

Adsorption Modeling of Thin-Film Molecularly Imprinted Polymers to Measure
Pyrene in Marine Environments

by

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Abstract

This thesis characterizes the adsorption properties of molecularly imprinted polymers (MIPs) for pyrene. MIPs are applied for monitoring organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and can be deployed in freshwater and marine (saline) water for detection of anthropogenic impacts. Exploiting a simple, low-tech method is of high priority as the fast detection of oil spill sources has become a challenge to analytical chemists and environmental scientists. Kinetic tests were conducted employing the developed MIPs in our group using an Ultra Performance Liquid Chromatography (UPLC) for the measurement of pyrene, PAHs, in both small and large volume studies.

Discussed will be the results obtained from kinetic and equilibrium adsorption experiments conducted using these films for measuring pyrene in distilled, tap water, and saline water. To gain an insight into the effects of temperature, pH, and salinity, the same experiments were conducted at varying temperature, pH, and salinity employing the standard batch equilibrium method. This research evaluates the adsorption capacity of the obtained polymers as a means to use MIPs for onsite detection without elaborate calibration making them suitable for use in early warning systems for oil spills.

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List of Symbols, Nomenclature or Abbreviations

$^{\circ}\text{C}$	Degrees Celsius
ΔH	Enthalpy of fusion
ΔS	Entropy of fusion
C_s	The concentration of an analyte in the stock solution
C_w	The concentration of a substance in the water phase
$C_{w,salt}^{sat}$	The saturated concentration of a solute in a saline aqueous phase
G	Gram
GC-MS	Gas chromatography-mass spectrometry
H	hour
HCl	Hydrochloric acid
$K_{ow, salt}$	Octanol-saline water partition coefficient
K_L	Langmuir constants
K_F	Freundlich constant
k_1	Pseudo first-order constant rate

K_2	Pseudo second order equation constant rate
Mg	mili gram
min	minute
mL	mili liter
N	The intensity of surface adsorption
Ng	Nanogram
NaCl	Sodium chloride
NaOH	Sodium hydroxide
PAH	Polycyclic aromatic hydrocarbon
ppb	Parts per billion
ppm	Parts per million
$Q(t)$	adsorbent concentration at any time
Q_e	adsorbent concentration at equilibrium
Q_{max}	Maximum MIP capacity

R	Universal gas constant
Rpm	Rotations per minute
S	Second
US	United States
US EPA	United States Environmental Protection Agency

Chapter 1

Introduction and Literature Review

1.1 Introduction

Accurate and rapid methods to monitor and measure the level of contaminants in seawater must be established in order to meet the discharge and water quality standards [1]. Polycyclic aromatic hydrocarbons (PAHs), a large group of stable organic compounds, produced naturally, and present in petroleum, are of great concern due to their carcinogenic, mutagenic and teratogenic effects [2]. The marine environment is a major concern as it is the main receptacle sink for PAH entering from various sources [3, 4].

Anthropogenic sources include products of petrogenic activities, such as crude oil, coke, and aluminum production, catalytic cracking towers, coal-tar pitch, coal gasification and liquefying plants, and the incomplete combustion of coal, oil, petrol, wood, gas, and the pyrolysis of organic matter [5]. Natural sources include leakage of petroleum or coal deposits, volcanic eruptions, forest fires, and hydrothermal processes [5]. Petrogenic sources of PAHs in industrial areas have been recorded to be 11.2 times greater than in urban areas [5].

Further study is needed concerning the effects of passive sampling and partitioning theory in order to assess the fluctuation of polycyclic aromatic hydrocarbons (PAHs) flux with regards to bioaccumulation and ecological risks in marine organisms [6]. Overall, this

study highlights an integrated use of passive sampling and monitoring methods as a fast and robust tool capable of being applied to assessing the effectiveness of molecularly imprinted polymers (MIPs) with quantitative, and qualitative insights in the environment port. This section aims at providing a general description and literature review of the concepts related to the techniques used for removing PAHs with further discussion on current ongoing research in analytical fields.

1.2 Scope and Objectives

Studies have been conducted using MIPs application in industry for PAH detection due to their advantage, compared to the conventional solid-phase extraction techniques (SPE), including more selective recognition along with high mechanical and chemical stability, simple preparation, low cost and minimal loss in operating activities [5, 7-9].

The main objectives of the research presented in the thesis are:

- To investigate of past studies on water pollution monitoring techniques for PAHs, specifically pyrene, through a comprehensive literature review.
- To design and conduct batch equilibrium adsorption tests using MIPs and to studying the effects of varying parameters for pyrene (Initial pH, temperature and salinity).
- To use adsorption isotherm modeling and kinetic studies to understand the nature and extent of adsorption for pyrene.

1.3 Thesis Structure

This thesis is divided into four chapters including the Introduction and Literature Review (Chapter 1), providing a comprehensive revision on the aforementioned subjects (See 1.2). and Conclusion (Chapter 4). Chapter 1 identifies the PAHs relevant to monitoring of oil spill in water while providing the context of MIP preparation and analysis. From this review, pyrene has been selected as the most representative of fresh inputs of crude oil contamination in water, and followingly scrutinized.

Chapter 2 includes the materials and methods used for objective work. Considering the previous reports of PAHs analysis using MIPs, and the current challenges to this type of analysis, thin-film MIPs using toluene as the pseudo-template were prepared. The MIP composition has been optimized and validated in previous work, for achieving a maximum response, which is yet to be measured as the main objective of this work. The applicability, excellent sensitivity, and recovery concentrations achieved previously, indicates that MIP compositions proposed can be readily used for the current tests.

Chapter 3 describes the data analyses result and subsequent discussion, explaining the effects of three parameters of pH, temperature, and salinity on pyrene adsorption. Chapter 4 provides suggestions for future work and conclusion over the work that has been done.

1.4 Introduction to the Literature Review

1.4.1 An overview of the importance of marine pollution studies

The health of our marine environment is deteriorating; the condition of marine resources, the situation for coastal communities, and associated economies. Marine pollution is, one of the major resources for the decline, and is primarily generated through inputs of nutrients, sediments, persistent toxic and organic substances [10, 11]. Efforts have been made to estimate the economic implications of marine degradation because of concern for food security with respect to marine products. Research shows that the coastal capacities to accommodate contamination has been reached; hence, there is a need for action [12]. Monitoring of marine pollution has been conducted since the early 1970s at national and regional levels, and, research results over the last several decades have laid the scientific foundation for the establishment of a comprehensive Global Ocean Observing System (GOOS). GOOS is being built around 5 modules, addressing the major concerns of oceans

and climate, living marine resources, the health of the ocean, marine pollution, coastal zones, and weather forecasting [12].

The ecotoxicology and human health-related issues of PAHs are of paramount importance, as some have been implicated as causative agents for lung, breast, esophageal, pancreatic, gastric, colorectal, bladder, skin, prostate, and cervical cancers in animal models and humans [13]. Acute and sub-acute exposures to PAHs in laboratory animals have shown neurobehavioral deficits results; however, several epidemiological studies have been conducted in proof of the hypothesis that exposures to PAHs will lead to behavioral deficits [14-18]. Most of the published literature on PAHs effects on human health have primarily discussed their potential in causing a plethora of cancers-including skin, lung, breast, scrotum, bladder, and colon [19, 20]. In addition to cancer, their capacity to cause reproductive neurotoxicity has come to attention, recently [21-23].

Sustainable use of the ocean and coastal areas, along with maintaining a healthy ocean must be considered in managing the various sectoral interests and actions of human society. An integrated approach to be able to deal with these interdependences is necessary, as the existing educational, economic and institutional structures and theories have been insufficient [24].

Scientists have realized that certain chemical pollutants are persistent in the environment, accumulate in the air, water, soil, and sediments. These are called persistent organic pollutants (POPs) [25]. POPs can be input into the environment from a number of

different resources including municipal and industrial waste discharge, surface runoff, inadvertent spills, and aerial deposition [26]. Their toxicity and tendency to accumulate in food chains make them a matter of concern [27].

1.4.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a family of ubiquitous environmental contaminants consisting of more than 100 discrete chemical structures [28]. PAHs have a uniquely stable structure and therefore persist in the environment [29, 30]. The United States Environmental Protection Agency (U.S. EPA) has designated 16 PAH (Table 1-1) compounds as priority pollutants for environmental monitoring purposes, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene [30]. Chemically, PAHs are composed of two or more benzene rings in the linear, cluster or angular forms. Their structures and physicochemical constants are given in Table (1-1).

Table 1-1 PAHs structures and physicochemical constants [18].




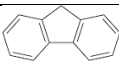
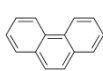
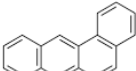
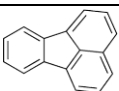

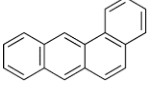
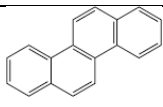
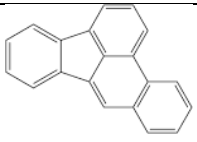
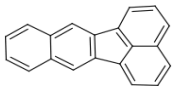
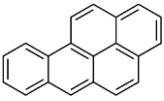
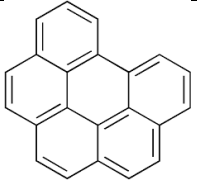
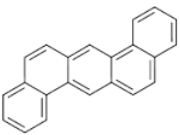
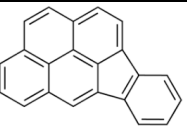
	Compound	Structure	MW (g/mol)	log K _{ow}	C _w ^{sat} (mg/L)
Low Molecular PAHs	Naphthalene		128.1	3.37	31.0
	Acenaphthylene		152.1	4.0	16.1
	Acenaphthene		154.2	3.92	3.80
	Fluorene		166.2	4.18	1.90
	Phenanthrene		178.2	4.57	1.10
	Anthracene		178.2	4.54	0.045
High Molecular PAHs	Fluoranthene		202.3	5.22	0.26
	Pyrene		202.3	5.18	0.132
	Benzo[a]anthracene		228.3	5.91	0.011

Table 1-2 PAHs structures and physicochemical constants [18].

High Molecular PAHs	Chrysene		228.3	5.65	0.002
	Benzo[b]fluoranthene		252.3	5.80	0.0015
	Benzo[k]fluoranthene		252.3	6.0	0.0008
	Benzo[a]pyrene		252.3	6.04	0.0038
	Benzo[g,h,i]perylene		276.3	6.5	0.0003
	Dibenz[a,h]anthracene		278.4	6.75	0.0006
	Indeno[1,2,3-cd]pyrene		276.3	7.66	0.062

PAH mobility in seawater is limited due to physicochemical properties, including low volatility, high lipophilicity, and low aqueous solubility [31]. Their fate in the marine environment is determined by two of these major physicochemical properties: solubility and vapor pressure [32]. It is worth mentioning that low exchange of water leads to increasing levels of PAHs. Temperature change reflects a significant effect on degradation, evaporation, and PAHs partitioning [40]. Temperature and salinity are the primary factors contributing to PAHs dissolution, adsorption, or transport in the marine ecosystem. PAH solubility in seawater increases with temperature and decreases with an increase in salinity, which is known as the “salting out” effect. Solubility also decreases with the increase in PAHs molecular weight and alkylation [33]. The structure of PAHs (relative positions of carbon atoms which constitutes this structure) determine their biological activity [13, 34].

PAHs are seldom released into the environment as individual compounds. PAHs typically coexist with a myriad of compounds including heavy metals, heterocyclic amines, and their own chlorinated, methylated, and alkylated analogs which are environmentally more persistent than the native PAHs [13]. High temperature increases the evaporation of PAHs fraction and decreases their sorption [35, 36]. Low temperature, in contrast, decreases solubility but increases deposition and adsorption, affecting their weathering process and leading to an increase in their lifetime [37].

Another important physicochemical property of PAHs is the octanol-water partition coefficient (K_{OW}), which is the ratio of the concentrations of a solute in immiscible octanol

and water phases at equilibrium condition [38]. This property is a good indicator of the solute's relative lipophilicity or hydrophobicity [39]. PAHs are considered large apolar or weakly mono-polar compounds, for the reason that they do not readily partition to the water phase from an organic phase. As the number of benzene rings increasing, the partitioning coefficients increase gradually, and subsequently lower levels of larger PAHs will be detected in the water phase [40].

The salinity of seawater also impacts solubility. The saturated concentration of a solute in a saline aqueous phase ($C_{w,salt}^{sat}$) can be calculated as:

$$C_{w,salt}^{sat} = C_w^{sat} \times 10^{-K'[\text{salt}]} \quad (1-1)$$

Similarly, the resultant partitioning coefficient ($K_{ow, salt}$) can be calculated as:

$$K_{ow, salt} = K_{ow} \times 10^{K'[\text{salt}]} \quad (1-2)$$

Where [salt] is the salinity of seawater (mol/L), $C_{w,sat}$ is the saturated solute concentration in pure water, and the K' is the Setschenow constant or salting constant (L/mol). Therefore, $\text{Log}(K_{ow, salt}) = \text{Log}(K_{ow}) + K'[\text{salt}]$.

Generally, PAHs are of low vapor pressure and aqueous solubilities, which decreases for each additional ring, or increased molecular weight; however, due to being highly soluble in water, low-molecular-weight PAHs, such as naphthalene, are dissolved in water

and could be transported to greater distances such as offshore, and polar regions through the movement of water masses [24, 42].

1.4.3 Sources of PAHs in the marine environment

Water is recovered from oil and gas wells on offshore platforms is termed "produced water" (PW), representing the largest volume of waste from production operations [41]. PW mostly contains organic materials of water-soluble low molecular acids and monocyclic aromatic hydrocarbons, including the concentrations of total PAHs, ranging from about 0.04 to 3 mg/L, as well as inorganic salts. The considerable concern about PW disposal is the result of the potential danger of chronic ecological damage [42]. PW and refinery effluents discharge PAHs into industrial bodies of water, while local discharge reuse distributed discharges [13]. They can also be released into the environment through volcanic eruptions, forest fires, coal and wood burning, incineration of municipal refuse, and expulsion of fumes from manufacturing industries such as coke, aluminum, graphite-electrodes, and petroleum [43]. A significant amount of PAHs carried to surface waters by sewers from urban run-off, petrogenic natural processes, roads, parking lots, roofs, and sidewalks. Mobile PAHs are deposited on surfaces, and rainfall acts as the transport mechanism that introduces toxic substances to the receptors.

