SYNTHESIS, CHARACTERIZATION AND ADSORPTION STUDIES OF DEEP-EUTECTIC SOLVENT MOLECULAR IMPRINTED POLYMER FOR THE REMOVAL OF BISPHENOL A

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ABSTRACT

Molecularly imprinted polymer (MIP) is a class of powerful materials with promising selective molecule recognition abilities. However, the conventional MIPs have a relatively low binding capacity and selectivity. To improve this characteristic of MIP, the addition of deep eutectic solvent (DES) as a functional monomer in the polymerization process was studied to synthesize potential MIP. The study focuses on the synthesis, characterization, and adsorption behavior of deep eutectic solvent molecularly imprinted polymer (DES-MIP), molecular imprinted polymer (MIP), and hybrid deep eutectic solvent molecular imprinted membrane (HDES-MIP) for the selective removal of bisphenol A (BPA) from aqueous medium. The potential of DES in MIP was studied by synthesizing DES-MIP using DES functional monomer. DES was synthesized by mixing choline chloride (ChCl) and methacrylic acid (MAA) by ratio of 1:2. DES-MIP was then compared with conventional MIP synthesized by MAA as a functional monomer. Both DES-MIP and MIP were prepared by the free radical polymerization process via a bulk polymerization method. Prepared DES-MIP was then hybridized with cellulose acetate (CA) to obtain the HDES-MIP membrane. The characterization results of X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC) confirmed the characteristics of synthesized DES-MIP, MIP and HDES-MIP. The DES-MIP has a higher selectivity for BPA (17.72 mg/g) than competing analogs, including bisphenol AP (9.78 mg/g), 2-naphthol (8.25), and 4-tertiary butyl-phenol (6.98 mg/g). The optimization parameters include adsorption pH, adsorption kinetics, adsorption isothermal, and thermodynamic studies were carried out. DES-MIP, MIP and HDES-MIP followed Pseudo-second order and Langmuir isothermal models. According to reusability tests, the DES-MIP can be recycled five times without losing significant adsorption capacity. As a result, the addition of DES in the polymerization process improved the physical and chemical properties and enhanced the recognition capacity of MIP, thus affecting the adsorption behavior.

ABSTRAK

Polimer pencetakan molekul (MIP) merupakan sejenis kelas bahan yang menakjubkan dengan jaminan kebolehan pengecaman terhadap molekul tertentu. Tetapi, MIP konvensional mempunyai kapasiti pengikat dan selektiviti yang rendah secara relatif. Untuk menambah baik ciri-ciri MIP, penambahan pelarut eutektik dalaman (DES) sebagai monomer berfungsi dalam proses pempolimeran telah dikaji untuk menghasilkan MIP yang baik. Kajian ini memfokuskan kepada penghasilan, pencirian, dan sifat penjerapan oleh pelarut eutektik dalaman polimer pencetakan (DES-MIP), polimer pencetakan molekul (MIP), dan pelarut eutektik hibrid dalaman membran cetakan molekul (HDES-MIP) sebagai penyingkiran khusus terhadap bisfenol A (BPA) daripada medium akueus. Potensi DES dalam MIP telah dikaji dengan menghasilkan DES-MIP dengan menggunakan kumpulan berfungsi DES. DES telah dihasilkan melalui campuran kolin klorida (ChCl) dan asid metakrilik (MAA) dengan nisbah 1:2. DES-MIP dibandingkan dengan MIP yang konvensional (dihasilkan dengan MAA sebagai monomer berfungsi). Kedua-dua DES-MIP dan MIP dihasilkan oleh proses pempolimeran radikal bebas melalui kaedah pempolimeran pukal. DES-MIP yang disediakan kemudian digabungkan dengan selulosa asetat (CA) untuk memperoleh membran HDES-MIP. Hasil pencirian oleh alat pembelauan sinar X (XRD), Spektroskopi inframerah fourier transformasi (FTIR), mikroskop electron pengimbas (SEM), thermal gravimetric analyzer (TGA), dan differential scanning calorimeter (DSC) telah mengesahkan ciri-ciri DES-MIP, MIP dan HDES-MIP yang dihasilkan. DES-MIP mempunyai pengkhususan yang tinggi terhadap BPA (17.72 mg/g) berbanding yang lain, seperti bisfenol AP (9.78 mg/g), 2-naftol (8.25), and 4-tertiari butil-fenol (6.98 mg/g). Pengoptimuman parameter termasuk kajian penjerapan pH, penjerapan kinetik, penjerapan isotherma dan termodinamik telah dijalankan. DES-MIP, MIP dan HDES-MIP mengikuti model tertib pseudo kedua dan tertib isoterma Langmuir. Menurut kepada ujian kebolehgunaan semula, DES-MIP boleh diguna semula selama lima kali tanpa kehilangan kapasiti penjerapan yang banyak. Penambahan DES dalam proses pempolimeran menambah baik sifat-sifat fizikal dan kimianya dan meningkatkan kapasiti pengecaman MIP yang akan mempengaruhi sifat penjerapannya.

