.50%) and neat PU 918 (55.40%) as control. Findings demonstrated that EE2 best fitted pseudo-second-order kinetics. Furthermore, the adsorption process was optimized via response surface methodology using a central composite design model by varying parameters such as pH, temperature, the concentration of adsorbate, and adsorbent dosage to determine. The model proved to be significant for optimizing the removal of the EE2 hormone with a high regression coefficient (R^2) of 0.983. The optimum parameters were found to be pH 7 (considering that wastewater or river water is in the range of pH 6–8), the temperature of 40 °C, 0.3 mg/L concentration of EE2, and 20 mg of PU-PANI-ES dosage. It was found that the modified PU membranes had a maximum adsorption capacity of 2.11 mg/g and high removal percentage

efficiency of ~82.20% for EE2. Adsorption mechanism and thermodynamics were also evaluated, and the results depicted the adsorption process of EE2 occurred via intraparticle diffusion and was exothermic in nature. Finally, a reusability study was done over six adsorption-desorption cycles to test the consistent effectiveness of the modified PU membrane, which remained above 80% removal capacity. Overall, the reported results proved that the modification of the spun PU nanofiber with PANI significantly improved hormone removal from water and can be considered a promising adsorbent membrane for the remediation of different steroid hormones from water. The results mentioned above were **reported and published in** "*Journal of Environmental Chemical Engineering*" 10, (**2022**), 107811, https://doi.org/10.1016/j.jece.2022.107811 (Web of Science Indexed [Chemical Engineering], Q1, J_{imp}: 7.968)

Article IV entitled ***"The adsorptive behaviour of electrospun hydrophobic polymers for optimized uptake of estrogenic sex hormones from aqueous media: Kinetics, thermodynamics and reusability study."*** This study focused on hydrophobic polymeric nanofibers of PSU, PVDF, and PLA, that were prepared via an electrospinning process and characterized using SEM, FTIR, TGA, BET, XRD, and porosimetry. Nanofibers possessed a mean fiber diameter of 149 - 183 nm and a specific surface area of 1.6 - 6.3 m^2/g. The adsorption efficiency of simultaneous removal of E1, E2, E3, and EE2 in a mixed concentration was investigated using HPLC. The preliminary study showed that PSU was the best among these polymers, with the highest percentage of removal (71.2%) of E1. The adsorption of hormones on PSU was significantly high compared to other polymers owing to the hydrogen bonding interactions. Therefore, five models (pseudo-first-order, pseudo-second-order, intraparticle diffusion, Elovich, and fractional power model) were deployed on experimental data to obtain the adsorption kinetics and to understand the characteristics of PSU fibers with contact time. The results indicated that spun PSU fibers exhibited the highest removal of all four estrogens, with a maximum removal efficiency of 71.2, 65.9, 56.9, and 36.1 % and adsorption capacity of 0.508, 0.703, 0.550, and 0.354 mg/g for E1, EE2, E2, and E3, respectively. Additionally, the adsorption was optimized by varying parameters such as concentration of adsorbate, pH, adsorbent dosage, and temperature to analyze one-way variance using ANOVA statistically. The pseudo-second-order is best fitted for E1, EE2, and E2, while the pseudo-first-order is for E3. The Langmuir-Freundlich isothermal model was most suitable for evaluation, and the thermodynamics depicted the adsorption of E1 on PSU was exothermic and spontaneous. The results indicated that spun PSU can be an

efficient adsorbent in the simultaneous elimination of estrogens from wastewater and exhibits high regeneration performance of over 60% after six adsorption-desorption cycles. These mentioned results were **reported and published in** "*Journal of Chemical Technology and Biotechnology*" (**2022**), https://doi.org/10.1002/jctb.7191 (Web of Science Indexed [Chemical Engineering], Q2, J_{imp}: 3.709)

Apart from the adsorption study of hormones on nanofibers, some photocatalyst materials (nanoparticles, nanowires, and nanorods) were prepared to test the photodegradation of these hormones as secondary work. The results of work with nanoparticles titled ***"Green synthesis of titanium and zinc oxide nanoparticles for simultaneous photocatalytic removal of estrogens in wastewater"*** was **reported and published in** "*AIP Proceedings of the 13th International Conference on Nanomaterials, Brno, Czech Republic*" 189-196, (**2021**), https://doi.org/10.37904/nanocon.2021.4333. In this study, titanium and zinc oxide nanoparticles (ZnO-NPs) were green synthesized using lemon juice and peel extract, zinc acetate, ethylene glycol, and titanium IV isopropoxide as precursors. The prepared TiO_2 and ZnO-NPs were characterized and subjected to the photocatalytic degradation of EH (E1, E2, EE2, and E3) under UV light irradiation at 365 nm, which resulted in promising photocatalytic activity. All four EH were significantly degraded owing to the photocatalytic activity combined with a slight contribution of hormonal adsorption (4-11 %) onto the surface of the photocatalysts. Overall hormonal degradation rates were in the range of 84-93 %, and approximately 99 % removal was achieved in 60 minutes under UV light irradiation by ZnO and TiO_2, respectively.