Concentrations of total PAHs in raw municipal wastewaters, which is another source of PAHs in surface waters, have been found to vary significantly, depending on the amount of industrial effluents co-treated with domestic wastewaters. Treated wastewaters usually

contain PAHs at much lower concentrations due to their removal by particles adsorption, volatilization, or biodegradation [43]. The high-molecular-weight PAHs are sparingly soluble in water and tend to associate with particulate matter. Hence, high-molecular-weight PAHs in marine waters are indicative of leading local inputs [24]. Higher concentrations of PAHs in urban run-off were found during autumn and winter due to the high incidence of vehicles in the streets, along with the use of heating systems [44].

Crude oil contains high levels of PAHs, but the relative concentration of each compound is highly dependent on the type and origin of the oil. Refining and petrochemical plant waste oils have been estimated to contribute ~ 200,000 metric tons of petroleum products and crude oil to the world's oceans annually [45]. Although specific sources are known to be responsible for the presence of PAHs in surface waters, their occurrence cannot always be related to a particular source. This is because of the fact that the currently available analytical techniques are limited.

The presence of PAHs in drinking water may also be due to the surface or groundwater used as raw water sources, or to the use of coal tar-coated pipes in public water supply systems, as is permitted in certain countries. Regarding the chlorination of drinking water, it has been found that this disinfection technique may lead to the formation of oxygenated and chlorinated PAHs, which are compounds that are more toxic than the parent PAHs. Depending on the surface water treatment process, different levels for PAHs in surface waters would be resulted [46].

With respect to human body burdens of PAHs, lifestyle/domestic activities such as smoking and cooking contribute significantly to the accumulation of PAHs. The PAH signature from one source can be mistakenly be identified from another source, studies show that the majority of PAHs emissions result from industrial and human activities [47-51].

PAHs concentrations in bodies of water in different geographical regions are presented in Figure (1-1), which clearly shows a higher level in the waters of developing nations, which mainly due to industrial discharges and specific petroleum sources [13]. PAHs contamination is a risk from industries such as power and desalination plants, petrochemical and fertilizers industries, and shipping tankers introducing innumerable minor oil spills [49].

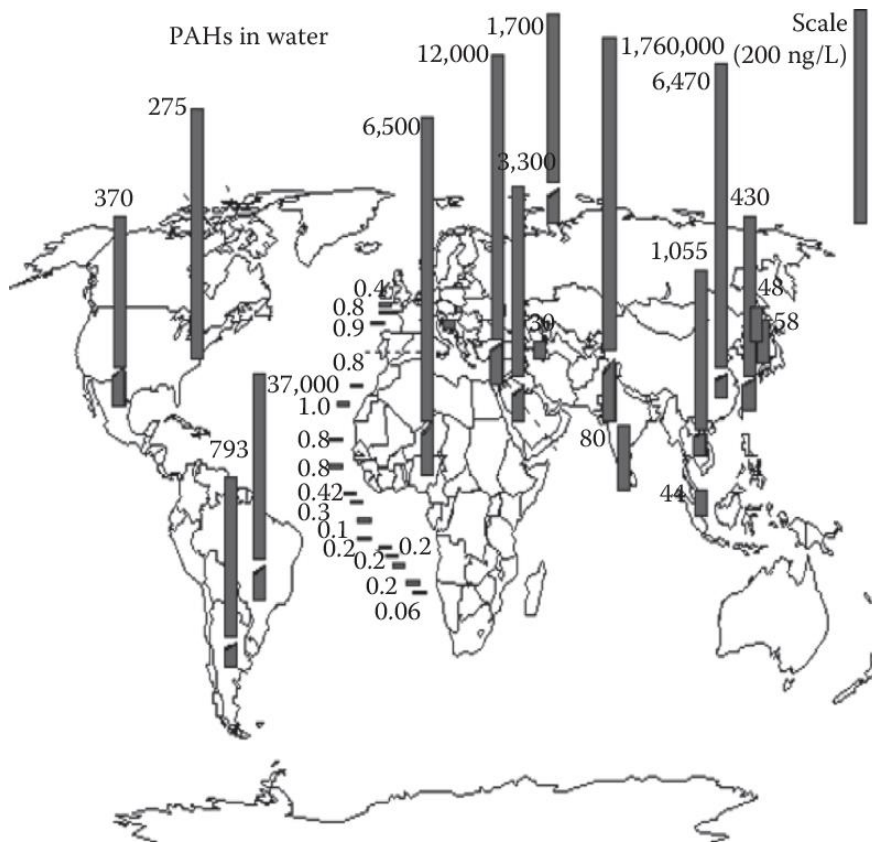


Figure 1-1 Global Environmental Distribution and Human Health Effects of Polycyclic Aromatic Hydrocarbons [24].

There have not been sufficient studies done on the effect of extreme temperature and salinity on the composition and concentrations of PAHs [52]. Most of the existing studies on composition and distribution of PAHs were based on single sampling and reported only the 16 EPA priority pollutant PAHs with the lowest link to current environmental conditions [52-54]. Recognizing the effects of temperature and composition on relative PAHs levels is crucial, and that is why a number of studies have been done observing the seasonal changes in PAHs composition and level changes in coastal sediments. From the

risk reduction perspective, human exposure to diffuse sources of PAHs such as automobile emissions, refuse burning, and residential wood burning are all of the equal importance [24]. Data achieved from the present literature review not only advance the knowledge on a critical environmental issue but also on the modeling studies of PAHs under varying environmental setups [49].

1.4.4 Why PAHs are problematic, with a focus on pyrene

Chronic exposure to even low concentrations to PAHs has been reported to have resulted in long-lasting damages such as cancers of the skin, lung, breast, scrotum, bladder, and colon, etc. PAHs concentrations/doses and the duration for which humans and wildlife are exposed to will have a huge impact on the health of the ecosystem and people living close to industrial sites or petroleum refineries [13]. The toxicity of these contaminants at low concentrations has attracted interest in environmental analysis and monitoring of trace pollutants in both drinking water and wastewater. However, the concentration of pyrene is lower than the detection limit of the usual spectroscopic methods and techniques used. Therefore, more applications of the instruments, namely: HPLC and liquid chromatography- fluorescence detection (LC-FLD), are to be discovered for pyrene detection [55].

In order to maintain a well-balanced ecosystem, identifying the possible contaminant sources of these contaminants is a must. That is why a continuous real-time monitoring system has been utilized in the study conducted by Hernandez-Ramirez for the provenance

of pollutants of the river. The more fascinating ability of the system is the ability to measure various water quality parameters, including temperature, pH, conductivity, turbidity, and dissolved oxygen, every 15 minutes. With these being said, the assessed results will be able to provide valuable information for both managing the river water quality and developing strict government policies for the sustainable conservation of specifically Atoyac River [56].

Containing harmful effects on ecosystem and organisms, PAHs carcinogenic potential is being assessed using a toxic equivalency factor, with the maximum being assigned to Benzo [a] Pyrene (BaP) and BaP equivalents. Risk quotient value is another factor potential of risk posing of certain PAHs. It must be kept in mind that different environmental matrices reveal different exposures; henceforth, considering the PAHs distribution pathways is of paramount importance [57]. Mahanty et al. used pyrene as the model compound for PAHs as its structure is found as a substrate of many PAH compounds [58, 59]. Kazunga et al. have studied the extracellular effects of pyrene metabolites from the partial transformation of one PAH substrate being able to decrease the metabolism of another PAHs with regards to their degradation [60]. In drinking water, the detected PAHs in the highest concentrations are fluoranthene, phenanthrene, pyrene, and anthracene [61].

Pyrene, as a major component of the PAH compounds, with four benzene rings and a flat aromatic system, has been of more consistent concentration in lakes and seawater. This makes more sense for pyrene to be the topic of most of the current studies. Makelane et al. developed and calibrated a dendritic electrochemical pyrene sensor, and applied it for

determination of pyrene in oil-polluted seawater following the United States Environmental Protection Agency's (EPA's) guidelines [55].

Stinga et al. investigated pyrene related experiments by using the measurements of UV-vis absorption, steady-state and time-resolved fluorescence, to further use the outcome for biomedical applications or wastewater treatment. In this specific work, they have devoted to investigating the aggregation state of the polymer using the fluorescence technique, which is both easy to operate and highly sensitive [62]. At the same time, this instrument is highly recommended for this PAH, due to its photophysical properties like high absorption coefficient, high fluorescence quantum yield, long excited-state fluorescence lifetime and remarkable monomer emission sensitive to the microenvironment changes.

1.4.5 PAHs detection and measurement in the marine environment and limitations

The interest of authorities in analyzing marine matrices began in the 19th century when the first oceanographic and fisheries laboratories were established for the analysis of seawater oxygen, pH, temperature, and composition (salts), as well as algae, bloom production measurements. This was because of growing populations and inadequate techniques for measuring treatments of domestic and industrial sewage [63].

PAH detection and measurement are typically done using gas chromatography-mass spectrometry (GC-MS) [64-66]. However, due to the complexity of matrices and low PAHs content, a high-efficiency clean-up pre-concentration procedure is required [67, 68].

Several pre-treatment processes for PAH extraction have been established, including liquid-liquid microextraction (LLME), solid-phase extraction (SPE), and solid-phase micro-extraction (SPME) [69-73].

SPE has been one of the most widely deployed methods for PAHs concentration in water sampling, because of its advantages. Its deficiencies include the use of traditional sorbents, which can have low adsorption capacities and selectivity. Nevertheless, the advantages, which are the great accuracy, safety, faster protocol, and considerable recoveries, outweigh its deficiencies [70, 71, 74-76].

Since the 1960s, chromatography has been an important tool in marine laboratories, and marine laboratories involved in the analysis of various types of contaminants and nutrients including PAHs. Column chromatography and liquid chromatography (LC) techniques have mainly used the clean-up phase, while gas chromatography (GC) has been extensively used in the final determination of these contaminants [63]. GC has been used in PAHs separation since the 1950s and 1960s with later and current work being conducted using capillary columns [77]. LC provides a cost-effective alternative for compliance testing or screening applications. Liquid chromatography also requires a huge amount of solvent and is time-consuming [63].

Rapid and cost-effective analytical methods, such as synchronous fluorescent spectroscopy (SFS) or fixed excitation/emission wavelength fluorescence (FF) both estimate PAHs metabolite concentrations in diluted bile samples without any previous chromatography separation and represent a suitable initial screening method [78, 79].

Ultrasonic extraction, supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), and microwave-assisted solvent extraction (MASE) are other sample preparation methods being deployed [63, 80-83].

Another spectroscopic method recently deployed to measure PAHs in situ is Surface-enhanced Raman scattering (SERS). Schmidt et al. applied SERS to detect six PAH species with a flow-through system at low concentrations of a few nanograms per liter. The high specificity and fingerprinting characteristics of Raman spectra is the reason behind the feasibility for substance identification in mixtures, which takes only 3-10 seconds. This is another reason making it suitable for in-situ measurements. The multiparametric in-situ spectroscopic measuring platform for coastal monitoring (MISPEC), being developed based on SERS, has been deployed for finding PAHs in harbour waters [84]. Mainly suited for stationary measurements, this sensor can still be improved in the sense of response time by addressing the sensors' surfaces. This would make SERS a capable tool for profiling while decreasing the detection limit to further reducing the power and weight consumption of the instruments [84].

A wide scope of in situ monitoring systems for measuring concentrations of various PAHs have been developed in recent decades; however, many of them are only at the laboratory or prototyping stages and require more time to be fully developed into commercially available products [85]. Harsh conditions in the marine environment also limit the application of these sensors. Research needs to be dedicated to deployment,

validation, and inter-calibration between sensors and other analytical measurement techniques [85].

Molecular imprinting as a versatile method for creating macromolecular pores matrices capable of displaying selective molecular recognition behaviour has recently surged [86]. Simple and low cost to prepare as well as being robust makes them ideal alternatives for molecular recognition [86]. This promising technology has yet to realize its full commercial potential, which will require the provision of a clear understanding of how physical factors affect the polymerization process and other fundamental parameters required in order to produce the artificial receptor reliability [87].

1.5 Molecularly Imprinted Polymers (MIPs)

The concept of molecular imprinting was initially proposed in the 1930s by Polyakov using silica particles. Since then, there have been significant advances in a number of aspects of imprinting of materials for selective recognition, including various templates ranging from metal ions, small molecules, peptides, proteins, and nucleic acids, to whole cells [88]. Wulff and Klotz in 1972, first demonstrated imprinting with organizing polymers and the idea of molecularly imprinted polymers (MIPs) [89, 90]. Molecular imprinting was inspired by the bio-interaction of “antigen-antibodies”, and is used as an artificial polymer receptor. MIPs are capable of molecular specific recognition through their functional nanocavities. They possess various superiorities in many real-world bioanalytical and biomedical approaches, such as low price, easy synthesis, good

repeatability, and considerable stability under harsh conditions when compared to biologically derived ligands such as antibodies [91-93]. Their main application involves chromatography, solid-phase extraction, biosensors, therapeutics, organic synthesis, and catalyses [94-99].

Numerous review studies about MIPs have been conducted, mostly as general introductions to the idea of imprinting and often describing chiral recognition. MIPs characterization, optimization, and evaluation are of priority in these studies[100-106]. Primarily, molecular imprinting refers to the polymerization of functional monomers in the presence of a template molecule. Imprinting between the template and functional monomer is dependent on the formation of a pre-polymerization complex around the template, imprinting the shape of the template within the polymer matrix upon polymerization. After template removal, the resulting cavities of MIPs are able to selectively rebind the template or related analogues, in this work, the targets are PAHs [107].

SPE is one of the most useful sample pretreatment/enrichment methods that MIPs have incorporated, thus it is a very active subfield within MIP research [108-110]. The potential of MIP-based analytical techniques in bio- and pharmaceutical analysis was reviewed by Owens, et. al [101]. These techniques are primarily utilized in areas such as SPE sorbent, the stationary phase for HPLC and cation-exchange columns, and as the recognition media in affinity analyses [97]. The demand for a pure template in a large quantity is regarded as the primary obstacle for MIP utilization, except in clinical approaches [97].

Despite being a synthetic host system capable of recognizing and binding the target molecule, one of MIPs challenges is their wide scope of affinity and selectivity; consequently, considerable attention has been allocated to molding desired recognition sites [111, 112]. Some of the work being conducted in this category includes the use of a metal ion as self-assembly pivot, auxiliary monomers, and optimization of polymerization temperature, as well as the strategy of molecular crowding [113-116].