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b	-	Langmuir constant
B_t	-	Boyd parameter
C_0	-	Concentration of the solute in the initial solution (mg /L)
C_i	-	Initial concentration of solution (mg/ L)
C_f	-	Final concentration of solution (mg /L)
C_e	-	Equilibrium concentration of BPA (mg /L)
C_t	-	Equilibrium concentration of solution (mg /L)
k_1	-	Pseudo-first order rate constant (min^{1})
k_2	-	Pseudo-second order rate constant ($g\ mg^{-1}min^{-1}$)
K_d	-	Distribution coefficients
K_F	-	Freundlich constant for sorption capacity (mg/g)
n	-	Freundlich constant for intensity
q_e	-	Amount of the BPA adsorbed at equilibrium (mg/g)
q_t	-	Amount of the BPA adsorbed at any time (mg/g)
Q_e	-	Binding capacity of BPA (mg/g)
R	-	Universal gas constant ($kJ\ mol^{-1}\ K^{-1}$)
R_L	-	Separation factor
T	-	Temperature (K)
t	-	Time (min)
$T_{1/2}$	-	Half adsorption time (min)
V	-	Volume of solution (L)
w	-	Mass of adsorbent particles (g)
BPA	-	Bisphenol A
BPO	-	Benzoyl peroxide
ChCl	-	Choline chloride
CEC	-	Capillary electro chromatography
DES	-	Deep eutectic solvent

DSC	-	Differential scanning calorimeter
DESs	-	Deep eutectic solvents
DES-MIP	-	Deep eutectic solvent molecular imprinted polymer
EDGMA	-	Ethylene glycerol dimethacrylate
EDC	-	Endocrine disturbing chemical
FRP	-	Free radical polymerization
FTIR	-	Fourier transform infrared spectroscopy
HBA	-	Hydrogen bond acceptor
HBD	-	Hydrogen bond donor
HPLC	-	High performance liquid chromatography
MAA	-	Methacrylic acid
MIPs	-	Molecular imprinted polymers
MIP	-	Molecular imprinted polymer
NIP	-	Non imprinted polymer
SPE	-	Solid phase extraction
PVC	-	Poly vinyl chloride
TGA	-	Thermogravimetric analysis
TRIM	-	Trimethylolpropane trimethacrylate
XRD	-	X-ray diffraction

LIST OF PUBLICATION

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Molecularly imprinted polymers (MIPs) have revolutionized and attracted attention as tailor-made adsorbents for specific recognition of target molecules (Hu *et al*., 2021). MIPs are synthetic polymers with biomimetic functionalities. MIPs are usually obtained through the polymerization of functional monomers around the target molecule (template) in a complementary fashion, bringing about an exceptional three-dimensional network (Pratiwi *et al*., 2018). MIPs are less expensive than other purification techniques, e.g., coagulation (Eslami *et al*., 2020), biological treatment (Saravanan *et al*., 2021), catalytic oxidations (Wang *et al*., 2021), ozonation solvent extraction (Yang *et al*., 2020), and adsorption distillation (Liu *et al*., 2021).