The second work entitled ***"ZnO nanowires and nanorods based ZnO/WO_3/Pt heterojunction for efficient photocatalytic degradation of Estriol (E3) hormone"*** was based on the removal of E3 hormone (which had least been adsorbed by nanofibers) by heterojunction photocatalytic nanowire and nanorod thin films. It was done because nanofibers possessed the least adsorption efficiency with this hormone. In this work, ZnO nanowires and nanorods based on ZnO/WO_3/Pt heterojunction were successfully grown on glass substrates via a facile hydrothermal method followed by spraying. The photocatalytic performance was evaluated by the degradation of the E3 hormone under UV light irradiation (~365 nm) in a closed continuous flow reactor. The as-prepared samples achieved an excellent photodegradation rate in the range of 23-37 % and 63- 86 % for the nanorods and nanowires morphology, respectively. This article provided new insight into the construction of suitable geometrically optimized

heterojunctions for the remediation of persistent bio toxicants such as E3, which are the most difficult to be removed from wastewaters by adsorption. The above-mentioned results were **reported and published in** "*Materials Letters*" (**2022**), 132291, https://doi.org/10.1016/j.matlet.2022.132291 (Web of Science Indexed [Applied Physics], Q2, J_{imp}: 3.574)

4.2 Contribution to science and practice

In the present scenario, a minuscule level of EH present are a severe threat to human and aquatic life through their exposure via food sources or drinking water. As a result, fish femininity, breast, ovarian, and prostate cancer caused by hormonal disorders is a serious threat and problem to society. The current European Union directive 2020/2184 concerning drinking water quality recommended a threshold limit of 1 ng/L as a benchmark for assessing the occurrence and treatment of EDCs. Thus, this doctoral work focuses on the preparation and characterization of smart materials that can be utilized for the simultaneous elimination of estrogenic hormones from wastewater by means of an adsorption technique for practical application.

The commonly used techniques are incapable of capturing EH at water treatment plants and result in secondary pollution due to insufficiently treated effluents, which demand secondary water treatment. Moreover, adsorbent nanoparticles which are promising for estrogens, have been reported in the literature, but they require an additional separation process from wastewater that raises the costs. In this regard, removing EH by adsorption via electrospun nanofibers offers a sustainable and relatively environmentally friendly solution for eliminating synthetic hormones with high efficiency and effectiveness of reusability for several adsorption-desorption cycles after regeneration. This brings a practical approach to large-scale production. Polymeric materials for water treatment applications are promising owing to their benefits, such as affordability, sustainability, efficient performance, durability, high surface area, high aspect ratio, and nanoporous structure. Furthermore, the nanofiber membrane functions precisely in different aquatic conditions without the accumulation of chemicals. In literature, commercially available nylon, PP, polytetrafluoroethylene, CA, regenerated cellulose, and glass microfiber filters have been reported for the removal of E1. Meanwhile, PA nanoparticles were employed to extract just EE2, PES nanofibers for the removal of E2, and PVDF doped with PVP and TiO_2 membranes prepared by the phase inversion process for the removal of E1 and E2. However, these studies were solely limited to the filtration of a single natural

or synthetic hormone. Therefore, different combinations of polymeric materials have been utilized to develop electrospun nanofibers, which can be utilized in simultaneous adsorption removal of four EH. Additionally, CBs were recycled to fabricate WCENFs that were used for comparison with the commercially available filters in the market. The studies were optimized using modeling to obtain the best conditions, understand interaction mechanisms, and apply kinetics, Isotherms, and thermodynamics. Also, the most promising lab synthesized polyurethane (PU 918) was surface coated with PANI/PVA to enhance adsorption removal capacity owing to ionic interaction and improved hydrogen bonding. Furthermore, ZnO and TiO_2 nanoparticles were green synthesized, considering environmental protection to test their photodegradation performance. Later these particles can be used in nanofibers for combining the photodegradation and adsorption processes. Finally, ZnO-based nanorods and nanowires thin films were prepared, characterized, and tested in a continuous cross-flow closed system for E3 hormone, which was least adsorbed by nanofiber membranes.

This doctoral study elaborated on the use of several hydrophilic and hydrophobic polymeric electrospun nanofibers, especially recycled WCENFs for adsorption and smartly functionalized polymers for optimized removal of hormones considering wastewater treatment applications. As a secondary work, nanoparticles, rods, and wires heterojunctions were tested for photodegradation of these hormones. This provides an opportunity for the next generation of scientific researchers to develop further modified and extremely specific polymeric nanofiber membranes incorporated with such photocatalysts intended for the eradication of micropollutants at wastewater treatment plants.

4.3 Future plans

The primary goal of this doctoral work was the ***development and characterization of electrospun nanofibrous polymeric materials that were tested for the elimination of estrogenic hormones from wastewater by means of an adsorption technique***. This aim was successfully achieved by preparing smart electrospun polymeric nanofibers for the adsorption removal of EH. However, the experimental work was restricted to batch adsorption study. Furthermore, as a secondary work, photocatalyst materials such as nanoparticles, nanorods, and nanowires were synthesized and were successful with a high performance of photocatalytic degradation of these EH but only in the presence of UV light. Additionally, the studies were limited to the use of these materials individually and separately for adsorption and photodegradation techniques. Thus, this

generates the following aims of studies that could be achieved before the final application of these studies can be implemented over large-scale use.