1.5.1 MIP Preparation

MIPs are prepared by a template-directed polymerization method., which involves a template-monomer pre-assembly stage using a functional monomer exploiting certain driving force(s), such as covalent bonding, hydrogen bonding, van der Waals forces, ionic interactions, metal coordination interactions, or hydrophobic effects. Subsequent copolymerization of the monomer-template complex with a crosslinking monomer is applied using a proper porogenic solvent. Despite the high specificity and affinity, covalent imprinting still suffers from template removal, slow binding kinetics, and limited template types [117, 118]. Noncovalent binding relies on weaker intermolecular interactions like hydrogen bonding, van der Waals forces, electrostatics, and hydrophobic forces. After the template removal from the resulting crosslinked polymer networks, MIPs with binding sites complementary to the template in shape, size, and distribution of functional groups will be obtained, with different selective template recognition capabilities [119].

Despite the significant progress made in MIPs development approaches, challenges still exist, such as the development of MIPs capable of selective recognition of small organic molecules in complex aqueous solutions [120]. Given that many real-world bioanalytical and biomedical applications are particularly dependent on aqueous systems, some useful strategies have been proposed for preparing water-compatible MIPs. These include improving their surface hydrophilicity, which reduces their hydrophobicity-induced nonspecific binding in aqueous media. Another approach includes the introduction of hydrophilic functional groups onto MIP surfaces by using hydrophilic functional monomers, crosslinkers or comonomers, or via surface chemical modification [120]. However, there are other challenges regarding MIPs relatively low binding performance, or low imprinting factor, which is defined as the binding affinity ratio of imprinted over nonimprinted polymers [121].

1.6 MIPs advantages in PAHs detection

According to the comprehensive literature review conducted by Vasapollo et al., MIPs have advantages in contaminants adsorption process due to their high mechanical strength, and resistance to high pressure and temperature, and compared to biological recognition material like antibodies. They are also inert with different chemicals (organic solvents, acids, bases, and metal ions). Their low production costs and long lifetimes at room temperature are additional benefits [97].

Potential applications of MIPs in various fields related to molecular recognition cannot be understated; these include separation and purification, biomimetic catalysis, chemo-sensing, and various biomedical applications, such as pseudo-immunoassays, drug delivery, and biomimetic nanomedicine [119]. MIPs have been used for separation of benzo[a]pyrene (BAP) from water and coffee samples, showing high-efficiency results with 4-VP-co-DVB polymer. The aforementioned study was aimed for BAP enrichment from tap water, lake water, and instant coffee samples, where no sample pre-treatment is required apart from filtration [122].

Reddithota studied the feasibility of PAHs removal from water by MIPs using groundwater spiked with PAHs while taking advantage of MIPs' reusability without any deterioration in performance, reported in at least ten repeated cycles [123]. Matsui et al have studied the use of an atrazine-MIP, prepared by suspension polymerization, for selective extraction of the related triazine herbicide simazine from water [123].

Adsorption, one of the most widely used technologies, especially in the environmental protection field, use the experimental data to model and predict the mechanism. Several models can be used to correlate the obtained data, namely: Langmuir, Freundlich, and Dubinin-Radushkevich, BET, and Langmuir-Freundlich (Sips). The next step is the error analysis to be undertaken upon the correlation coefficient (r-squared) and standard errors (S.E.). The model having the highest relative r, squared value, and smaller S.E. will be determined as the best fit, for the equilibrium predictions [124].

Most binding models applied to MIPs are homogeneous, whereas, MIPs are heterogeneous materials containing binding sites with a wide array of binding affinities and selectivity. MIPs binding behavior can be accurately modeled and demonstrated by the heterogeneous hybrid Langmuir–Freundlich (LF) isotherm by using five representative MIPs, both homogeneous and heterogeneous [125]. Such comparisons have required the use of several different binding models and analyses, including the Langmuir and the Freundlich model, alongside with numerical approximation techniques. In contrast, the LF model enabled direct comparisons of MIPs binding characteristics under different conditions having very different underlying distributions [125]. LF fitting coefficients yield a measure of the total number of binding sites, mean binding affinity, and heterogeneity using binding parameters calculations, with respect to association constant. Moreover, a unimodal heterogeneous distribution is an accurate approximation of the distribution found in homogeneous and heterogeneous MIPs [125].

Over the years, a wide variety of kinetic models, such as pseudo-first-order (PFO), pseudo-second-order (PSO), Langmuir, Freundlich, Elovich, Flory-Huggins, and Dubinin-Radushkevich, Temkin, and Hill have been formulated as two-parameter models for adsorption isotherms. Likewise, several reviews have been conducted over three-parameter adsorption models (Redlich-Peterson, Sips, Toth, Koble-Corrigan, Khan, Radke-Pirauznitz, Brunauer-Emmett-Teller, Frenkel-Halsey-Hill) to study multi-layer physisorption. [126]. In this case study, however, two-parameter models were analyzed. MIPs, artificial antibodies, have long been distinctive due to their robustness, storage

endurance, short development time, and high selectivity for the target molecule. There are conditions that can affect their extraction efficiency, including the PAHs concentration, media condition such as pH, temperature, and salinity. The equilibrium time will be evaluated based on these conditions. This method can be applied to determining probable PAHs in industrial zones, namely: environmental monitoring, food, and beverage analysis and industrial process surveillance [127-129].

Chapter 2

Materials and Methods

2.1 Introduction

Understanding the operative processes for the fate and transport of PAHs from numerous sources has been a national issue, including municipal waste disposal, industrial discharges, accidental spills, leaky underground storage tanks to mitigate PAHs exposure risks to humans and the environment, as well as assessing efficient, cost-effective rectifying strategies [130]. Sorption has always been the primary chemical control process over these contaminants fate and transport. The main controlling sorption factors include the hydrophobicity of the solute, mineral composition, and the surface area of the sorbent, and its secondary factors consist of sample temperature, salinity, and pH [131-134].

The annual mean temperature of saturated groundwater regimes in the northern United States and Canada is $\sim 10^{\circ}\text{C}$; however, most laboratory sorption experiments are performed at room temperature $\sim 25^{\circ}\text{C}$, which is higher than groundwater temperatures [135]. The equilibrium and kinetic parameters determined at this condition may not be applicable to real systems at lower temperatures. This is why adsorption kinetic experiments have been done as a function of temperature: to probe the feasibility of MIPs for the purpose of adsorption [136, 137].

pH sensitivity has not been thoroughly investigated for MIPs based on 4-VP. However, a reasonable explanation might well be that the highly cross-linked structure of MIPs restricts the pH response. It is worth mentioning that in order to obtain rigid recognition sites, a large amount of cross-linker is required in the synthesis of MIPs, commonly 1: 4: 20 for the molar ratio of template to the functional monomer to cross-linker. Mobility of the ions and pyrene in the sample, their density charge, presence of ligands in the solution, as well as protonation that leads to less available retention are all the factors that should be considered in this case [138, 139].

There has not been sufficient work performed concerning the effects of temperature, pH, and salinity on the kinetics of sorption of PAHs, especially pyrene, to model MIPs. This study seeks to quantify the effect of the aforementioned parameter on the magnitude and rate of sorption of pyrene, specifically. Batch sorption experiments were performed as the technique for determination of equilibrium distribution coefficients and sorption rate constants at 4, 10 and 35 °C. The resulting constants/coefficients may be used as process-related parameters in contaminant transport models to help predict the MIPs accessibility over the PAHs measurement in groundwater [130].

2.2 Materials

Pyren standard (99%) was purchased from Sigma-Aldrich (St. Louis, Mo, USA) and used without further purification. All organic solvents (toluene, acetonitrile, methanol) were of HPLC grade or higher and purchased from Fisher Scientific. All compounds used

in the preparation of the thin-film MIPs, including the 2,2-dimethoxy-2-phenylacetophenone (DMPA) initiator, ethylene glycol dimethacrylate (EGDMA) cross-linker, 4-vinyl pyridine (4-VP) monomer were purchased from Sigma-Aldrich and were used without further purification. A stock solution of 110 ppm pyrene in acetonitrile: water (v:v, 80%:20%) was prepared and working solutions were prepared by appropriate dilution of the stock solution with water. The prepared MIPs were utilized for the following experiments, considering their net weight as the adsorbate.

2.3 Preparation of MIP films

Cut glass microscope slides were prepared in sizes of 18 × 30 mm by washing in acidified water with methanol and drying with a flow of nitrogen. The pre-polymerization solution was prepared by pipetting 4.25 μL toluene, as the pseudo- template, 17 μL 4-VP, 151 μL EGDMA, 200 μL 1-octanol, and 3.2 mg DMPA into a 2-mL vial.

An 8.0-μL aliquot of the pre-polymerization solution was dispensed on the frosted glass surface and covered with a glass microscope cover-slide of 18 × 18 mm size, to minimize oxygen interference in the polymerization process. Then, the slides were placed directly under a handheld UV lamp ($\lambda = 254$ nm, 6 watts) at ambient temperature (~20 °C) for 40 minutes. Subsequently, the imprinted polymers were soaked in methanol for 30 minutes to remove the pseudo-template.

2.4 Batch kinetic experiments

The stock solution of pyrene was diluted by adding specific amounts of water to yield working solutions of 10.0, 25.0, 50.0, and 100.0 ng/mL. Based on a calibration curve from UPLC analysis of pyrene, in order to study the aforementioned parameters, a concentration of 25.0 ng/mL was chosen.

The impact of adsorption parameters including pH, temperature, and salinity, were studied. Each parameter was studied while keeping other factors constant. For the adsorption isotherm experiment, the MIPs were immersed in 20.0-mL of aqueous pyrene solution in a disposable scintillation vial under continuous stirring at 1400 rpm using Teflon-coated stir bars at room temperature (~20 °C) for specified time intervals. The MIPs were then removed from the vials at different time intervals, rinsed with a small volume of distilled water and dried at room temperature. The adsorbed pyrene was then extracted into 4.0-mL of methanol using a vortex for 30 minutes at 1400 rpm. The solution was filtered through a 0.22 μm filter into a 2.0mL vial for analysis. The MIPs were soaked in methanol for 1 h for regeneration and subsequent reuse.

2.5 pH experiments

The solution pH effect on pyrene adsorption at pH 3.5, 7.0, and 10.5 was examined. An aqueous pyrene solution of 25.0 ppb for adsorbate mass of 2.5-3 mg over 300 minutes of stirring, at a rate of 1400 rpm. Each of the adsorption tests was replicated five times. The

pH of the samples was adjusted using a 1M HCl solution and 1M sodium hydroxide, both prepared in distilled water.

2.6 Large scale system experiment

The same adsorption/desorption experiments were done, but in larger volume (aquarium with a volume of 29.4 liters), using tap water with pyrene from a stock solution (110 ppm), with 3 replicates. A holder for 33 MIPs was used to keep the MIPs in the same position for time intervals of 15, 30, 60, 120, 180, 240, 300, and 360 minutes, and then runs of 12, 24, 36, and 48 hours were conducted to make sure that equilibrium had been reached. During the experiment, the concentration of the tap water was checked to keep the tank concentration at 10.0 ppb. Additional pyrene was spiked during the experiment to make sure the concentration in solution remained constant. In each run, the three MIPs were removed, and desorption and analyses were conducted on each.

2.6.1 PAH Analysis

The adsorbed concentrations of pyrene on MIPs were measured by UPLC (Waters Acquity) equipped with a PDA detector and a 50 mm × 2.1 mm BEH C₁₈ column, using acetonitrile with 0.1% formic acid as the mobile phase at a flow rate of 0.400 mL/min. The PDA was set to monitor a single wavelength for pyrene at 272 nm. Calibration of the UPLC was performed by injecting standard solutions at five different concentrations. Identification of analytes was based on the retention time for pyrene. Concentrations of

PAHs are reported as ng pyrene per mg on a dry polymer film mass. For quality assurance/quality control studies, analyses included triplicate injection of each sample.

2.6.2 Data Analysis

The removal efficiency (RE) of pyrene, and the capacity can be calculated using the following equation:

$$RE = \frac{m_{\text{pyrene adsorbed on MIP}}}{m_{\text{initial pyrene in solution}}} \times 100\% \quad (2-1)$$

$$Q_{(t)} = \frac{m_{\text{pyrene adsorbed on MIP}}}{m_{\text{MIP}}} \quad (2-2)$$

Additionally, the Langmuir, Freundlich, and Langmuir- Freundlich isotherms were used in adsorption isotherm analyses, demonstrated by the following equations:

$$Q_e = K_F \times C_e^{1/n} \quad (2-3)$$

$$Q_e = \frac{K_L \times Q_{max} \times C_e}{(1 + Q_{max} \times C_e)} \quad (2-4)$$

$$Q_e = \frac{Q_L \times (K_L \times C_e)^{1/n}}{1 + (K_L \times C_e)^{1/n}} \quad (2-5)$$

In the above equation, Q_e (ng/mg) is the equilibrium capacity of the correlated MIP, Q_{max} (ng/mg) is the maximum MIP capacity, K_L (mL/ng), K_F ($\frac{\text{ng}^{(1-\frac{1}{n})} \cdot \text{mL}^{\frac{1}{n}}}{\text{mg}}$) is the Langmuir

and Freundlich constants that express surface adsorption capacity, and n is the constant showing the intensity of surface adsorption.

The Langmuir model had originally been developed to describe gas–solid-phase adsorption onto activated carbon, assuming a monolayer coverage of the solute by the sorbent, occurring at a finite (fixed) number of definite localized sites. This empirical model considers that the binding sites have the same affinity for adsorption and no interaction between adsorbed molecules occurs. It refers to homogeneous adsorption, where each molecule possesses constant enthalpies and sorption activation energy (all sites possess an equal affinity for the adsorbate) [140-143].

The Freundlich isotherm model, the earliest known relationship between non-ideal and reversible adsorption processes, accounts for heterogeneous adsorbent surfaces and non-uniform binding sites distribution. This model is not restricted to the monolayer formation, demonstrating the ratio of the adsorbate onto a given mass of adsorbent to the solute, which is not a constant at different solution concentrations. Therefore, the adsorbed amount would be the summation of adsorption on all sites (each site having bond energy), with the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of the adsorption process [144-147].