MIPs are based on molecular recognition, which occurs naturally. The interaction between antibodies and antigens is one example. MIPs are precise for selective identification and binding of a given guest molecule (Huang *et al*., 2014). The extraordinary molecular interaction between monomer receptor and desired analyte is a result of MIPs well-designed molecular recognition. The synthesis of MIPs usually starts with the pre-assembly of monomers in the presence of template in a suitable soluble medium. The monomer is arranged around the template in a fixed position during the process, which is followed by copolymerization of crosslinker and initiation (Zhao *et al*., 2019). The template molecule is eliminated after polymerization leaving behind tri-dimensional structure with size, shape, and functional group complementary to the template molecule.

MIPs showed applications as separation materials for the analysis of various compounds, including drugs (Walshe *et al*., 1997), pesticides (Yang *et al*., 2006) an

amino acids (Dinu & Apetrei, 2022). The MIP membrane is a specific detection technology that has been increasing in the last few years. Several articles have been published on the preparation of MIP membranes, showing specific permeability and separation for template/ligands such as cholesterol (Ciardelli *et al*., 2006), nucleotides, and various drugs (Trotta *et al*., 2005). The transport properties and applications of MIP membranes in sensor technology have also been investigated (Algieri *et al*., 2014).

Besides all the advantages, conventional MIPs are still facing the problem of low binding capacity and low selectivity (Arabi *et al*., 2020). Deep eutectic solvents (DESs) are emerging solvents gradually introduced as functional monomers in molecular imprinting (Jablonský *et al*., 2020). DESs are comprised of mixture of two or more constituents that have a low melting point as compared to their components (Wang *et al*., 2018). One component behaved as a hydrogen bond donor (HBD) while the other one acted as a hydrogen bond acceptor (HBA). These components are held together with each other by either hydrogen bond or van der Waals interaction. DESs possess excellent properties, such as functional capacity, low cost, and low toxicity (Fu *et al*., 2017). DESs enhance the aggregate of the imprinting site marking the selective adsorption capacity of the surface.

Additionally, DESs have distinct properties, including easy preparation, low vapour pressure, and favourable biodegradability (Qin *et al*., 2019). The selectivity and adsorption capacity of target material is successfully enhanced by the introduction of DESs on the surface of molecular imprinted polymer (MIP) and this system is called deep eutectic solvent molecularly imprinted polymer (DES-MIP). DES-MIP showed good stability, excellent compatibility, improved selectivity, reusability, better imprinting factor, quick binding kinetics, and greater adsorption capacity. The excellent improvement of MIPs upon modification with DES is due to the controlled structure and homogeneity of the binding site (Wang *et al*., 2018).

Bisphenol A (BPA) is an emerging organic, synthetic, and chemical intermediate used in certain plastics and epoxy resins (Fan *et al*., 2021). BPA is the most widespread endocrine disruptor which caused chronic health conditions related to the reproductive system (Shamhari *et al*., 2021), metabolic function, nervous system, immune function, growth, and development of progeny (Ma *et al*., 2019). The general population may directly or indirectly exposed to BPA through food, water, air, cosmetics, and thermal. Eventually, these products are biodegraded by sunlight and

converted into microplastics. Due to its non-biodegradability and resistance to chemical degradation, it is essential to remove BPA from the environment (Huang *et al*., 2017).

In this study profoundly specific and proficient DES based on choline chloride-methacrylic acid (ChCl-MAA) as a functional monomer was developed. The obtained DES was used as a functional monomer to produce (DES-MIP). A conventional MIP based on MAA monomer was also produced. The prepared DES-MIP was hybridized with cellulose acetate (CA) to obtain the hybrid DES-MIP membrane (HDES-MIP).