- Optimized fabrication jointly of high-performing electrospun nanofiber membranes (PU and WCENFs) incorporated with highly efficient photocatalysts that can operate at both UV and visible light conditions to have rapid simultaneous adsorption removal and photocatalytic degradation of micropollutants such as EH from wastewater.
- Determination of the possible enhanced adsorption activity by surface functionalization in the presence of an incorporated photocatalyst and observing the stability of nanofibers in different mediums.
- Determination of contact time study to apply suitable kinetic models in continuous crossflow and dead-end flow closed systems to obtain high flux and true removal percentages in natural water samples for complete wastewater remediation.
- Testing the reusability of material for at least ten cycles to be economically viable where the performance must remain high above 90% and the recovery of EH is significantly possible.
- Optimization study with variation in experimental condition parameters such as the influence of competing ions and interacting media, the concentration of adsorbate, adsorbent dosage, pH of the solution, the temperature of interaction, and time of contact to precisely evaluate the types of the mechanism involved, apply thermodynamics, Isothermal models, identify the most suitable cost-effective operating conditions, and determine the economic feasibility.
- Observe the adsorption and photodegradation capacities of the prepared materials to analyze their performance in capturing EH and compare them with the best materials reported in the literature.

REFERENCES

[1] Uddin, Z.; Ahmad, F.; Ullan, T.; Nawab, Y.; Ahmad, S.; Azam, F.; Rasheed, A.; Zafar, M. S.: Recent trends in water purification using electrospun nanofibrous membranes. International Journal of Environmental Science and Technology, (2021). http://doi:10.1007/s13762-021-03603-9.

[2] Dongre, R. S.; Sadasivuni, K. K.; Deshmukh, K.; Mehta, A.; Basu, S.; Meshram, J. S.; Al-Maadeed, M. A. A.; Karim, A.: Natural polymer based composite membranes for water purification: a review. Polymer-Plastics Technology and Materials, **58**, 1295–1310 (2019). http://doi:10.1080/25740881.2018.1563116.

[3] Mishra, R. K.; Sabu, A.; Tiwari, S. K.: Materials chemistry and the futurist eco-friendly applications of nanocellulose: Status and prospect. Journal of Saudi Chemical Society, **22**, 949–978 (2018). http://doi:10.1016/j.jscs.2018.02.005.

[4] Alim, M. A.; Rahman, A.; Tao, Z.; Samali, B.; Khan, M. M.; Shirin, S.: Suitability of roof harvested rainwater for potential potable water production: A scoping review. Journal of Cleaner Production, **248** (2020). http://doi:10.1016/j.jclepro.2019.119226.

[5] Wadhawan, S.; Jain, A.; Nayyar, J.; Mehta, S. K.: Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. Journal of Water Process Engineering, **33**, 101038 (2020). http://doi:10.1016/j.jwpe.2019.101038.

[6] Jain, P.; Pradeep, T.: Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. Biotechnology and Bioengineering, **90**, 59–63 (2005). http://doi:10.1002/bit.20368.

[7] Matilainen, A.; Gjessing, E. T.; Lahtinen, T.; Hed, L.; Bhatnagar, A.; Sillanpää, M.: An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere, **83**, 1431–1442 (2011). http://doi:10.1016/j.chemosphere.2011.01.018.

[8] Jiang, J. Q.: The role of coagulation in water treatment. Current Opinion in Chemical Engineering, **8**, 36–44 (2015). http://doi:10.1016/j.coche.2015.01.008.

[9] Turner, T.; Wheeler, R.; Stone, A.; Oliver, I.: Potential Alternative Reuse Pathways for Water Treatment Residuals. Water, Air, and Soil Pollution, **230** (2019).

[10] Glaze, W. H.; Kang, J. W.; Chapin, D. H.: The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone: Science & Engineering, **9**, 335–352 (1987). http://doi:10.1080/01919518708552148.

[11] Rice, R. G.: The use of ozone to control trihalomethanes in drinking water

treatment. Ozone: Science & Engineering, **2**, 75–99 (1980). http://doi:10.1080/01919518008550870.
[12] Kim, J.; Chung, Y.; Shin, D.; Kim, M.; Lee, Y.; Lim, Y.; Lee, D.: Chlorination by-products in surface water treatment process. Desalination, **151**, 1–9 (2003). http://doi:10.1016/S0011-9164(02)00967-0.
[13] Shi, P.; Jia, S.; Zhang, X. X.; Zhang, T.; Cheng, S.; Li, A.: Metagenomic insights into chlorination effects on microbial antibiotic resistance in drinking water. Water Research, **47**, 111–120 (2013). http://doi:10.1016/j.watres.2012.09.046.
[14] Golob, V.; Vinder, A.; Simonič, M.: Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. Dyes and Pigments, **67**, 93–97 (2005). http://doi:10.1016/j.dyepig.2004.11.003.
[15] Sher, F.; Malik, A.; Liu, H.: Industrial polymer effluent treatment by chemical coagulation and flocculation. Journal of Environmental Chemical Engineering, **1**, 684–689 (2013). http://doi:10.1016/j.jece.2013.07.003.
[16] Yang, Y.; Zhu, G.; Zhang, H.; Chen, J.; Zhong, X.; Lin, Z.; Su, Y.; Bai, P.: Triboelectric Nanogenerator for Harvesting Wind Energy and as Self-. ACS Nano, **7**, 9461–9468 (2013).
[17] Rengaraj, S.; Yeon, K. H.; Moon, S. H.: Removal of chromium from water and wastewater by ion exchange resins. Journal of Hazardous Materials, **87**, 273–287 (2001). http://doi:10.1016/S0304-3894(01)00291-6.
[18] Dąbrowski, A.; Hubicki, Z.; Podkościelny, P.; Robens, E.: Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere, **56**, 91–106 (2004). http://doi:10.1016/j.chemosphere.2004.03.006.
[19] Joss, A.; Keller, E.; Alder, A. C.; Göbel, A.; McArdell, C. S.; Ternes, T.; Siegrist, H.: Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Research, **39**, 3139–3152 (2005). http://doi:10.1016/j.watres.2005.05.031.
[20] Oller, I.; Malato, S.; Sánchez-Pérez, J. A.: Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. Science of the Total Environment, **409**, 4141–4166 (2011). http://doi:10.1016/j.scitotenv.2010.08.061.
[21] Ting, Y. F.; Praveena, S. M.: Sources, mechanisms, and fate of steroid estrogens in wastewater treatment plants: a mini review. Environmental Monitoring and Assessment, **189** (2017). http://doi:10.1007/s10661-017-5890-x.
[22] Qu, X.; Alvarez, P. J. J.; Li, Q.: Applications of nanotechnology in water and wastewater treatment. Water Research, **47**, 3931–3946 (2013). http://doi:10.1016/j.watres.2012.09.058.
[23] Lee, J.; Yoon, J.; Kim, J. H.; Lee, T.; Byun, H.: Electrospun PAN–GO composite nanofibers as water purification membranes. Journal of Applied