To study adsorption kinetics, the PFO model was used. The PFO kinetic model equation is as follows [148] :

$$Q(t) = Q_e \times e^{-k_1 t} \quad (2-6)$$

The variable $Q(t)$ (ng/mg) is the adsorbent concentration at any time t (min), and k_1 (min^{-1}) is the constant rate of the PFO equation.

The PSO kinetic model equation, given below shows Q_e as the adsorbent concentration at equilibrium, and K_2 (mg/ng.min) as the PSO equation constant rate [148]:

$$Q(t) = \frac{Q_e^2 \times K_2 \times t}{Q_e \times K_2 \times t + 1} \quad (2-7)$$

Comparing the results, we can conclude the type of adsorption: chemisorption or physisorption. Chemisorption, or chemical adsorption, involves valence forces, the same as those operating in the formation of chemical compounds; whereas physisorption takes in intermolecular or van der Waals forces. Each of the phenomenons is characterized by either chemical or physical specificity. The obvious distinguishable feature between them is the reversible capability, which does not exist for chemisorption.

Chapter 3

Results and Discussion

3.1 The Effect of pH on pyrene adsorption by MIPs

As described in the Materials and Methods, a simple concept was used to generate results demonstrating the competitive pH effect. Further data from pyrene adsorption is summarized in Figure (3-1) in the form Recovery% vs time, and Figure (3-2) as a function capacity vs time.

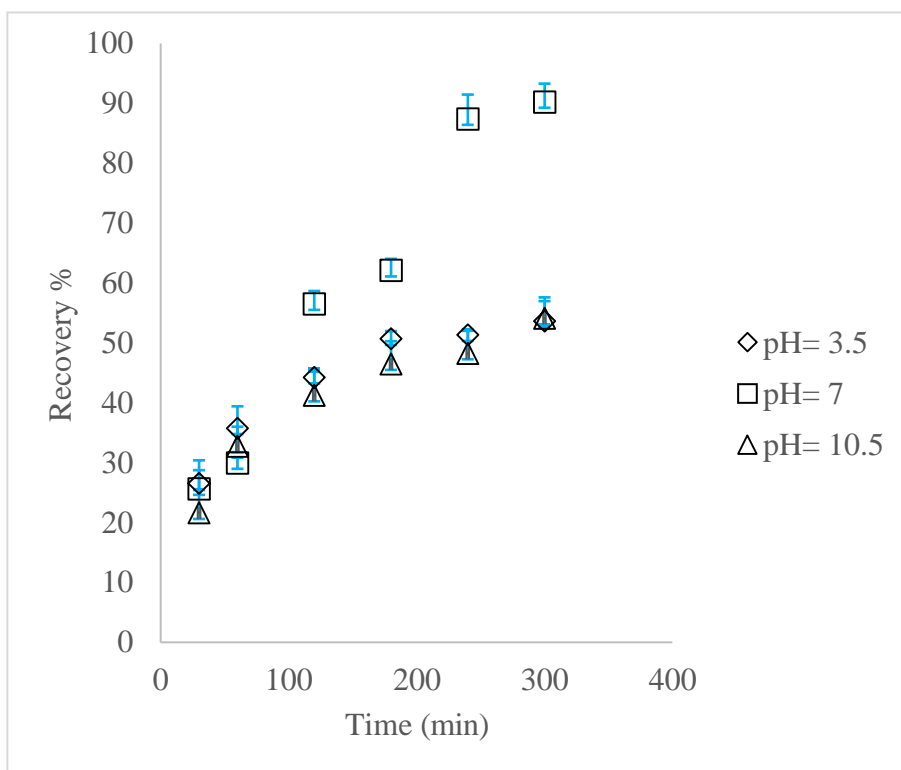


Figure 3-1 MIPs Recovery% as a function of pH at different time intervals.

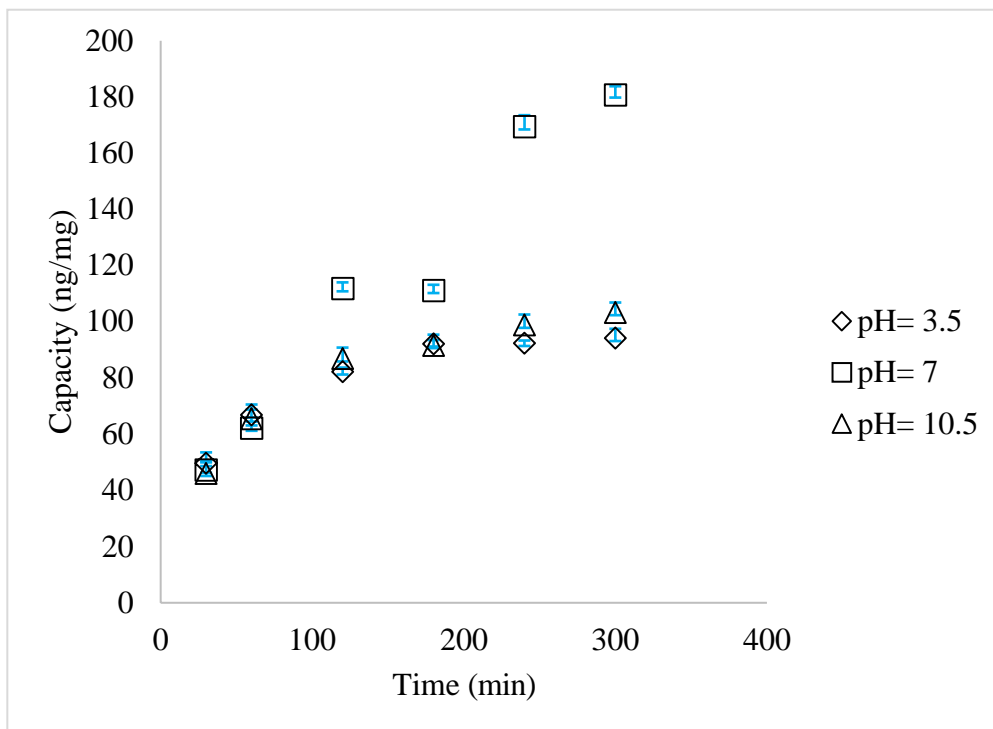


Figure 3-2 MIPs capacity as a function of pH at different time intervals.

According to the figures, MIPs would operate more efficiently in neutral water samples as compared with acidic or basic water. The maximum capacity reached was 180.76 ng/mg at pH = 7.0. Comparing the results obtained from each graph, the rate of adsorption is also faster at pH=7.0; whereas, in the other two conditions, the rate is almost the same. It can be concluded that despite the slight differences in adsorption behavior observing from percent recovery and capacity graphs, acidic and basic conditions do not lead to an improvement, and MIPs operate better in the neutral condition. The reason behind this incident might be due to the deprotonation of the surface.

This phenomenon of not observing an actual change in the rate can be explained by the net charge of pyrene and MIPs at different pH values. In the family of PAHs, pyrene itself is known as an electron donor; however, due to the lack of functional groups, no remarkable discussion can be conducted on its ionic interactions [149]. In acidic or basic condition, more ions may be in the solution that might occupy the sorbent surface, leading to less adsorption capacity or recovery.

3.2 The effect of sample salinity on pyrene adsorption by MIPs

In this experiment, solutions with salinities of 0%, 1%, 2%, 3.5%, and 7%, using NaCl were with pyrene at 25.0 ng/mL. Figures (3-3) and (3-4) outline the results adsorption as a function of time and salinity.

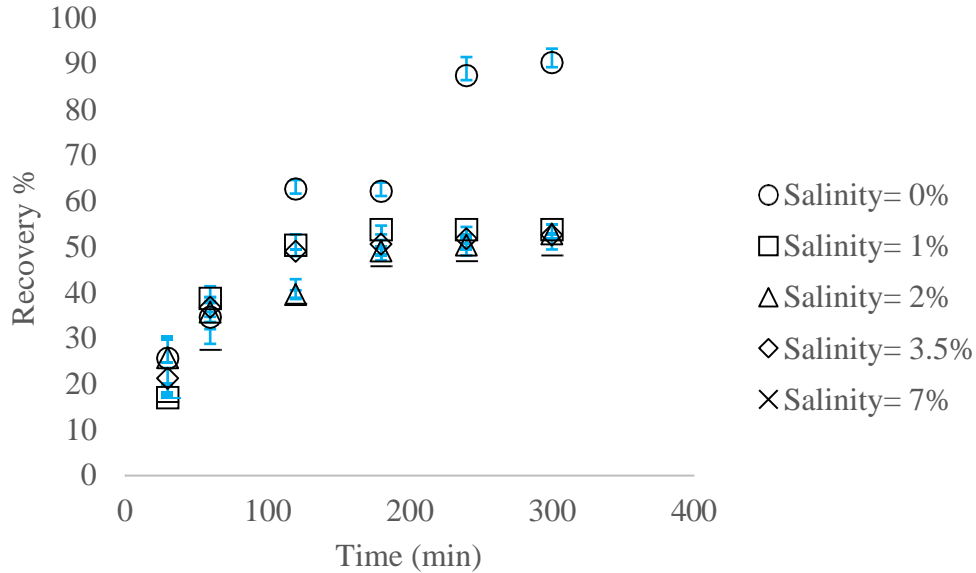


Figure 3-3 MIPs Recovery% as a function of salinity at different time intervals.

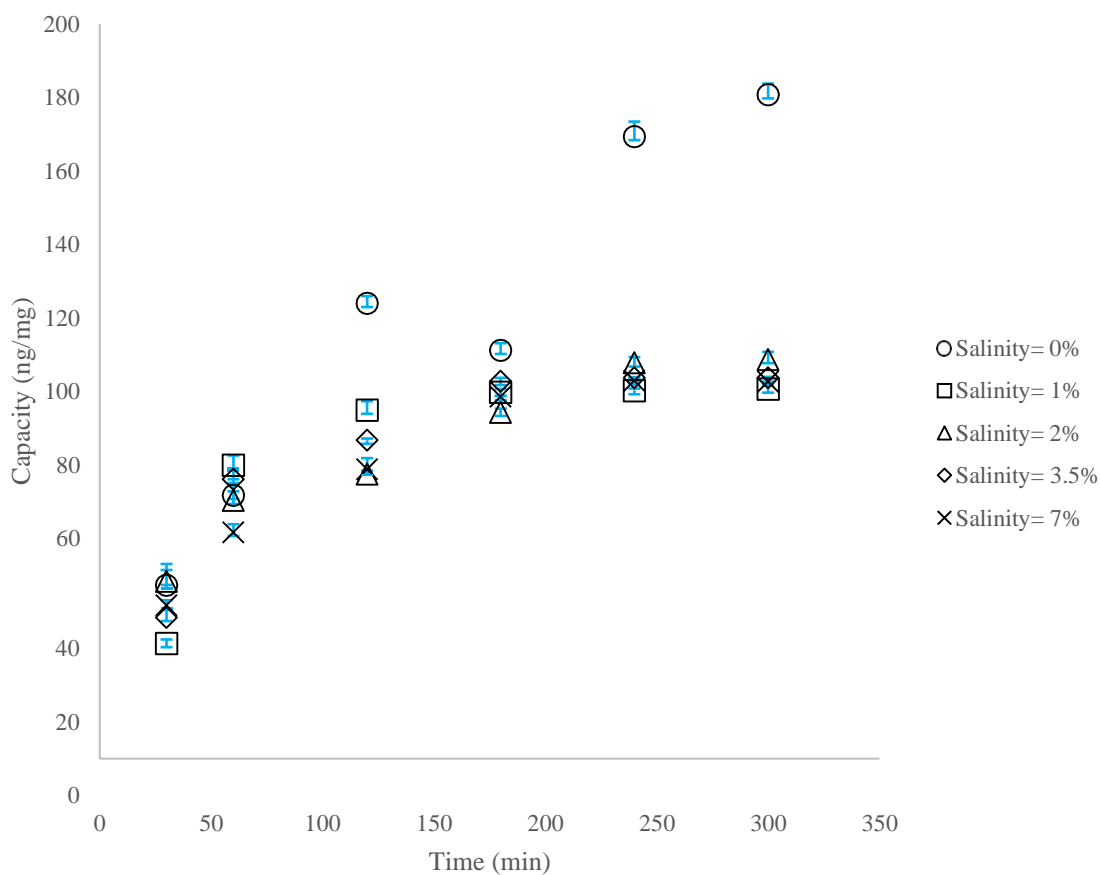


Figure 3-4 MIPs capacity as a function of salinity at different time intervals.

The maximum adsorption capacity of 180.76 ng/mg at a 0.0% salinity. Interactions between major ions present in saline water and the polymeric material, in the form of rebinding of the polymer to pyrene particles within the solution, are discussed in the following paragraphs.

The effect of salt can be also attributed to the dimerization of reactive components in the sample, being related to a number of intermolecular forces explaining this aggregation, including van der Waals forces, ionic-dipole forces, and dipole-dipole forces. These occur

between the molecules in the solution, being reported that they increase upon the addition of salt to the solution. It has also been reported that this can be attributed to the aggregation of molecules induced by the action of salt ions, as these ions force the molecules to aggregate, leading to an increase to the extent of the sorption on the sorbent surface. However, the adsorption capacity might be sensitive or insensitive to the ionic strength of the solution and pH intensity of the solution [139]. Pyrene participation in water sample also needs to be taken into account, especially when equilibrium is reached.

It is also observed that an increase in the salt concentration can increase the percent of adsorption recovery by MIPs; however, the increase is less than 10% at the equilibrium time. The ions from NaCl were placed between the surface of MIPs and the pyrene molecules, producing a screening effect of the surface charge, as well as making the adsorbate-adsorbent interactions favored and enhancing pyrene adsorption. The proposed mechanisms of the enhanced adsorption involve interactions between water ion and adsorbate ion in this system. Sodium chloride dissociates into Na and Cl in aqueous solution. There is a strong electrostatic field around the anions and cations being dissociated from sodium chloride, which results in the formation of an oriented array of water molecules around these ions.

At the same time, the existence of these ions enhances the combining powers between water molecules and reinforces the hydrophobicity of the adsorbate in the opposite direction being beneficial for adsorption. In addition, the water solubility of the hydrophobic compound is reduced by an increase in ionic strength, being known as “salting

out” effect, leading to an enhancement of the adsorbate, pyrene, onto the surface of MIPs. This study is mainly important for the application of the adsorption process to saline industry wastewater treatment systems [150, 151].