1.2 Problem statement

MIPs are synthetic polymers that contain artificial receptor sites for a specific target template. Many researchers have investigated MIPs for BPA (Alnaimat *et al*., 2019; Ardekani *et al*., 2020; Poliwoda *et al*., 2016; Y. Wang *et al*., 2019). Most of these studies used conventional functional monomers such as methacrylic acid (MAA), acrylamide (AAM) and 4-vinyl pyridine (4-PV). MIPs obtained through conventional monomers still face limitations. Poor selectivity, irregular shape, and slow mass transfer lead to poor binding capacity for the target template (Tian *et al*., 2018).

The release of a wide range of chemical pollutants with potential toxicity into water is an ecological threat to humans. BPA is one of the major chemical manufactured worldwide due to the growing market of polycarbonates and epoxy resins (Huang *et al*., 2012). The estimated use of BPA was 7.7 million metric tons in 2015 and is projected to reach 10.6 million metric tons by 2022. Commonly, BPA is used to synthesize polycarbonates, phenolics, and epoxies. Industrial wastes, effluents and household products are some of the common sources of pollution of BPA in the environment (Kwiatkowska *et al*., 2017). It is negligibly released into the environment mixed up with drinking water and food by contacting polycarbonates and resins, glassware, food cans, baby bottles, and storage buckets.

BPA is responsible for causing tumors in humans, even taking a minor concentration every day. It is extremely important to remove BPA as the exposure leads to severe health and environmental effects (Corrales *et al*., 2015). BPA has been banned in the production of baby bottles along with any other food contact items for children under the age of three. The European Chemical Agency (ECHA) has

classified BPA as a chemical of very high concern. Recent rules have placed even more restrictions on the use of BPA that's why food manufacturers are steadily looking for an alternative to eliminate BPA from their goods (Wassenaar *et al*., 2021). The European Commission approved a regulation in 2018 that restricted the use of BPA as a packing material (Zhang *et al*., 2020). The Specific Migration Limit (SML) per kilogram of food was reduced from 0.6 mg to 0.05 mg. Per body weight, 4 ug/kg was set as the new Tolerable Daily Intake (t-TDI).

A new generation of functional DES monomers has some unique characteristics compared to traditional monomers, such as the creation of inclusion complexes by host-guest interaction DES forms a complex with the target analyte through various types of intermolecular interactions such as Van der Waals force, hydrophobic interactions, electrostatic affinity, dipole-dipole and hydrogen bond interaction during the imprinting Phases (Grecco *et al*., 2021). Thus, DES is the alternative approach that eliminates the drawbacks faced by using traditional monomers.

1.3 Objectives of study

The main objective of this study is to improve the selectivity and binding capacity of molecular imprinted polymer (MIP) by introducing a choline chloride/methacrylic base functional monomer. Meanwhile, the specific objectives are as follows:

i. To synthesize and characterize the deep eutectic solvent molecular imprinted polymer (DES-MIP) for the removal of bisphenol A (BPA).
ii. To prepare and characterize the hybrid DES-MIP membrane (HDES-MIP) for the removal of BPA.
iii. To study the optimum parameters for DES-MIP and hybrid DES-MIP membrane (HDES-MIP) for the removal of BPA.

1.4 Significance of study

The conventional MIPs faced several problems, including low selectivity and low binding capacity. Application of new functional monomer for MIP enhanced selectivity and binding capacity for BPA. DES is an excellent choice as a functional

monomer for the preparation of DES-MIP due to less toxic, low cost and easy preparation made. Molecular imprinting technology (MIT) was revolutionized after the utilization of DES, which proved to be an effective source to overcome the drawbacks of traditional molecular imprinting. Factors like incomplete template removal, irregular shape and low binding capacity can be improved by the introduction of DES for the MIP synthesis. The proposed method for the synthesis of DES-MIP's remarkably enhanced binding capacity. Consequently, excellent template recognition, as well as adsorption capacity have been achieved.