Polymer Science, **135**, 1–9 (2018). http://doi:10.1002/app.45858.
[24] Yalcinkaya, F.: A review on advanced nanofiber technology for membrane distillation. Journal of Engineered Fibers and Fabrics, **14** (2019). http://doi:10.1177/1558925018824901.
[25] Ma, H.; Burger, C.; Hsiao, B. S.; Chu, B.: Ultra-fine cellulose nanofibers: New nano-scale materials for water purification. Journal of Materials Chemistry, **21**, 7507–7510 (2011). http://doi:10.1039/c0jm04308g.
[26] Zhang, M.; Song, L.: Mechanisms and parameters affecting flux decline in cross-flow microfiltration and ultrafiltration of colloids. Environmental Science and Technology, **34**, 3767–3773 (2000). http://doi:10.1021/es990475u.
[27] Koyuncu, I.; Sengur, R.; Turken, T.; Guclu, S.; Pasaoglu, M. E.: *Advances in water treatment by microfiltration, ultrafiltration, and nanofiltration*; Vol. 2019; ISBN 9781782421269.
[28] Islam, M. S.; Sultana, A.; Saadat, A. H. M.; Islam, M. S.; Shammi, M.; Uddin, M. K.: Desalination Technologies for Developing Countries: A Review. Journal of Scientific Research, **10**, 77–97 (2018). http://doi:10.3329/jsr.v10i1.33179.
[29] Bjorge, D.; Daels, N.; De Vrieze, S.; Dejans, P.; Van Camp, T.; Audenaert, W.; Hogie, J.; Westbroek, P.; De Clerck, K.; Van Hulle, S. W. H.: Performance assessment of electrospun nanofibers for filter applications. Desalination, **249**, 942–948 (2009). http://doi:10.1016/j.desal.2009.06.064.
[30] Barhate, R. S.; Ramakrishna, S.: Nanofibrous filtering media: Filtration problems and solutions from tiny materials. Journal of Membrane Science, **296**, 1–8 (2007). http://doi:10.1016/j.memsci.2007.03.038.
[31] Mahdi A. Shirazi, M.; Bazgir, S.; Meshkani, F.: Electrospun Nanofibrous Membranes for Water Treatment. Advances in Membrane Technologies, (2020). http://doi:10.5772/intechopen.87948.
[32] Schäfer, A. I.; Stelzl, K.; Faghih, M.; Sen Gupta, S.; Krishnadas, K. R.; Heißler, S.; Pradeep, T.: Poly(ether sulfone) Nanofibers Impregnated with β-Cyclodextrin for Increased Micropollutant Removal from Water. ACS Sustainable Chemistry and Engineering, **6**, 2942–2953 (2018). http://doi:10.1021/acssuschemeng.7b02214.
[33] McLachlan, J. A.; Simpson, E.; Martin, M.: Endocrine disrupters and female reproductive health. *Best Pract. Res. Clin. Endocrinol. Metab.* (2006), *20*, 63–75.
[34] Montes-Grajales, D.; Olivero-Verbel, J.: EDCs databank: 3D-structure database of endocrine disrupting chemicals. Toxicology, **327**, 87–94 (2015). http://doi:10.1016/j.tox.2014.11.006.
[35] Gyllenhammar, I.; Glynn, A.; Jönsson, B. A. G.; Lindh, C. H.; Darnerud, P. O.; Svensson, K.; Lignell, S.: Diverging temporal trends of human exposure to bisphenols and plastizisers, such as phthalates, caused by