3.3 The effect of temperature on pyrene equilibrium adsorption studies

Two commonly used isotherm models, including Langmuir-Freundlich (Sips), were used to fit adsorption data isotherms of pyrene concentrations ranging from 10.0 to 100.0 ppb, on MIPs, (Fig. 3-5). Table 3-1 outlines the results of the model fits and Figure 4-5 Compares the models to experimental data.

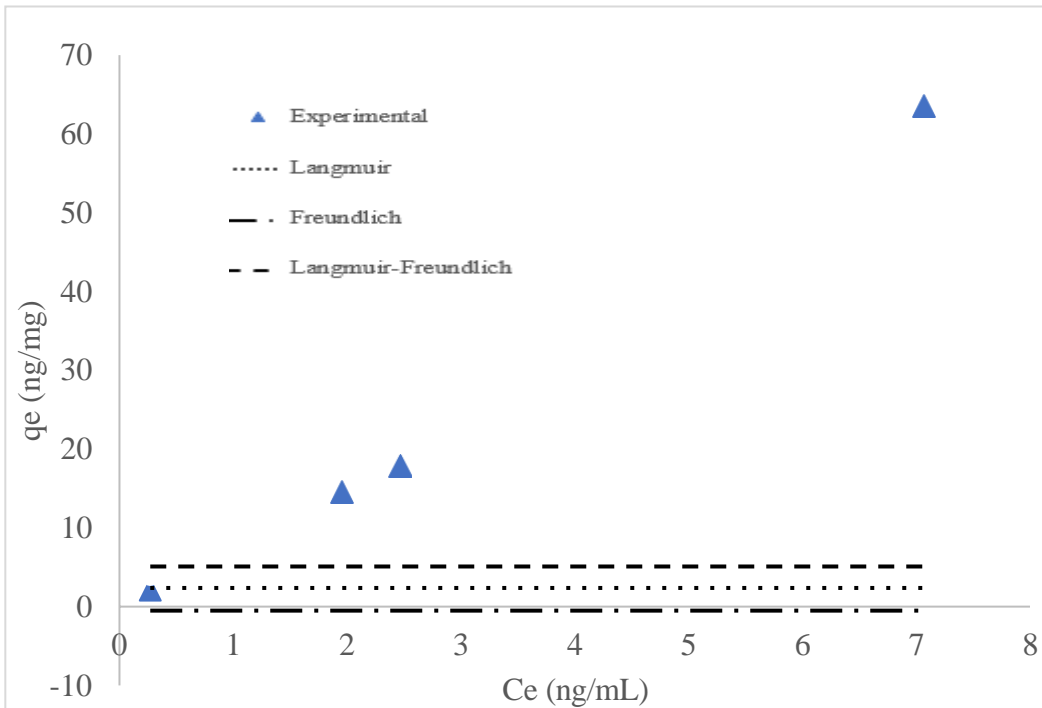


Figure 3-5 Adsorption of pyrene on MIP, experimental data, simulated by Langmuir, Freundlich, and Sips isotherms.

Table 3-1 Isotherm model parameters for pyrene adsorption from water.

Langmuir			Freundlich		
Q_{\max} (ng/mg)	K_L (mL/ng)	R^2	K_F (ng/mg)	1/n	R^2
1319.13	66010.0	0.9888	6.358	1.176	0.9992
Langmuir-Freundlich					
Q_L (ng/mg)	K_L (mL/ng)	1/n	R^2		
200.053	240400	0.8635	0.9612		

According to the values of R^2 in the Table (3-1), the Freundlich model is more suitable for describing the adsorption isotherm of pyrene on MIPs. This represents that the binding sites have different affinities for adsorption of a multimolecular layer. The value of “1/n” indicates favourability of adsorption (>1 indicates favorable adsorption), K_F , as the indicator of adsorption capacity shows the maximum MIP capacity. However, due to not reaching maximum capacity or equilibrium, K_F does not make logical sense with what it represents; therefore, future work should be mostly dedicated to this part of the study to reach equilibrium for data validation. Another worth mentioning fact about this isotherm is that it is derived strictly for trace adsorption of an ion participating in an exchange reaction,

uniquely corresponding to a distribution of relative adsorption site affinities containing empirical parameters for characterizing the size distribution function mathematically. Sips isotherm model, is based on the assumption that the MIPs surface is heterogeneous and that each class of the sites adsorbs individually accordingly to the Langmuir isotherm [152].

The results shown in Figures (3-6) and (3-7) illustrate the adsorbed concentration of pyrene in different time intervals and varying sample temperatures, by means of capacity and recovery% variables.

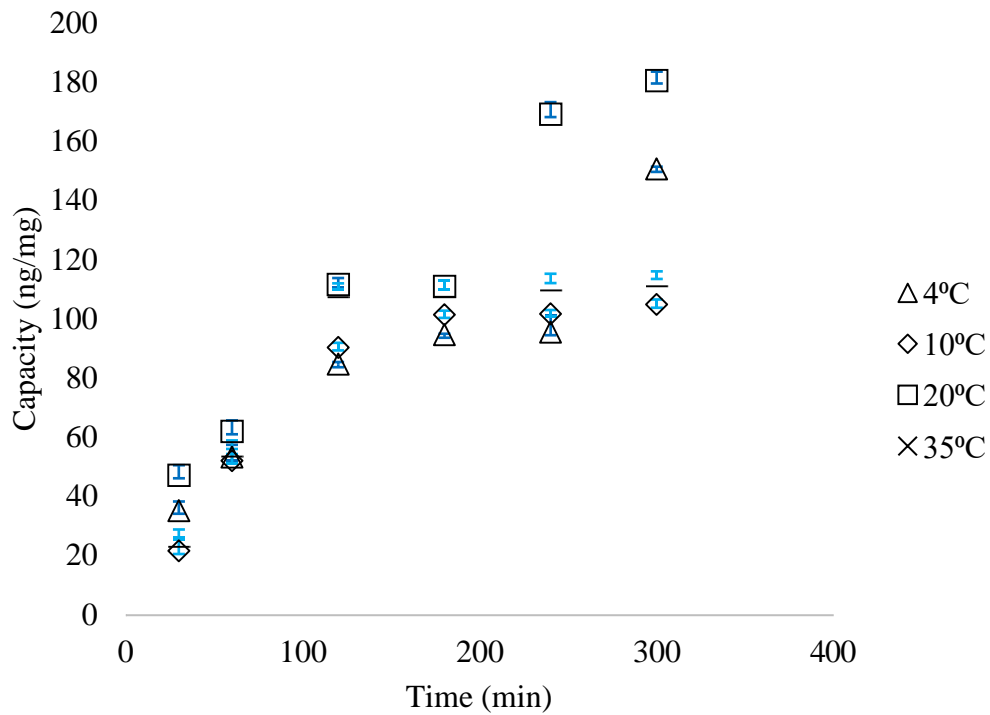


Figure 3-6 MIPs capacity as a function of temperature for initial concentration of pyrene.

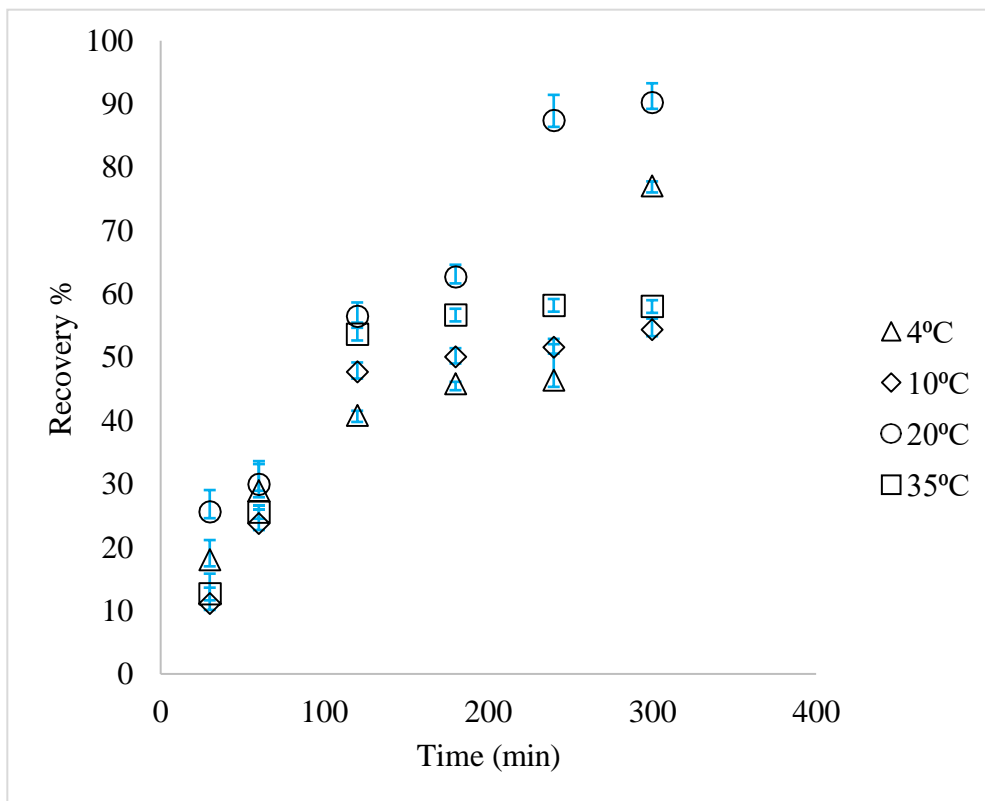


Figure 3-7 MIPs Recovery% as a function of temperature for an initial concentration of pyrene.

The temperature does not have a significant impact on the adsorption capacity, which could be due to the constant driving force leading to no change in pyrene molecules onto MIPs. More studies can be conducted over a broader range of temperatures, to observe the maximum capacity of MIPs through reaching the equilibrium condition as well as the effect of temperature, if there is any. Moreover, the enthalpy and entropy of the reaction can be calculated, consequently. Conducting more experiments in this area, to decide on the ΔG also helps figure out the feasibility of the process and the spontaneous nature of the

adsorption. The “solvent effect” is the other noteworthy factor to be mentioned, which occurs because of pyrene-water interactions leading to a probable change of energies in the adsorption of MIP components by water [151].

3.4 Pyrene adsorption kinetic studies

Adsorption kinetic studies at four different concentrations (10.0 ppb, 25.0 ppb, 50.0 ppb, and 100.0 ppb) were carried out and two conventional kinetic models (PFO and PSO) compared to experimental data. Table (3-2) and Figure (3-8) compares the data to the models.

Table 3-2 Calculated adsorption kinetic model parameters.

Initial Concentration (ng.mL ⁻¹)	Pseudo-first-order kinetic		
	q _e (ng/mL)	K ₁ (min ⁻¹)	R ²
10	34.841	0.0033	0.9946
25	64.357	0.0042	0.9944
50	138.66	0.0045	0.9928
100	256.82	0.0042	0.9989

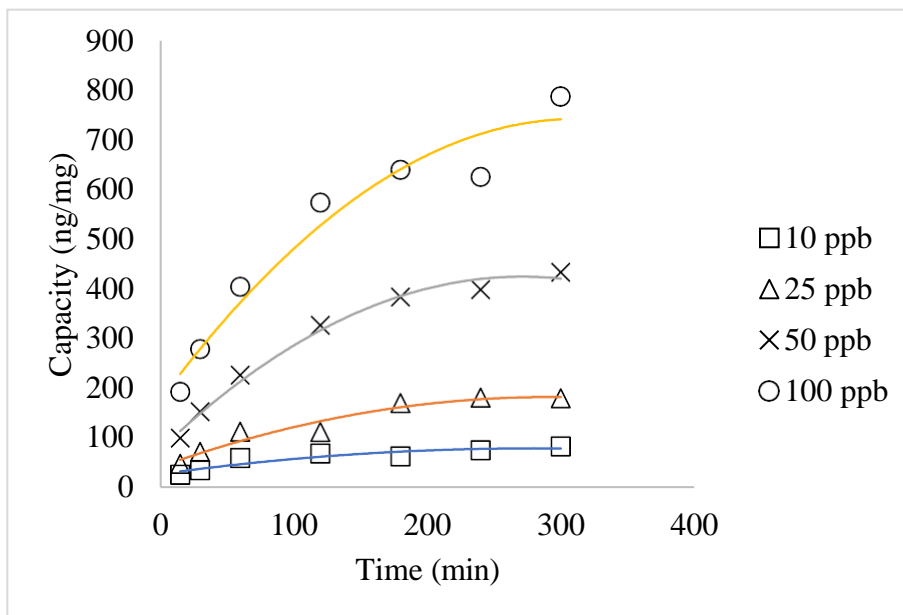


Figure 3-8 The application of PFO kinetic adsorption model for experimental data.

The sorption kinetics of pyrene on MIPs fits a pseudo-first-order model, with R^2 values close to unity for all concentrations. This model can be used to describe and validate the experimental data set. Competitive adsorption experiments demonstrate that the synthesized MIPs display excellent selectivity toward targeted molecule, which was pyrene in this case [153].

3.5 Results from a large-scale system approach

Studies in an aquarium (volume of 29.4 L) using tap water, on 10.0 ng/mL concentration at a stirring rate of 2000 rpm were conducted. According to the data, the equilibrium capacity of MIPs has not been reached, indicating probable new binding sites being appeared resulting in more adsorption. Hence, more experiments are required to reach

equilibrium resulting in the maximum capacity, for the adsorption studies to be based on true assumptions.

The results are shown in the graphs below:

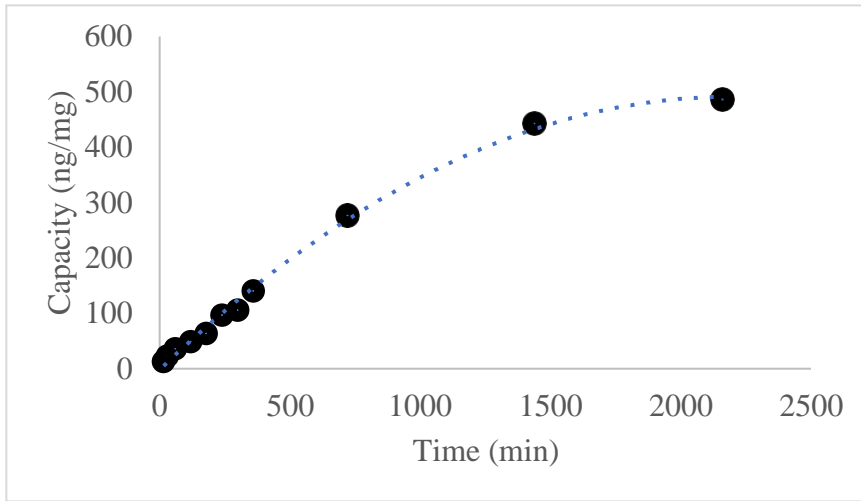


Figure 3-9 The application of PFO kinetic adsorption model for experimental data.