Additionally, the wide range of polarity of DESs makes it possible to construct analytical platforms for several compounds for which it has previously been impossible to do so due to solubility issues. For example, DESs have recently been employed as extraction solvents for the pre-concentration of pesticide residues in food and environmental samples, followed by instrumental analysis. Finally, DESs are non-toxic and eco-friendly, making them desirable for use as green media in the creation of devices for the pharmaceutical, agrochemical, and food sectors. The advantages of the existence of high content functional groups in DES monomers provide excellent interaction with template molecules which tend to enhance the selectivity and affinity of DES-MIP. The effective extraction ability of DES-MIP is due to the presence of natural process action hydrogen bonding, hydrophobic nature, and electrostatic interaction (Li *et al*., 2015)

1.5 Scope of study

In order to achieve the research objectives, the scopes of study have been determined are:

i. Synthesis of DES-MIP and DES-NIP by preparing a new functional monomer which is combination of choline chloride-methacrylic acid (ChCl-MAA) as a DES compound.
ii. Synthesis of the conventional MIP and NIP as control by using methacrylic acid (MAA) as functional monomer.
iii. Synthesis and characterization of hybrid deep eutectic solvent molecular imprinted polymer membrane (HDES-MIP).

iv. Evaluation of interaction between functional groups of DES, MIPs, NIPs and HDES-MIP was done by using Fourier transform infrared spectrometer (FTIR).

v. Evaluation of morphology of synthesized MIPs, NIPs and HDES-MIP was analyzed by using a scanning electron microscope (SEM).

vi. Evaluation of crystalline properties of MIPs and NIPs were carried out by using X-ray diffraction (XRD) analysis.

vii. Determination of heating behavior of MIPs and NIPs was carried out by Differential scanning calorimetry (DSC).

viii. Evaluation of thermal stability with respect to temperature was carried out by Thermogravimetric analysis (TGA) for MIPs and NIPs

ix. Evaluation of optimum parameters including pH, kinetic, isothermal and thermodynamic of MIPs and HDES-MIP was carried out by a batch adsorption experiment using UV-vis spectrophotometry.

x. Determination of selectivity of MIPs and NIPs was carried out by comparing the adsorption of structurally similar molecules.

xi. Evaluation of reusability of MIPs was carried out by performing five adsorption cycles.

CHAPTER 2

LITERATURE REVIEW

2.1 Molecularly imprinted polymer (MIPs)

2.1.1 Overview of MIPs

Molecular imprinting is an outstanding approach for the synthesis of polymers with high selectivity and specificity for the target molecule, which involves the attachment of polymerizable functional monomers around the template molecules (Bates *et al*., 2017). Molecularly imprinted polymers (MIPs) have a specific ability to determine and separate specific molecules (target template) from other molecules that contain similar structures. Due to specific recognition, easy preparation and low-cost MIPs find their application in the areas of purification, separation, biosensing, catalysis, drug delivery, and degradation (Chen *et al*., 2016).Three major approaches are used to synthesize MIPs (i) covalent, (ii) non-covalent, and (iii) semi-covalent.

The noncovalent imprinting approach is frequently used to prepare MIPs due to its flexibility and ease of handling. The noncovalent interactions involve Van der Waals forces, hydrogen bonding and π–π interactions (Zhang *et al*., 2021). Most common functional monomer for this type of MIP is methacrylic acid (MAA), which interacts through hydrogen bonding. The imprint molecules interact with the MIPs during the imprinting procedure and the rebinding process via non-covalent interactions. Simple and economical experimental procedures of noncovalent approach allow a wide range of functional monomers to interact with almost every kind of template available commercially (Martín-Esteban, 2016). A major limitation of this approach is the formation of complexes with multiple template–monomer stoichiometries. Such complexes may have binding sites with different affinities. However, the simplicity of operation, kinetics of binding removal and versatility of the

non-covalent approach have made it more popular in the recent past (Arabi *et al*., 2020). Figure 2.1 shows the schematic synthesis of MIPs.