substitution of legacy EDCs? Environmental Research, **153**, 48–54 (2017). http://doi:10.1016/j.envres.2016.11.012.
[36] Sood, S.; Shekhar, S.; Santosh, W.: Dimorphic placental stress: A repercussion of interaction between endocrine disrupting chemicals (EDCs) and fetal sex. Medical Hypotheses, **99**, 73–75 (2017). http://doi:10.1016/j.mehy.2017.01.002.
[37] Luo, L.; Yang, Y.; Xiao, M.; Bian, L.; Yuan, B.; Liu, Y.; Jiang, F.; Pan, X.: A novel biotemplated synthesis of TiO2/wood charcoal composites for synergistic removal of bisphenol A by adsorption and photocatalytic degradation. Chemical Engineering Journal, **262**, 1275–1283 (2015). http://doi:10.1016/j.cej.2014.10.087.
[38] Chen, Y.; Zhang, Y.; Luo, L.; Shi, Y.; Wang, S.; Li, L.; Long, Y.; Jiang, F.: A novel templated synthesis of C/N-doped β-Bi2O3 nanosheets for synergistic rapid removal of 17α-ethynylestradiol by adsorption and photocatalytic degradation. Ceramics International, **44**, 2178–2185 (2018). http://doi:10.1016/j.ceramint.2017.10.173.
[39] Han, J.; Qiu, W.; Gao, W.: Adsorption of estrone in microfiltration membrane filters. Chemical Engineering Journal, **165**, 819–826 (2010). http://doi:10.1016/j.cej.2010.10.024.
[40] European Commission: Directive (EU) 2020/2184 of the European Parlliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal of the European Union, **2019**, 1–61 (2020).
[41] Yazdan, M. S.; Kumar, R.; Leung, S. W.: The Environmental and Health Impacts of Steroids and Hormones in Wastewater Effluent , as Well as Existing Removal Technologies : A Review. , 206–224 (2022).
[42] Nghiem, L. D.; Schäfer, A. I.: Adsorption and transport of trace contaminant estrone in NF/RO membranes. Environmental Engineering Science, **19**, 441–451 (2002). http://doi:10.1089/109287502320963427.
[43] Solomon, G. M.; Schettler, T.: Environment and health: 6. Endocrine disruption and potential human health implications. *Cmaj* (2000), *163*, 1471–1476.
[44] Cartinella, J. L.; Cath, T. Y.; Flynn, M. T.; Miller, G. C.; Hunter, K. W.; Childress, A. E.: Removal of natural steroid hormones from wastewater using membrane contactor processes. Environmental Science and Technology, **40**, 7381–7386 (2006). http://doi:10.1021/es060550i.
[45] Johnson, A. C.; Aerni, H. R.; Gerritsen, A.; Gibert, M.; Giger, W.; Hylland, K.; Jürgens, M.; Nakari, T.; Pickering, A.; Suter, M. J. F.; Svenson, A.; Wettstein, F. E.: Comparing steroid estrogen, and nonylphenol content across a range of European sewage plants with different treatment and management practices. Water Research, **39**, 47–58 (2005). http://doi:10.1016/j.watres.2004.07.025.
[46] Sarmah, A. K.; Northcott, G. L.; Leusch, F. D. L.; Tremblay, L. A.: A

survey of endocrine disrupting chemicals (EDCs) in municipal sewage and animal waste effluents in the Waikato region of New Zealand. Science of the Total Environment, **355**, 135–144 (2006). http://doi:10.1016/j.scitotenv.2005.02.027.

[47] Vymazal, J.; Březinová, T.; Koželuh, M.: Occurrence and removal of estrogens, progesterone and testosterone in three constructed wetlands treating municipal sewage in the Czech Republic. Science of the Total Environment, **536**, 625–631 (2015). http://doi:10.1016/j.scitotenv.2015.07.077.

[48] Han, J.; Qiu, W.; Cao, Z.; Hu, J.; Gao, W.: Adsorption of ethinylestradiol (EE2) on polyamide 612: Molecular modeling and effects of water chemistry. Water Research, **47**, 2273–2284 (2013). http://doi:10.1016/j.watres.2013.01.046.

[49] Braga, O.; Smythe, G. A.; Schäfer, A. I.; Feitz, A. J.: Fate of steroid estrogens in Australian inland and coastal wastewater treatment plants. Environmental Science and Technology, **39**, 3351–3358 (2005). http://doi:10.1021/es0501767.

[50] Limpiyakorn, T.; Homklin, S.; Ong, S. K.: Fate of estrogens and estrogenic potentials in sewerage systems. Critical Reviews in Environmental Science and Technology, **41**, 1231–1270 (2011). http://doi:10.1080/10643380903488680.

[51] Aris, A. Z.; Shamsuddin, A. S.; Praveena, S. M.: Occurrence of 17α-ethynylestradiol (EE2) in the environment and effect on exposed biota: A review. *Environ. Int.* (2014), *69*, 104–119.

[52] Adeel, M.; Song, X.; Wang, Y.; Francis, D.; Yang, Y.: Environmental impact of estrogens on human, animal and plant life: A critical review. *Environ. Int.* (2017), *99*, 107–119.

[53] Siegenthaler, P. F.; Bain, P.; Riva, F.; Fent, K.: Effects of antiandrogenic progestins, chlormadinone and cyproterone acetate, and the estrogen 17α-ethinylestradiol (EE2), and their mixtures: Transactivation with human and rainbowfish hormone receptors and transcriptional effects in zebrafish (Danio reri. Aquatic Toxicology, **182**, 142–162 (2017). http://doi:10.1016/j.aquatox.2016.11.001.

[54] Srinivasan, J.; Ramakrishnan, G.; Mukhopadhyay, S.; Manoharan, S.: A study of knitted fabrics from polyester microdenier fibres. Journal of the Textile Institute, **98**, 31–35 (2007). http://doi:10.1533/joti.2005.0180.