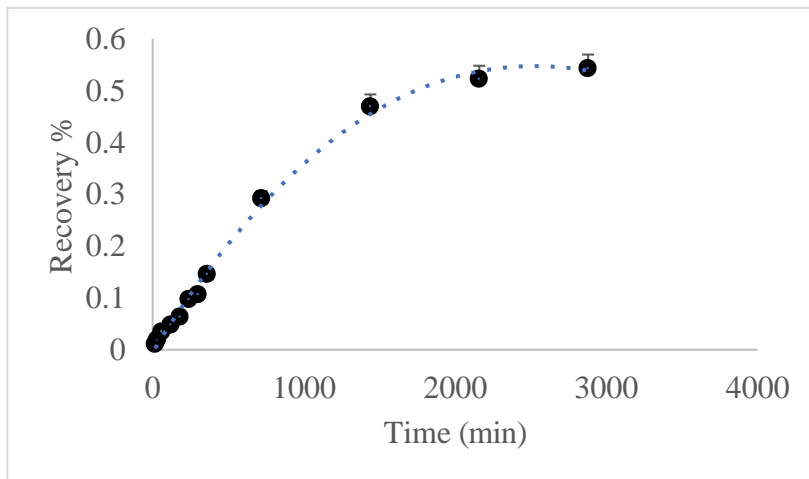


Figure 3-10 Recovery% change with time on large scale experiment.

Table 3-3 Calculated PFO model parameters for a large scale experiment.

		Q _e (ng/mg)	K ₁ (min ⁻¹)	R ²
PFO	model	42.533	0.0014	0.9878
parameters				

According to the parameters represented in table 3-3, it was determined that the data is well suited to PFO model, demonstrating a physisorption reaction.

Chapter 4

Conclusions and Future Work

This study explored the characterization of MIPs on distilled water with injected pyrene as the studied PAH by deploying laboratory-scale experiments. The equilibrium and adsorption behavior topics were studied as a function of time, temperature, salinity and pH to determine the adsorption capacity. Previous studies conducted using naphthalene, as the targeted analyte within the solution, provided the information on MIPs adsorption capacity and the evaporated amount of the matrix in the solution. Here, some gaps in knowledge were observed, requiring more studies to be performed on other PAHs, that are not as volatile as naphthalene. Moreover, the information on MIPs behaviour with a single analyte is required in order to discuss their operation in samples containing a mixture of PAHs.

The results show that the capacity and recovery of MIPs are unaffected with a change in salinity or temperature; however, they do operate best at a pH of 7.0. This can be explained through the polarity increase of organic material with an increase in pH, leading to a lower affinity for hydrophobic compounds. Likewise, a higher pH could increase water mineral dispersion, resulting in more dissociated water minerals and organic matter. These incidents neutralize each other, with considering pyrene molecule dispersion in the solution as well [154]. This study is a novel one in adsorption chemistry that needs to be delved more by applying different polymer materials to the experiments, to observe the possible reactions between the monomer and acid/base. Also, different types of acid and base are

suggested to be used to measure the level of pH effect on the reactions and adsorption capacity.

Regarding the salinity study, as mentioned earlier, when there are more ions within the solution, more surface of the sorbent would be occupied by them, and less capacity will be left for pyrene to be adsorbed. Over the temperature experiments, the MIPs function does not change severely in varying temperatures. Conducting more experiments with different initial concentrations of the adsorbent (pyrene) is suggested for future work, as it affects the solubility of pyrene in water which leads to more adsorbent mass in the solution.

For the batch experiments, the time dependence of sorptive uptake of pyrene was observed by measuring the decrease in aqueous concentration over approximately 6 hours, which is the approximate time of equilibrium. At the conclusion of each experiment, there was at least a 50% recovery of MIPs as compared to the initial values of pyrene. This assured that a significant capacity of the films had been reached; however, the assumption that some adsorption sites might be occupied by something else than pyrene should be considered. Factors such as an affection of mobility of pyrene in water solution should also be undertaken as the reasons behind observed behaviors.

The dispersion of MIPs in water plays an important role in their adsorption performance toward pyrene in the aqueous phase, that can be associated with their incorporation of hydrophilic functional monomer 4-VP, as well as the high surface area of MIP, and their excellent dispersion in aqueous solution, along with strong interaction

between pyrene and MIPs which is not disturbed by water molecules [155]. Studies of the pore surface areas of the adsorbent relative to the weight of the sorbent and affinity which is highly dependant on the molecular characteristics of the adsorbate in the fluid are suggested for future work [156]. These characteristics include size, shape, and polarity, the partial pressure or concentration in the fluid, as well as the system conditions, such as the temperature.

Moreover, to study the feasibility of real scale sampling, an experiment was conducted including 18 MIPs, with the result operating well with the PFO model, similar to small-batch scale samples. Comparing the results from this experiment and the batch ones, the maximum capacity was not reached, as it is still increasing. Hence, the first step for future work would be to reach equilibrium in order to validate the isotherm data and studies in this section.

Molecular imprinting is a promising technique for designing smart materials containing molecular recognition properties involving copolymerization of functional and cross-linking monomers in the presence of a template molecule and a suitable porogenic solvent, with the further process of template removal. Hence, future work should be allocated to testing these MIPs for various sampling environments, such as a blood environment, produced water, or any type of oil spills requiring specific contamination detection and measurement, through the versatile approach for the fabrication of high-performance MIPs for application in aqueous environments provided in this work. To evaluate the effectiveness of MIPs for adsorption of pyrene from the aqueous phase, the

adsorption capacity and equilibrium time can be investigated at different temperatures, with the resulted in the adsorption kinetic curves, indicative of mass transfer rates and recognition sites. With the same results obtained, the standard free-energy change (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) can be calculated from the temperature-dependent adsorption isotherms providing in-depth information on the internal energy changes concerning adsorption.

This study has taken advantage of the adsorption process utilizing the tendency of a component of a solution to be collected on the surface of a solid sorbent, with the objective of purifying valuable feed stream and waste treatment, as the later future works.

References

1. Resh, V.H. and J.D. Unzicker, *Water quality monitoring and aquatic organisms: the importance of species identification*. Journal (Water Pollution Control Federation), 1975: p. 9-19.
2. Huang, D.-L., R.-Z. Wang, Y.-G. Liu, G.-M. Zeng, C. Lai, P. Xu, B.-A. Lu, J.-J. Xu, C. Wang, C.J.E.S. Huang, and P. Research, *Application of molecularly imprinted polymers in wastewater treatment: a review*. 2015. **22**(2): p. 963-977.
3. Jernelöv, A.J.A., *The threats from oil spills: now, then, and in the future*. 2010. **39**(5-6): p. 353-366.
4. Haupt, K., *Peer reviewed: molecularly imprinted polymers: the next generation*. 2003, ACS Publications.
5. Abdel-Shafy, H.I. and M.S. Mansour, *A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation*. Egyptian Journal of Petroleum, 2016. **25**(1): p. 107-123.
6. Li, J.-Y., W. Yu, J. Yin, Y. Chen, Q. Wang, and L. Jin, *Reduced bioavailability and ecological risks of polycyclic aromatic hydrocarbons in Yangshan port of East China Sea: Remediation effectiveness in the transition from construction to operation*. Science of The Total Environment, 2019. **687**: p. 679-686.
7. Claude, B., P. Morin, M. Lafosse, A.-S. Belmont, and K. Haupt, *Selective solid-phase extraction of a triterpene acid from a plant extract by molecularly imprinted polymer*. Talanta, 2008. **75**(2): p. 344-350.
8. Tanaka, M.N., S.T.S. Santos, M. Gouveia, M. dos Santos Filho, I.C. Cosentino, J.B.B. Neto, S. Tufik, J. do Rosário Matos, and L.P. Mercuri, *Encapsulation study of citalopram and risperidone into nanostructured silica SBA-15 for in vitro release evaluation*. Journal of Thermal Analysis and Calorimetry, 2017. **127**(2): p. 1725-1732.
9. Hassan, S.S., H.I.A. Shafy, M.S. Mansour, and H.E. Sayour, *Quercetin Recovery from Onion Solid Waste via Solid-Phase Extraction Using Molecularly Imprinted Polymer Nanoparticles*. International Journal of Food Engineering, 2019. **15**(1-2).
10. Cordes, R. *Is grey literature ever used? Using citation analysis to measure the impact of GESAMP, an international marine scientific advisory body*. in *Proceedings of the Annual Conference of CAIS/Actes du congrès annuel de l'ACSI*. 2013.

11. Steel, B.S., C. Smith, L. Opsommer, S. Curiel, and R. Warner-Steel, *Public ocean literacy in the United States*. Ocean & Coastal Management, 2005. **48**(2): p. 97-114.
12. Kullenberg, G., *Approaches to addressing the problems of pollution of the marine environment: an overview*. Ocean & coastal management, 1999. **42**(12): p. 999-1018.
13. Ramesh, A., A.E. Archibong, D.B. Hood, Z. Guo, and B.G. Loganathan, *Global environmental distribution and human health effects of polycyclic aromatic hydrocarbons*. 2011, CRC Press: Boca Raton, FL, USA. p. 95-124.
14. Wormley, D.D., A. Ramesh, and D.B. Hood, *Environmental contaminant–mixture effects on CNS development, plasticity, and behavior*. Toxicology and applied pharmacology, 2004. **197**(1): p. 49-65.
15. La’Nissa, A.B., H. Khoubouei, J.S. Goodwin, C.V. Irvin-Wilson, A. Ramesh, L. Sheng, M.M. McCallister, G.C. Jiang, M. Aschner, and D.B. Hood, *Down-regulation of early ionotropic glutamate receptor subunit developmental expression as a mechanism for observed plasticity deficits following gestational exposure to benzo (a) pyrene*. Neurotoxicology, 2007. **28**(5): p. 965-978.
16. McCallister, M.M., M. Maguire, A. Ramesh, Q. Aimin, S. Liu, H. Khoshbouei, M. Aschner, F.F. Ebner, and D.B. Hood, *Prenatal exposure to benzo (a) pyrene impairs later-life cortical neuronal function*. Neurotoxicology, 2008. **29**(5): p. 846-854.
17. Bouayed, J., F. Desor, H. Rammal, A.K. Kierner, E. Tybl, H. Schroeder, G. Rychen, and R. Soulimani, *Effects of lactational exposure to benzo [a] pyrene (B [a] P) on postnatal neurodevelopment, neuronal receptor gene expression and behaviour in mice*. Toxicology, 2009. **259**(3): p. 97-106.
18. Dutta, K., D. Ghosh, A. Nazmi, K.L. Kumawat, and A. Basu, *A common carcinogen benzo [a] pyrene causes neuronal death in mouse via microglial activation*. PLoS One, 2010. **5**(4): p. e9984.
19. Menzie, C.A., B.B. Potocki, and J. Santodonato, *Exposure to carcinogenic PAHs in the environment*. Environmental science & technology, 1992. **26**(7): p. 1278-1284.
20. Mastrangelo, G., E. Fadda, and V. Marzia, *Polycyclic aromatic hydrocarbons and cancer in man*. Occupational Health and Industrial Medicine, 1997. **3**(36): p. 113.
21. Hood, D.B., A. Ramesh, and M. Aschner, *Polycyclic Aromatic Hydrocarbons: Exposure from Emission Products and from Terrorist Attacks on US Targets–*

- Implications for Developmental Central Nervous System Toxicity*, in *Handbook of Toxicology of Chemical Warfare Agents*. 2009, Elsevier. p. 229-243.
22. Hood, D.B., D. Campbell, and P. Levitt, *An Emerging Gene–Environment Interaction Model: Autism Spectrum Disorder Phenotypes Resulting from Exposure to Environmental Contaminants during Gestation*. *Developmental Neurotoxicology Research: Principles, Models, Techniques, Strategies, and Mechanisms*, 2011: p. 543-562.
23. Hood, D.B., A. Ramesh, S. Chirwa, H. Khoshbouei, and A.E. Archibong, *Developmental toxicity of polycyclic aromatic hydrocarbons*, in *Reproductive and developmental toxicology*. 2011, Elsevier. p. 593-606.
24. Session, F., *IOC/WESTPAC Co-ordinating Committee for the North-East Asian Regional-Global Ocean Observing System*. 1999.
25. Manahan, S., *Environmental chemistry*. 2017: CRC press.
26. Storelli, M., A. Storelli, R. D'Addabbo, G. Barone, and G. Marcotrigiano, *Polychlorinated biphenyl residues in deep-sea fish from Mediterranean Sea*. *Environment International*, 2004. **30**(3): p. 343-349.
27. El-Shahawi, M., A. Hamza, A. Bashammakh, and W. Al-Saggaf, *An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants*. *Talanta*, 2010. **80**(5): p. 1587-1597.
28. Bojes, H.K. and P.G. Pope, *Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas*. *Regulatory Toxicology and Pharmacology*, 2007. **47**(3): p. 288-295.
29. Wakasugi, T., T. Nagai, M. Kapoor, M. Sugita, M. Ito, S. Ito, J. Tsudzuki, K. Nakashima, T. Tsudzuki, and Y. Suzuki, *Complete nucleotide sequence of the chloroplast genome from the green alga *Chlorella vulgaris*: the existence of genes possibly involved in chloroplast division*. *Proceedings of the National Academy of Sciences*, 1997. **94**(11): p. 5967-5972.
30. Yan, J., L. Wang, P.P. Fu, and H. Yu, *Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list*. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, 2004. **557**(1): p. 99-108.