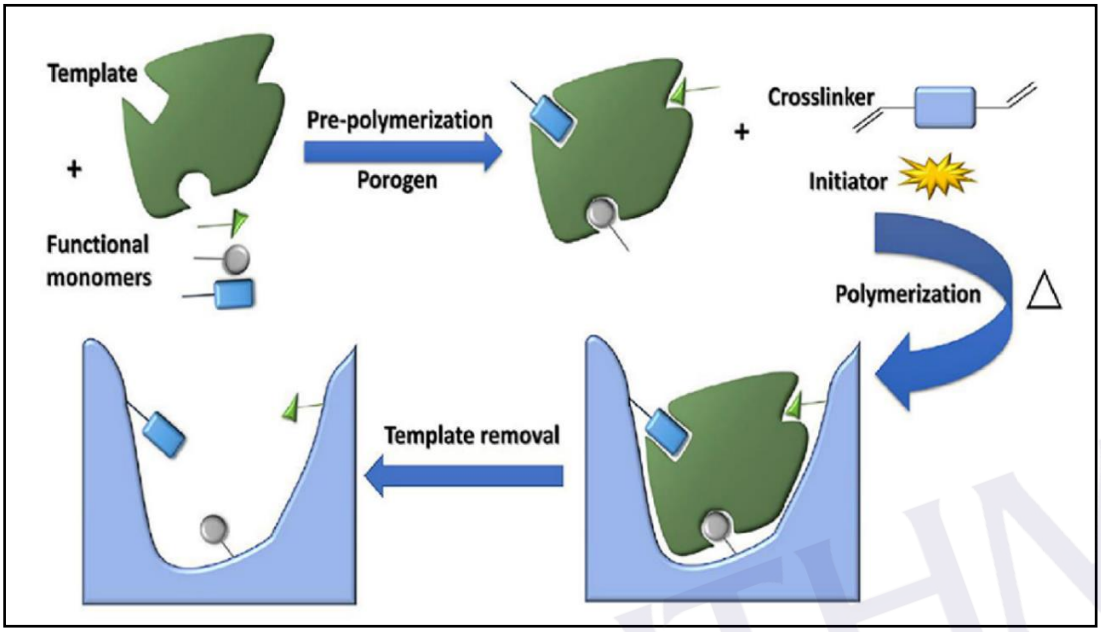

Figure 2.1: Schematic preparation of MIP by non-covalent approach (Gao *et al*., 2020)

The covalent approach was first introduced by Wulff and coworkers (Wulff, 1977). It is the second most popular approach used for the synthesis of MIPs. The covalent approach indicates that the cleavage of the covalent reversible bond occurs to remove MIPs from the resulting matrix, which is reformed upon rebinding of the analyte (Parisi *et al*., 2019). The covalent bonds must be cleaved for the template to be extracted via chemical interaction, resulting in well-defined binding cavities with complementary steric and functional topography to the target molecule. The exact stoichiometry of the template-monomer complexes allows the preparation of polymers with binding groups exclusively located in the imprinted cavities, decreasing the possibility of non-specific interactions. There are some limitations associated with the covalent approach for MIPs. The application of the covalent approach is restricted to a limited number of functional monomers and templates such as alcohols, amines, aldehydes, ketones and carboxylic acids (Marfà *et al*., 2021). Moreover, template-monomer complex formation before polymerization is attributed to higher effort for template cleavage after MIP synthesis. The repeated use and slow rebinding kinetics are due to the need to establish the covalent bond for target recognition

The covalently BPA-imprinted polymer was prepared using BPA as a template, dimethacrylate as the monomer, ethylene glycol dimethacrylate (EGDMA) as the crosslinker, and 2,2'-azobis (isobutyronitrile) as the initiator. The polymerization was polymerized by UV initiation by using chloroform as a solvent. The BPA was separated from the resulting polymer by hydrolysis of the ester bonds with aqueous sodium hydroxide, generating the carboxylic acid residues in the polymer. The ester bonds of the obtained polymer were hydrolyzed to generate carboxyl group-based binding sites. The resulting polymer exhibited a high affinity for BPA. Table 2.1 shows the advantages and disadvantages of the three approaches used in the synthesis of MIPs (Ikegami *et al*., 2004).