[55] Aende, A.; Gardy, J.; Hassanpour, A.: Seawater desalination: A review of forward osmosis technique, its challenges, and future prospects. Processes, **8** (2020). http://doi:10.3390/PR8080901.

[56] Semião, A. J. C.; Schäfer, A. I.: Xenobiotics Removal by Membrane Technology: An Overview. In; (2010); pp. 307–338.

[57] Luo, Y.; Guo, W.; Ngo, H. H.; Nghiem, L. D.; Hai, F. I.; Zhang, J.; Liang, S.; Wang, X. C.: A review on the occurrence of micropollutants in the

aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* (2014), *473–474*, 619–641.
[58] Tijani, J. O.; Fatoba, O. O.; Petrik, L. F.: A review of pharmaceuticals and endocrine-disrupting compounds: Sources, effects, removal, and detections. Water, Air, and Soil Pollution, **224** (2013). http://doi:10.1007/s11270-013-1770-3.
[59] Onesios, K. M.; Yu, J. T.; Bouwer, E. J.: Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: A review. *Biodegradation* (2009), *20*, 441–466.
[60] Pham, T. T.; Nguyen, V. A.; Van der Bruggen, B.: Pilot-Scale Evaluation of GAC Adsorption Using Low-Cost, High-Performance Materials for Removal of Pesticides and Organic Matter in Drinking Water Production. Journal of Environmental Engineering, **139**, 958–965 (2013). http://doi:10.1061/(asce)ee.1943-7870.0000704.
[61] ALI, H.; MASAR, M.; URBANEK, M.; GULER, A. C.; URBANEK, P.; MACHOVSKY, M.; KURITKA, I.: Effect of annealing on luminescence and photocatalytic activity of ZnS nanocrystals under UV light irradiation. NANOCON 2020 Conference Proeedings, **2020**, 261–266 (2020). http://doi:10.37904/nanocon.2020.3707.
[62] Pendergast, M. M.; Hoek, E. M. V.: A review of water treatment membrane nanotechnologies. *Energy Environ. Sci.* (2011), *4*, 1946–1971.
[63] Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marĩas, B. J.; Mayes, A. M.: Science and technology for water purification in the coming decades. *Nature* (2008), *452*, 301–310.
[64] Augusto, F.; Hantao, L. W.; Mogollón, N. G. S.; Braga, S. C. G. N.: New materials and trends in sorbents for solid-phase extraction. TrAC - Trends in Analytical Chemistry, **43**, 14–23 (2013). http://doi:10.1016/j.trac.2012.08.012.
[65] Bhardwaj, N.; Kundu, S. C.: Electrospinning: A fascinating fiber fabrication technique. *Biotechnol. Adv.* (2010), *28*, 325–347.
[66] Yang, Z.; Peng, H.; Wang, W.; Liu, T.: Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites. Journal of Applied Polymer Science, **116**, 2658–2667 (2010). http://doi:10.1002/app.
[67] Yudanova, T. N.; Filatov, I. Y.; Afanasov, I. M.: Production of ultrafine cellulose acetate fibers. Theoretical Foundations of Chemical Engineering, **50**, 508–512 (2016). http://doi:10.1134/S004057951604031X.
[68] Dzenis, Y.: Spinning continuous fibers for nanotechnology. *Science (80-.).* (2004), *304*, 1917–1919.
[69] Shabafrooz, V.; Mozafari, M.; Vashaee, D.; Tayebi, L.: Electrospun nanofibers: From filtration membranes to highly specialized tissue engineering scaffolds. *J. Nanosci. Nanotechnol.* (2014), *14*, 522–534.
[70] Hemamalini, T.; Karunakaran, S. A.; Siva Elango, M. K.; Senthil Ram, T.;

Giri Dev, V. R.: Regeneration of cellulose acetate nanofibrous mat from discarded cigarette butts. Indian Journal of Fibre and Textile Research, **44**, 248–252 (2019).
[71] Kimmer, D.; Vincent, I.; Lovecka, L.; Kazda, T.; Giurg, A.; Skorvan, O.: Some aspects of applying nanostructured materials in air filtration, water filtration and electrical engineering. In *AIP Conference Proceedings*; (2017); Vol. 1843.
[72] F. Cengiz, TA. Dao, O. Jirsak: Influence of solution properties on the roller electrospinning of poly(vinyl alcohol). Society, , 1–10 (2010). http://doi:10.1002/pen.
[73] Haider, A.; Haider, S.; Kang, I.: REVIEW A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology. Arabian Journal of Chemistry, **11**, 1165–1188 (2018). http://doi:10.1016/j.arabjc.2015.11.015.
[74] Sagitha, P.; Reshmi, C. R.; Manaf, O.; Sundaran, S. P.; Juraij, K.; Sujith, A.: *Development of nanocomposite membranes by electrospun nanofibrous materials*; Elsevier Inc.; ISBN 9780128167106.
[75] Wasim, M.; Sabir, A.; Shafiq, M.; Jamil, T.: *Chapter 11 - Electrospinning: A Fiber Fabrication Technique for Water Purification*; Elsevier Inc.; ISBN 9780128139264.
[76] Ray, S. S.; Chen, S.; Li, C.; Nguyen, C.: RSC Advances A comprehensive review : electrospinning technique for fabrication and surface modi fi cation. RSC Advances, **6**, 85495–85514 (2016). http://doi:10.1039/C6RA14952A.
[77] Schiffman, J. D.; Schauer, C. L.: A Review : Electrospinning of Biopolymer Nanofibers and their Applications A Review : Electrospinning of Biopolymer Nanofibers and their Applications. **3724** (2008). http://doi:10.1080/15583720802022182.
[78] Eng, J. T. S.; Lin, T.: Journal of Textile Science & Engineering Needleless Electrospinning : A Practical Way to Mass Production of Nanofibers. **2**, 2–4 (2012). http://doi:10.4172/2165-8064.1000e109.