31. Kwon, H.-O. and S.-D. Choi, *Polycyclic aromatic hydrocarbons (PAHs) in soils from a multi-industrial city, South Korea*. *Science of the Total Environment*, 2014. **470**: p. 1494-1501.
32. Douben, P.E., *PAHs: an ecotoxicological perspective*. 2003: John Wiley & Sons.
33. Abrajano Jr, T., B. Yan, and V. O'Malley, *High molecular weight petrogenic and pyrogenic hydrocarbons in aquatic environments*. *Treatise on geochemistry*, 2003. **9**: p. 612.
34. Akyüz, M. and H. Çabuk, *Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey*. *Science of the total environment*, 2010. **408**(22): p. 5550-5558.
35. Chiou, C.T. and C. Chiou, *Partition and adsorption of organic contaminants in environmental systems*. 2002: Wiley Online Library.
36. Wang, L., Z. Yang, and J. Niu, *Temperature-dependent sorption of polycyclic aromatic hydrocarbons on natural and treated sediments*. *Chemosphere*, 2011. **82**(6): p. 895-900.
37. Mu, Q., M. Shiraiwa, M. Octaviani, N. Ma, A. Ding, H. Su, G. Lammel, U. Pöschl, and Y. Cheng, *Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs*. *Science advances*, 2018. **4**(3): p. eaap7314.
38. Sangster, J., *Octanol-water partition coefficients: fundamentals and physical chemistry*. 1997: John Wiley & Sons.
39. Carballa, M., G. Fink, F. Omil, J.M. Lema, and T. Ternes, *Determination of the solid-water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge*. *Water research*, 2008. **42**(1-2): p. 287-295.
40. Berthod, A. and S. Carda-Broch, *Determination of liquid-liquid partition coefficients by separation methods*. *Journal of chromatography A*, 2004. **1037**(1-2): p. 3-14.
41. Yin, Y.B., K.N. Heck, C.L. Coonrod, C.D. Powell, S. Guo, M.A. Reynolds, and M.S. Wong, *PdAu-catalyzed Oxidation through in situ Generated H₂O₂ in Simulated Produced Water*. *Catalysis Today*, 2019.
42. Neff, J., K. Lee, and E.M. DeBlois, *Produced water: overview of composition, fates, and effects*, in *Produced water*. 2011, Springer. p. 3-54.

43. Manoli, E. and C. Samara, *Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis*. TrAC Trends in Analytical Chemistry, 1999. **18**(6): p. 417-428.
44. Bomboi, M. and A. Hernandez, *Hydrocarbons in urban runoff: their contribution to the wastewaters*. Water research, 1991. **25**(5): p. 557-565.
45. J.W. Moore, S.R., *Organic Chemicals in Natural Waters: Applied Monitoring and Impact Assessment*.
46. Shiraishi, H., N.H. Pilkington, A. Otsuki, and K. Fuwa, *Occurrence of chlorinated polynuclear aromatic hydrocarbons in tap water*. Environmental science & technology, 1985. **19**(7): p. 585-590.
47. Ramesh, A., S.A. Walker, D.B. Hood, M.D. Guillén, K. Schneider, and E.H. Weyand, *Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons*. International journal of toxicology, 2004. **23**(5): p. 301-333.
48. Humans, I.W.G.o.t.E.o.C.R.t., *Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures*. IARC Monographs on the evaluation of carcinogenic risks to humans, 2010. **92**: p. 1.
49. Soliman, Y.S., E.M. Alansari, J.L. Sericano, and T.L. Wade, *Spatio-temporal distribution and sources identifications of polycyclic aromatic hydrocarbons and their alkyl homolog in surface sediments in the central Arabian Gulf*. Science of The Total Environment, 2019. **658**: p. 787-797.
50. Mumtaz, M., J. George, K. Gold, W. Cibulas, and C. Derosa, *ATSDR evaluation of health effects of chemicals. IV. Polycyclic aromatic hydrocarbons (PAHs): understanding a complex problem*. Toxicology and industrial health, 1996. **12**(6): p. 742-971.
51. Masih, J., R. Singhvi, K. Kumar, V. Jain, and A. Taneja, *Seasonal variation and sources of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air in a semi arid tract of northern India*. Aerosol Air Qual Res, 2012. **12**: p. 515-525.
52. de Mora, S., I. Tolosa, S.W. Fowler, J.-P. Villeneuve, R. Cassi, and C. Cattini, *Distribution of petroleum hydrocarbons and organochlorinated contaminants in marine biota and coastal sediments from the ROPME Sea Area during 2005*. Marine pollution bulletin, 2010. **60**(12): p. 2323-2349.
53. Tolosa, I., S.J. De Mora, S.W. Fowler, J.-P. Villeneuve, J. Bartocci, and C. Cattini, *Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from*

- the Gulf and the Gulf of Oman*. Marine pollution bulletin, 2005. **50**(12): p. 1619-1633.
54. Soliman, Y., E. Al Ansari, and T. Wade, *Concentration, composition and sources of PAHs in the coastal sediments of the exclusive economic zone (EEZ) of Qatar, Arabian Gulf*. Marine pollution bulletin, 2014. **85**(2): p. 542-548.
55. Makelane, H., T. Waryo, U. Feleni, and E. Iwuoha, *Dendritic copolymer electrode for second harmonic alternating current voltammetric signalling of pyrene in oil-polluted wastewater*. Talanta, 2019. **196**: p. 204-210.
56. Hernandez-Ramirez, A., E. Martinez-Tavera, P. Rodriguez-Espinosa, J. Mendoza-Pérez, J. Tabla-Hernandez, D. Escobedo-Urías, M. Jonathan, and S. Sujitha, *Detection, provenance and associated environmental risks of water quality pollutants during anomaly events in River Atoyac, Central Mexico: A real-time monitoring approach*. Science of the Total Environment, 2019. **669**: p. 1019-1032.
57. Hussain, K., R.R. Hoque, S. Balachandran, S. Medhi, M.G. Idris, M. Rahman, and F.L. Hussain, *Monitoring and Risk Analysis of PAHs in the Environment*. Handbook of Environmental Materials Management, 2019: p. 973-1007.
58. Mahanty, B., K. Pakshirajan, and V.V. Dasu, *Biodegradation of pyrene by Mycobacterium frederiksbergense in a two-phase partitioning bioreactor system*. Bioresource technology, 2008. **99**(7): p. 2694-2698.
59. Mahanty, B., K. Pakshirajan, and V.V. Dasu, *Pyrene encapsulated alginate bead type for sustained release in biodegradation: preparation and characteristics*. Polycyclic Aromatic Compounds, 2009. **29**(1): p. 56-73.
60. Kazunga, C. and M.D. Aitken, *Products from the incomplete metabolism of pyrene by polycyclic aromatic hydrocarbon-degrading bacteria*. Appl. Environ. Microbiol., 2000. **66**(5): p. 1917-1922.
61. Organization, W.H., *Polynuclear aromatic hydrocarbons in drinking water*. Background document for development of WHO Guidelines for Drinking-water Quality. Geneva: WHO, 2003.
62. Stîngă, G., A. Băran, A. Iovescu, L. Aricov, and D.-F. Anghel, *Monitoring the confinement of methylene blue in pyrene labeled poly (acrylic acid)*. Journal of Molecular Liquids, 2019. **273**: p. 125-133.
63. de Boer, J. and R.J. Law, *Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and*

- polycyclic aromatic hydrocarbons*. Journal of Chromatography A, 2003. **1000**(1-2): p. 223-251.
64. Plaza-Bolaños, P., A.G. Frenich, and J.L.M. Vidal, *Polycyclic aromatic hydrocarbons in food and beverages. Analytical methods and trends*. Journal of Chromatography A, 2010. **1217**(41): p. 6303-6326.
65. Hyder, M., L.L. Aguilar, J. Genberg, M. Sandahl, C. Wesén, and J.Å. Jönsson, *Determination of polycyclic aromatic hydrocarbons (PAHs) from organic aerosols using hollow fiber micro-porous membrane liquid-liquid extraction (HF-MMLLE) followed by gas chromatography-mass spectrometry analysis*. Talanta, 2011. **85**(2): p. 919-926.
66. Ras, M.R., F. Borrull, and R.M. Marcé, *Sampling and preconcentration techniques for determination of volatile organic compounds in air samples*. TrAC Trends in Analytical Chemistry, 2009. **28**(3): p. 347-361.
67. Farré, M., S. Pérez, C. Gonçalves, M. Alpendurada, and D. Barceló, *Green analytical chemistry in the determination of organic pollutants in the aquatic environment*. TrAC Trends in Analytical Chemistry, 2010. **29**(11): p. 1347-1362.
68. Beltran, A., F. Borrull, R. Marcé, and P. Cormack, *Molecularly-imprinted polymers: useful sorbents for selective extractions*. TrAC Trends in Analytical Chemistry, 2010. **29**(11): p. 1363-1375.
69. Xie, J., C. Cai, S. Lai, L. Yang, L. Luo, H. Yang, Y. Chen, and X. Chen, *Synthesis and application of a molecularly imprinted polymer as a filter to reduce polycyclic aromatic hydrocarbon levels in mainstream cigarette smoke*. Reactive and Functional Polymers, 2013. **73**(12): p. 1606-1611.
70. Ma, J., R. Xiao, J. Li, J. Yu, Y. Zhang, and L. Chen, *Determination of 16 polycyclic aromatic hydrocarbons in environmental water samples by solid-phase extraction using multi-walled carbon nanotubes as adsorbent coupled with gas chromatography-mass spectrometry*. Journal of Chromatography A, 2010. **1217**(34): p. 5462-5469.
71. Ma, J., M. Li, C. Rui, J. Li, Q. Xue, L. Chen, and Y. Xin, *Bamboo charcoal as adsorbent for SPE coupled with monolithic column-HPLC for rapid determination of 16 polycyclic aromatic hydrocarbons in water samples*. Journal of chromatographic science, 2011. **49**(9): p. 683-688.
72. Krüger, O., U. Kalbe, E. Richter, P. Egeler, J. Römbke, and W. Berger, *New approach to the ecotoxicological risk assessment of artificial outdoor sporting grounds*. Environmental pollution, 2013. **175**: p. 69-74.

73. King, A.J., J.W. Readman, and J.L. Zhou, *Behaviour of polycyclic aromatic hydrocarbons in dissolved, colloidal, and particulate phases in sedimentary cores*. International Journal of Environmental and Analytical Chemistry, 2007. **87**(3): p. 211-225.
74. Li, J., Z. Cai, S. Xu, C. Liao, X. Song, and L. Chen, *Analysis of urinary porphyrins by high performance liquid chromatography-electrospray ionization mass spectrometry*. Journal of Liquid Chromatography & Related Technologies, 2011. **34**(15): p. 1578-1593.
75. Gosetti, F., U. Chiuminatto, E. Mazzucco, E. Robotti, G. Calabrese, M.C. Gennaro, and E. Marengo, *Simultaneous determination of thirteen polycyclic aromatic hydrocarbons and twelve aldehydes in cooked food by an automated on-line solid phase extraction ultra high performance liquid chromatography tandem mass spectrometry*. Journal of Chromatography A, 2011. **1218**(37): p. 6308-6318.
76. Galán-Cano, F., V. Bernabé-Zafón, R. Lucena, S. Cárdenas, J.M. Herrero-Martínez, G. Ramis-Ramos, and M. Valcárcel, *Sensitive determination of polycyclic aromatic hydrocarbons in water samples using monolithic capillary solid-phase extraction and on-line thermal desorption prior to gas chromatography-mass spectrometry*. Journal of Chromatography A, 2011. **1218**(14): p. 1802-1807.
77. Finlayson-Pitts, B.J. and J.N. Pitts, *Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles*. Science, 1997. **276**(5315): p. 1045-1051.
78. Sherrington, R., E. Rogaev, Y.a. Liang, E. Rogaeva, G. Levesque, M. Ikeda, H. Chi, C. Lin, G. Li, and K. Holman, *Cloning of a gene bearing missense mutations in early-onset familial Alzheimer's disease*. Nature, 1995. **375**(6534): p. 754.
79. Lin, E.L., S.M. Cormier, and J.A. Torsella, *Fish biliary polycyclic aromatic hydrocarbon metabolites estimated by fixed-wavelength fluorescence: comparison with HPLC-fluorescent detection*. Ecotoxicology and environmental safety, 1996. **35**(1): p. 16-23.
80. Fuoco, R., M.P. Colombini, and E. Samcova, *Individual determination of ortho and non-ortho substituted polychlorobiphenyls (PCBs) in sediments by high performance liquid chromatographic pre-separation and gas chromatography/ECD detection*. Chromatographia, 1993. **36**(1): p. 65-70.
81. Reutergårdh, L., *An overview on organic contaminants, focusing on monitoring of a few chlorinated organic pollutants, through immission studies*. Resources, conservation and recycling, 1996. **16**(1-4): p. 361-382.

82. Burford, M.D., S.B. Hawthorne, and D.J. Miller, *Extraction rates of spiked versus native PAHs from heterogeneous environmental samples using supercritical fluid extraction and sonication in methylene chloride*. Analytical Chemistry, 1993. **65**(11): p. 1497-1505.
83. Carvalhaes, G.K., P. Brooks, C.G. Marques, G.C. Azevedo, J.T. Azevedo, and M. Machado, *P035 The Use of Accelerated Extraction Techniques for Citrus Pulp Pellets PCDD/F Monitoring Program*. ORGANOHALOGEN COMPOUNDS, 2001. **50**: p. 225-228.
84. Schmidt, H., N.B. Ha, J. Pfannkuche, H. Amann, H.-D. Kronfeldt, and G. Kowalewska, *Detection of PAHs in seawater using surface-enhanced Raman scattering (SERS)*. Marine pollution bulletin, 2004. **49**(3): p. 229-234.
85. Mills, G. and G. Fones, *A review of in situ methods and sensors for monitoring the marine environment*. Sensor Review, 2012. **32**(1): p. 17-28.
86. Cormack, P.A. and K. Mosbach, *Molecular imprinting: recent developments and the road ahead*. Reactive and Functional Polymers, 1999. **41**(1-3): p. 115-124.
87. Piletska, E.V., A.R. Guerreiro, M.J. Whitcombe, and S.A. Piletsky, *Influence of the polymerization conditions on the performance of molecularly imprinted polymers*. Macromolecules, 2009. **42**(14): p. 4921-4928.
88. Polyakov, M., *Adsorption properties and structure of silica gel*. Zhur Fiz Khim, 1931. **2**: p. 799-805.
89. Wulff, G., *The use of polymers with enzyme-analogous structures for the resolution of racemates*. Angew. Chem. Internat. Edit., 1972. **11**(4): p. 341.
90. Wulff, G., T. Gross, and R. Schönfeld, *Enzyme models based on molecularly imprinted polymers with strong esterase activity*. Angewandte Chemie International Edition in English, 1997. **36**(18): p. 1962-1964.
91. Niu, H., Y. Yang, and H. Zhang, *Efficient one-pot synthesis of hydrophilic and fluorescent molecularly imprinted polymer nanoparticles for direct drug quantification in real biological samples*. Biosensors and Bioelectronics, 2015. **74**: p. 440-446.
92. Zhang, Z., X. Zhang, D. Niu, Y. Li, and J. Shi, *Large-pore, silica particles with antibody-like, biorecognition sites for efficient protein separation*. Journal of Materials Chemistry B, 2017. **5**(22): p. 4214-4220.