Table 2.1: Summary of different approaches used for the synthesis of MIPs

Imprinting type	Benefits	Limitations	References
Covalent	Provide homogeneous binding sites with a definite shape. Polymerization ensures the maximization of the number of specific binding sites.	The removal of template and rebinding is very difficult.	(Hasanah *et al*., 2021; Yi *et al.*, 2013)
Semi-covalent	Random distribution and association of functional monomers to template molecules.	There may be template bleeding when hydrolysis is unable to remove the template.	(Hasanah *et al* ., 2021)
Non-covalent	Experimental simplicity. Easy removal of the template under mild conditions. Fast template binding and release kinetics.	The weak average affinity of the binding site. Formation of nonselective binding sites because of random incorporation of	(Torres-Cartas *et al.*, 2020)

The semi-covalent approach is a protocol for producing MIPs that combines the covalent and noncovalent approaches. This alternative approach can provide a higher imprinting factor and a faster adsorption value. (Zhang *et al.*, 2020) applied a semi covalent approach for MIP to fabricate the mesoporous fluorescent molecularly imprinted sensor for detecting BPA from food samples. To achieve rapid identification of BPA, an imprinting precursor1-(benzofuran-2-yl)-2-propylaminopentane (BPAP) was formulated via thermally reversible isocyanate bonding that worked as an alternative template molecule for BPA detection.

2.2 Synthesis of MIPs

MIPs are commonly synthesized by free radical polymerization (FRP). The other components involved in the synthesis process are functional monomer, template, crosslinker and initiator.

2.2.1 Free radical polymerization (FRP)

FRP is widely used in the industrial preparation of polymers. FRP-prepared materials have distinct functionalities. As a result, approximately 50% of the world's polymer production is typically carried out using this method (Marfà *et al*., 2021). MIPs are often synthesized by FRP which is the most important method for their production. In the presence of a suitable solvent, the reaction is carried out under the normal condition of temperature and pressure.

Typically, the synthesis technique is carried out in bulk or solution at mild reaction temperatures lower than 80 °C. This range of temperature is quite favorable for wide range of functional groups and templates (Kouki *et al.*, 2022). Typically, the polymerization reaction happens quite quickly. A popular azo-initiator used in this reaction is azo N-N′-bis isobutyronitrile (AIBN), which can initiate a reaction thermally or chemically. Previous studies demonstrated that photo-initiated polymerization at low temperature decreases the kinetic energy of the pre-polymerization complex which increased the stability and allowing greater binding capacity and specificity than thermal initiated polymerization which requires temperatures higher than 40 °C.

As shown in Figure 2.2, free FRP consists of three steps: (i) initiation, (ii) propagation, and (iii) termination. Initiation is the first step in which the formation of free radicals occurs by the decomposition of an initiator under heating. The second major step is the propagation, where the addition of a monomer to a growing macro radical contributes to the growth of the chain. The final step is termination, which takes place in two ways. First is the recombination of two macro radicals and secondly, the disproportionation that gives the double bonds C=C and C-H at the end of the chain of polymer (Datta & Włoch, 2019).

REFERENCES

Abbas, M. (2020). Modeling of adsorption isotherms of heavy metals onto Apricot stone activated carbon: Two-parameter models and equations allowing determination of thermodynamic parameters. *Materials Today: Proceedings*, *43*, 3359–3364.

Abbott, A. P., Al-Barzinjy, A. A., Abbott, P. D., Frisch, G., Harris, R. C., Hartley, J., & Ryder, K. S. (2014). Speciation, physical and electrolytic properties of eutectic mixtures based on $CrCl_3 \cdot 6H_2O$ and urea. *Physical Chemistry Chemical Physics*, *16*(19), 9047–9055.

Abramian, L., & El-Rassy, H. (2009). Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel. *Chemical Engineering Journal*, *150*(2–3), 403–410.