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LIST OF ABBREVIATIONS AND SYMBOLS

Alphabetically ordered

BC	Borax and citric acid
Borax	Sodium tetra-borate decahydrate
CA	Cellulose acetate
CBs	Cigarette butts
ECDs	Endocrine disrupting compound
EH	Estrogenic hormones
E1	Estrone
E2	Estradiol
EE2	Ethinylestradiol
E3	Estriol
GMF	Glass microfiber
HPLC	High performance liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
NF	Nanofiltration
NPs	Nanoparticles
PA	Polyamide

PAN	Polyacrylonitrile
PANI	Polyaniline
PEO	Polyethylene oxide
PES	Polyethersulfone
PET	Polyethylene terephthalate
PLA	Polylactide
PSU	Polysulfone
PU Elasollan	Polyurethane Elastollan
PU 918	Polyurethane 918
PU-PANI-ES	Polyurethane modified with polyaniline emeraldine salt
PU-PANI-EB	Polyurethane modified with polyaniline emeraldine base
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	Polyvinyl pyrrolidone
PP	Polypropylene
PTFE	Polytetrafluoroethylene
RC	Regenerated cellulose
RO	Reverse osmosis
SEM	Scanning electron microscopy
TiO_2	Titanium dioxide
WCENFs	Waste cigarette electrospun nanofibers
ZnO	Zinc oxide

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Education

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Doctoral degree
Centre of polymer systems, Tomas Bata University in Zlin (Czech Republic)
Material Science and Engineering
Biomaterials and Biocomposites

2015 – 2017
Master´s degree
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Petroleum Engineering

2011 – 2015
Bachelor´s degree
School of Chemical and Materials Engineering, National University of Sciences and Technology (Pakistan)
Materials Engineering

2008 – 2010
A-Levels
Beaconhouse educational complex, Islamabad (Pakistan)
(University of Cambridge Examination, England)

2006 – 2008
O-Levels
Beaconhouse school system, Islamabad (Pakistan)
(University of Cambridge Examination, England)

Work experience

2017 – 2018

Lecturer (TVF)
School of Chemical and Materials Engineering and School of Art Design and Architecture, National University of Sciences and Technology (Pakistan)

2017 – 2018
Coach for O & A-Levels
Internik Academy

2008 – 2015
Private home tutor
O & A-Levels

Internships

2022 (8 weeks)
Research traineeship (Ph.D. degree)
Leibniz Institute of Surface Engineering (IOM), Germany

2017 (4 weeks)
Corrosion control and maintenance (Master's degree)
MOL GROUP, Hungary

2014 (6 weeks)
Quality control (Bachelor's degree)
Velosi Integrity & Safety Pakistan (PVT) LTD, Pakistan

Work on projects of Internal Grant Agency (IGA)

2022 – present
Project IGA/CPS/2022/003,
Member of project team

2021
Project IGA/CPS/2021/002, Preparation and characterization of nanocomposite systems
Member of project team

2020
Project IGA/CPS/2020/002, Bioactive polymer systems for environmental applications

Member of project team

2019
Project IGA/CPS/2019/006, Polymeric composites for bio-applications
Member of project team

Network and membership

2017 – present
Registered Materials Engineer
Pakistan Engineering Council, Islamabad, Pakistan

2013 – 2014
NUST Bazm-e-Pakistan
National University of Sciences and Technology (NUST), Islamabad, Pakistan

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Conferences and Seminars

Nanocon2021 (**20th – 22nd October 2021**)
International scientific conference Brno, Czech Republic

Academic English writing for Research and Publication (Webinar) (**26th – 29th April 2021**)
Department of English, University of Liverpool, England, United Kingdom

Tips and Tricks for Handling Reference Materials (**8th December 2020**)
RESTEK (Webinar), France

HPLC Troubleshooting – Part 2 (**1st December 2020**)
RESTEK (Webinar), France

HPLC Troubleshooting – Part 1 (**24th November 2020**)
RESTEK (Webinar), France

Nanocon2020 (**21st – 23rd October 2020**)
International scientific conference Brno, Czech Republic

Model United Nations (LUMUN) (**27th – 31st December 2009**)

Lahore University of Management Sciences (LUMS), Lahore, Pakistan

The Champion's Leadership Summit (**14th September 2008**) Islamabad, Pakistan

Honours and awards

UESTP Overseas PhD Scholarship (**2018**)
Higher Education Commission (HEC), Pakistan

Monash PhD Research Scholarship (**2018**)
Faculty of Engineering International Postgraduate Research Scholarship (FEIPRS), Australia

Bronze Medal (**2017**)
M.Sc Petroleum Engineering, University of Miskolc, Hungary