93. Kryscio, D.R. and N.A. Peppas, *Critical review and perspective of macromolecularly imprinted polymers*. Acta biomaterialia, 2012. **8**(2): p. 461-473.
94. Zhang, Z. and J. Liu, *Molecular Imprinting with Functional DNA*. Small, 2019: p. 1805246.
95. Hoshino, Y., H. Koide, T. Urakami, H. Kanazawa, T. Kodama, N. Oku, and K.J. Shea, *Recognition, neutralization, and clearance of target peptides in the bloodstream of living mice by molecularly imprinted polymer nanoparticles: a plastic antibody*. Journal of the American Chemical Society, 2010. **132**(19): p. 6644-6645.
96. Ogiso, M., N. Minoura, T. Shinbo, and T. Shimizu, *Detection of a specific DNA sequence by electrophoresis through a molecularly imprinted polymer*. Biomaterials, 2006. **27**(22): p. 4177-4182.
97. Cheong, W.J., S.H. Yang, and F. Ali, *Molecular imprinted polymers for separation science: a review of reviews*. Journal of separation science, 2013. **36**(3): p. 609-628.
98. Attia, M. and M. Abdel-Mottaleb, *Polymer-Doped Nano-Optical Sensors for Pharmaceutical Analysis*. Handbook of Polymers for Pharmaceutical Technologies: Processing and Applications, 2015. **2**.
99. Ye, L., *Molecularly imprinted polymers with multi-functionality*. Analytical and bioanalytical chemistry, 2016. **408**(7): p. 1727-1733.
100. Vasapollo, G., R.D. Sole, L. Mergola, M.R. Lazzoi, A. Scardino, S. Scorrano, and G. Mele, *Molecularly imprinted polymers: present and future prospective*. International journal of molecular sciences, 2011. **12**(9): p. 5908-5945.
101. Owens, P.K., L. Karlsson, E. Lutz, and L.I. Andersson, *Molecular imprinting for bio- and pharmaceutical analysis*. TrAC Trends in Analytical Chemistry, 1999. **18**(3): p. 146-154.
102. Ersahin, M.E., H. Ozgun, R. Kaya, B.K. Mutlu, C. Kinaci, and I. Koyuncu, *Treatment of produced water originated from oil and gas production wells: a pilot study and cost analysis*. Environmental Science and Pollution Research, 2018. **25**(7): p. 6398-6406.
103. Spivak, D.A., *Optimization, evaluation, and characterization of molecularly imprinted polymers*. Advanced drug delivery reviews, 2005. **57**(12): p. 1779-1794.
104. Karim, K., F. Breton, R. Rouillon, E.V. Piletska, A. Guerreiro, I. Chianella, and S.A. Piletsky, *How to find effective functional monomers for effective molecularly*

- imprinted polymers?* Advanced drug delivery reviews, 2005. **57**(12): p. 1795-1808.
105. Yan, H. and K. Row, *Characteristic and synthetic approach of molecularly imprinted polymer*. International journal of molecular Sciences, 2006. **7**(5): p. 155-178.
106. Lee, W.-C., C.-H. Cheng, H.-H. Pan, T.-H. Chung, and C.-C. Hwang, *Chromatographic characterization of molecularly imprinted polymers*. Analytical and bioanalytical chemistry, 2008. **390**(4): p. 1101-1109.
107. Alexander, C., H.S. Andersson, L.I. Andersson, R.J. Ansell, N. Kirsch, I.A. Nicholls, J. O'Mahony, and M.J. Whitcombe, *Molecular imprinting science and technology: a survey of the literature for the years up to and including 2003*. Journal of Molecular Recognition: An Interdisciplinary Journal, 2006. **19**(2): p. 106-180.
108. Stevenson, D., *Molecular imprinted polymers for solid-phase extraction*. TrAC Trends in Analytical Chemistry, 1999. **18**(3): p. 154-158.
109. Qiao, F., H. Sun, H. Yan, and K.H. Row, *Molecularly imprinted polymers for solid phase extraction*. Chromatographia, 2006. **64**(11-12): p. 625-634.
110. Dias, A., E. Figueiredo, V. Grassi, E. Zagatto, and M. Arruda, *Molecularly imprinted polymer as a solid phase extractor in flow analysis*. Talanta, 2008. **76**(5): p. 988-996.
111. Cieplak, M. and W. Kutner, *Artificial biosensors: how can molecular imprinting mimic biorecognition?* Trends in biotechnology, 2016. **34**(11): p. 922-941.
112. Chen, L., X. Wang, W. Lu, X. Wu, and J. Li, *Molecular imprinting: perspectives and applications*. Chemical Society Reviews, 2016. **45**(8): p. 2137-2211.
113. Li, Z.Y., Z.S. Liu, Q.W. Zhang, and H.Q. Duan, *Chiral separation by (S)-naproxen imprinted monolithic column with mixed functional monomers*. Chinese Chemical Letters, 2007. **18**(3): p. 322-324.
114. Sellergren, B., C. Dauwe, and T. Schneider, *Pressure-induced binding sites in molecularly imprinted network polymers*. Macromolecules, 1997. **30**(8): p. 2454-2459.
115. Sellergren, B., *Molecular imprinting by noncovalent interactions. Enantioselectivity and binding capacity of polymers prepared under conditions favoring the formation of template complexes*. Die Makromolekulare Chemie: Macromolecular Chemistry and Physics, 1989. **190**(11): p. 2703-2711.

116. Ban, L., L. Zhao, B.-L. Deng, Y.-P. Huang, and Z.-S. Liu, *Preparation and characterization of an imprinted monolith by atom transfer radical polymerization assisted by crowding agents*. Analytical and bioanalytical chemistry, 2013. **405**(7): p. 2245-2253.
117. Ye, L. and K. Mosbach, *Molecular imprinting: synthetic materials as substitutes for biological antibodies and receptors*. Chemistry of Materials, 2008. **20**(3): p. 859-868.
118. Komiyama, M., T. Mori, and K. Ariga, *Molecular imprinting: Materials nanoarchitectonics with molecular information*. Bulletin of the Chemical Society of Japan, 2018. **91**(7): p. 1075-1111.
119. Ma, Y., J.-F. Gao, C. Zheng, and H. Zhang, *Well-defined biological sample-compatible molecularly imprinted polymer microspheres by combining RAFT polymerization and thiol-epoxy coupling chemistry*. Journal of Materials Chemistry B, 2019.
120. Zhang, H., *Water-compatible molecularly imprinted polymers: promising synthetic substitutes for biological receptors*. Polymer, 2014. **55**(3): p. 699-714.
121. Sellergren, B. and A.J. Hall, *Molecularly imprinted polymers*. Supramolecular chemistry: from molecules to nanomaterials, 2012.
122. Dickert, F.L., M. Tortschanoff, W.E. Bulst, and G. Fischerauer, *Molecularly imprinted sensor layers for the detection of polycyclic aromatic hydrocarbons in water*. Analytical Chemistry, 1999. **71**(20): p. 4559-4563.
123. Krupadam, R.J., M.S. Khan, and S.R. Wate, *Removal of probable human carcinogenic polycyclic aromatic hydrocarbons from contaminated water using molecularly imprinted polymer*. Water research, 2010. **44**(3): p. 681-688.
124. Chen, X., *Modeling of experimental adsorption isotherm data*. Information, 2015. **6**(1): p. 14-22.
125. Umpleby, R.J., S.C. Baxter, Y. Chen, R.N. Shah, and K.D. Shimizu, *Characterization of molecularly imprinted polymers with the Langmuir-Freundlich isotherm*. Analytical chemistry, 2001. **73**(19): p. 4584-4591.
126. Foo, K.Y. and B.H. Hameed, *Insights into the modeling of adsorption isotherm systems*. Chemical engineering journal, 2010. **156**(1): p. 2-10.

127. Li, H. and L. Wang, *Highly selective detection of polycyclic aromatic hydrocarbons using multifunctional magnetic–luminescent molecularly imprinted polymers*. ACS applied materials & interfaces, 2013. **5**(21): p. 10502-10509.
128. Krupadam, R.J., B. Bhagat, and M.S. Khan, *Highly sensitive determination of polycyclic aromatic hydrocarbons in ambient air dust by gas chromatography-mass spectrometry after molecularly imprinted polymer extraction*. Analytical and bioanalytical chemistry, 2010. **397**(7): p. 3097-3106.
129. Mahony, J., K. Nolan, M. Smyth, and B. Mizaikoff, *Molecularly imprinted polymers—potential and challenges in analytical chemistry*. Analytica chimica acta, 2005. **534**(1): p. 31-39.
130. Piatt, J.J., D.A. Backhus, P.D. Capel, and S.J. Eisenreich, *Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments*. Environmental science & technology, 1996. **30**(3): p. 751-760.
131. Voice, T.C. and W.J. Weber Jr, *Sorption of hydrophobic compounds by sediments, soils and suspended solids—I. Theory and background*. Water Research, 1983. **17**(10): p. 1433-1441.
132. Karickhoff, S.W., *Organic pollutant sorption in aquatic systems*. Journal of hydraulic engineering, 1984. **110**(6): p. 707-735.
133. Karickhoff, S.W., *Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils*. Chemosphere, 1981. **10**(8): p. 833-846.
134. Schwarzenbach, R.P. and P.M. Gschwend, *Environmental organic chemistry*. 2016: John Wiley & Sons.
135. Driscoll, C.T., G.B. Lawrence, A.J. Bulger, T.J. Butler, C.S. Cronan, C. Eagar, K.F. Lambert, G.E. Likens, J.L. Stoddard, and K.C. Weathers, *Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies: The effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota*. BioScience, 2001. **51**(3): p. 180-198.
136. MacFarlane, D., J. Cherry, R. Gillham, and E. Sudicky, *Migration of contaminants in groundwater at a landfill: a case study: 1. Groundwater flow and plume delineation*. Journal of Hydrology, 1983. **63**(1-2): p. 1-29.
137. Bennett, P. and D. Siegel, *Increased solubility of quartz in water due to complexing by organic compounds*. Nature, 1987. **326**(6114): p. 684.

138. Abollino, O., M. Aceto, M. Malandrino, C. Sarzanini, and E. Mentasti, *Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances*. Water research, 2003. **37**(7): p. 1619-1627.
139. Al-Degs, Y.S., M.I. El-Barghouthi, A.H. El-Sheikh, and G.M. Walker, *Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon*. Dyes and pigments, 2008. **77**(1): p. 16-23.
140. Langmuir, I., *The constitution and fundamental properties of solids and liquids. Part I. Solids*. Journal of the American chemical society, 1916. **38**(11): p. 2221-2295.
141. Vijayaraghavan, K., T. Padmesh, K. Palanivelu, and M. Velan, *Biosorption of nickel (II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models*. Journal of hazardous materials, 2006. **133**(1-3): p. 304-308.
142. Kundu, S. and A. Gupta, *Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization*. Chemical Engineering Journal, 2006. **122**(1-2): p. 93-106.
143. Pérez-Marín, A., V.M. Zapata, J. Ortuno, M. Aguilar, J. Sáez, and M. Lloréns, *Removal of cadmium from aqueous solutions by adsorption onto orange waste*. Journal of hazardous materials, 2007. **139**(1): p. 122-131.
144. Freundlich, H., *Over the adsorption in solution*. J. Phys. Chem, 1906. **57**(385471): p. 1100-1107.
145. Adamson, A.W. and A.P. Gast, *Physical chemistry of surfaces*. Vol. 15. 1967: Interscience New York.
146. Ahmaruzzaman, M., *Adsorption of phenolic compounds on low-cost adsorbents: a review*. Advances in colloid and interface science, 2008. **143**(1-2): p. 48-67.
147. Zeldowitsch, J., *Adsorption site energy distribution*. Acta phys. chim. URSS, 1934. **1**: p. 961-973.
148. Ren, Y., X. Wei, and M. Zhang, *Adsorption character for removal Cu (II) by magnetic Cu (II) ion imprinted composite adsorbent*. Journal of hazardous materials, 2008. **158**(1): p. 14-22.
149. Shiyanovskaya, I., K.D. Singer, V. Percec, T.K. Bera, Y. Miura, and M. Glodde, *Charge transport in hexagonal columnar liquid crystals self-organized from supramolecular cylinders based on acene-functionalized dendrons*. Physical Review B, 2003. **67**(3): p. 035204.

150. Weill, F.-X., D. Domman, E. Njamkepo, A.A. Almesbahi, M. Naji, S.S. Nasher, A. Rakesh, A.M. Assiri, N.C. Sharma, and S. Kariuki, *Genomic insights into the 2016–2017 cholera epidemic in Yemen*. *Nature*, 2019. **565**(7738): p. 230.
151. Mohamed, E.F., G. Awad, C. Andriantsiferana, and H. Delmas, *Effect of Salinity and PH on the industrial effluent treatment by activated carbon: modeling of the kinetic adsorption and equilibrium isotherms*. *Environmental Management and Sustainable Development*, 2019. **8**(1): p. 77-94.
152. Sposito, G., *Derivation of the Freundlich Equation for Ion Exchange Reactions in Soils I*. *Soil Science Society of America Journal*, 1980. **44**(3): p. 652-654.
153. Duan, F., C. Chen, X. Zhao, Y. Yang, X. Liu, and Y. Qin, *Water-compatible surface molecularly imprinted polymers with synergy of bi-functional monomers for enhanced selective adsorption of bisphenol A from aqueous solution*. *Environmental Science: Nano*, 2016. **3**(1): p. 213-222.
154. Zheng, C. and P.P. Wang, *MT3DMS: a modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide*. 1999, Alabama Univ University.
155. Liu, X., Y. Wang, L. Li, and R. Li, *Synthesis and characterization of azoxystrobin hydrophilic molecularly imprinted microspheres*. *Journal of Macromolecular Science, Part A*, 2019: p. 1-11.
156. Bagreev, A., T.J. Bandosz, and D.C. Locke, *Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer*. *Carbon*, 2001. **39**(13): p. 1971-1979.