Laptop winner (**2016**)
5th position in Materials engineering batch
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Name twice on the dean's list (**2014**)
High GPA achievement in 2 consecutive semesters (Collected certificate and scholarship)
National University of Sciences and Technology (NUST)

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1. M. Yasir, T. Sopik, L. Lovecka, D. Kimmer, V. Sedlarik, The adsorption, kinetics, and interaction mechanisms of various types of estrogen on electrospun polymeric nanofiber membranes, Nanotechnology 33 (2021) 75702, https://doi.org/10.1088/1361-6528/ac357b.
2. M. Yasir, T. Sopik, R. Patwa, D. Kimmer, V. Sedlarik, Adsorption of estrogenic hormones in aqueous solution using electrospun nanofibers from waste cigarette butts: Kinetics, mechanism, and reusability, Express Polymer Letters 16 (2022) 624–648, https://doi.org/10.3144/expresspolymlett.2022.46.
3. M. Yasir, M. Masar, T. Sopik, H. Ali, M. Urbanek, J. Antos, M. Machovsky, I. Kuritka, ZnO nanowires and nanorods based ZnO/WO_3/Pt heterojunction for efficient photocatalytic degradation of Estriol (E3) hormone, Materials Letters (2022) 132291, https://doi.org/10.1016/j.matlet.2022.132291.
4. M. Yasir, F. A. Ngwabebhoh, T. Sopík, H. Ali, V. Sedlarik, Electrospun polyurethane nanofibers coated with polyaniline/polyvinyl alcohol as ultrafiltration membranes for the removal of ethinylestradiol hormone micropollutant from aqueous phase, Journal of Environmental Chemical Engineering 10 (2022) 107811, https://doi.org/10.1016/j.jece.2022.107811.
5. M. Yasir, F. A. Ngwabebhoh, T. Sopik, L. Lovecka, D. Kimmer, V. Sedlarik, The adsorptive behaviour of electrospun hydrophobic polymers for optimized uptake of estrogenic sex hormones from aqueous media: Kinetics, thermodynamics and reusability study. in the Journal of Chemical Technology and Biotechnology. (2022) https://doi.org/10.1002/jctb.7191.

Papers published in international conferences:

1. M. Yasir, T. Sopik, D. Kimmer, V. Sedlarik, Facile HPLC technique for simultaneous detection of estrogentic hormones in wastewater. in 'Proceedings of the 12th International Conference on Nanomaterials, Brno, Czech Republic' 272–276 (2020). https://doi.org/10.37904/nanocon.2020.3710.

2. M. Yasir, T. Sopik, H. Ali, D. Kimmer, V. Sedlarik, Green synthesis of titanium and zinc oxide nanoparticles for simultaneous photocatalytic removal of estrogens in wastewater. in 'Proceedings of the 13th International Conference on Nanomaterials, Brno, Czech Republic' 189-196 (2021). https://doi.org/10.37904/nanocon.2021.4333.
3. H. Ali, M. Masar, M. Yasir, T. Sopik, P. Urbanek, M. Machovsky, I. Kuritka, Silica supported WO_3/Cu_2O heterostructured nanoparticles for photocatalytic degradation of hormones. in 'Proceedings of the 13th International Conference on Nanomaterials, Brno, Czech Republic' 104-109 (2021). https://doi.org/10.37904/nanocon.2021.4343.
4. Z. Krchnackova, D. Kimmer, L. Lovecka, M. Kovarova, H. Pistekova, D. Vesela, I. Vincent, M. Yasir, V. Sedlarik, Antimicrobial properties of polymeric nanofibrous membranes containing ferrous sulphate. in 'Proceedings of the 13th International Conference on Nanomaterials, Brno, Czech Republic' 317-322 (2021). https://doi.org/10.37904/nanocon.2021.4347.
5. H. Ali, M. Masar, M. Yasir, F. A. Ngwabebhoh, O. Zandraa, T. Sopik, M. Machovsky, I. Kuritka, Silica supported visible light active graphitic carbon nitride (g-C3N4) photocatalyst for estrogenic hormones removal and antibacterial activity, submitted in 'Proceedings of the 2nd International Conference on Energy Fuels Environment, Krakow, Poland' (2022).

Papers accepted as coauthor in international journals with impact factor:

1. B. Ahmad, N. M. Ahmad, M. Yasir, Z. A. Khan, S. Rafiq, High-Performance Anticorrosive Polyester Coatings on Mild Steel in Mixed Acid Mixtures Environments. in Advances in Polymer Technology. (2019) https://doi.org/10.1155/2019/3954784
2. A. Salim, M. A. Abbas, M. I. Khan, M. Z. Khan, F. Javaid, S. Mushtaq, M. Batool, M. Yasir, A. L. Khan, A. U. Khan, K. M. Deen, N. M. Ahmad, Graphene Oxide incorporated Polyether Sulfone Nanocomposite Antifouling Ultrafiltration Membranes with Enhanced Hydrophilicity. in Materials Research Express. (2022) https://doi.org/10.1088/2053-1591/ac81a3.
3. P. Drohsler, M. Yasir, D. R. C. Fabian, J. Cisar, Z. Yadollahi, V. Sedlarik, Comparative degradation study of a biodegradable composite based on polylactide with halloysite nanotubes and a polyacrylic acid copolymer. in the Journal of Materials Today Communications. (2022) https://doi.org/10.1016/j.mtcomm.2022.104400.

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