Abu-Alsoud, G. F., Hawboldt, K. A., & Bottaro, C. S. (2020). Comparison of four adsorption isotherm models for characterizing molecular recognition of individual phenolic compounds in porous tailor-made molecularly imprinted polymer Films. *ACS Applied Materials and Interfaces*, *12*(10), 11998–12009.

Acosta, R., Nabarlatz, D., Sánchez-Sánchez, A., Jagiello, J., Gadonneix, P., Celzard, A., & Fierro, V. (2018). Adsorption of Bisphenol A on KOH-activated tyre pyrolysis char. *Journal of Environmental Chemical Engineering*, *6*(1), 823–833.

Ahmed, M. J., & Dhedan, S. K. (2012). Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons. *Fluid Phase Equilibria*, *317*, 9–14.

Algieri, C., Drioli, E., Guzzo, L., & Donato, L. (2014). Bio-mimetic sensors based on molecularly imprinted membranes. *Sensors*, *14*(8),

Almoselhy, R. I. M. (2020). Applications of Differential Scanning Calorimetry (DSC) in Oils and fats research. A Reviewa. *American Research Journal of Agriculture*, *6*(1), 1–9.

Alnaimat, A. S., Barciela-Alonso, M. C., & Bermejo-Barrera, P. (2019). Determination of bisphenol A in tea samples by solid phase extraction and liquid

chromatography coupled to mass spectrometry. *Microchemical Journal*, *147*(January), 598–604.

Amin, S., Damayanti, S., & Ibrahim, S. (2018). synthesis and characterization molecularly imprinted polymers for analysis of dimethylamylamine using acrylamide as monomer functional. *Jurnal Kefarmasian Indonesia*, *November*, 76–84.

Androvič, L., Bartáček, J., & Sedlák, M. (2016). Recent advances in the synthesis and applications of azo initiators. *Research on Chemical Intermediates*, *42*(6), 5133–5145.

Ansell, R. J. (2015). Characterization of the binding properties of molecularly imprinted polymers. *Advances in Biochemical Engineering/Biotechnology*, *150*, 51–93.

Arabi, M., Ostovan, A., Bagheri, A. R., Guo, X., Wang, L., Li, J., Wang, X., Li, B., & Chen, L. (2020). Strategies of molecular imprinting-based solid-phase extraction prior to chromatographic analysis. In *TrAC - Trends in Analytical Chemistry*, *128*, 115923.

Arca, H. C., Mosquera-Giraldo, L. I., Bi, V., Xu, D., Taylor, L. S., & Edgar, K. J. (2018). Pharmaceutical applications of cellulose ethers and cellulose ether esters. *Biomacromolecules*, *19*(7), 2351–2376.

Ardekani, R., Borhani, S., & Rezaei, B. (2020). Selective molecularly imprinted polymer nanofiber sorbent for the extraction of bisphenol A in a water sample. *Polymer International*, *69*(9), 780–793.

Asman, S., Mohamad, S., & Sarih, N. M. (2016a). Study of the morphology and the adsorption behavior of molecularly imprinted polymers prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization process based on two functionalized β-cyclodextrin as monomers. *Journal of Molecular Liquids*, *214*, 59–69.

Asman, S., Mohamad, S., & Sarih, N. M. (2016b). Study of the morphology and the adsorption behavior of molecularly imprinted polymers prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization process based on two functionalized β-cyclodextrin as monomers. *Journal of Molecular Liquids*, *214*, 59–69.

Balayan, S., Chauhan, N., Chandra, R., & Jain, U. (2022). Electrochemical based c-reactive protein (Crp) sensing through molecularly imprinted polymer (mip) pore

structure coupled with bi-metallic tuned screen-printed electrode. *Biointerface Research in Applied Chemistry*, *12*(6), 7697–7714.

Bates, F., Busato, M., Piletska, E., Whitcombe, M. J., Karim, K., Guerreiro, A., del Valle, M., Giorgetti, A., & Piletsky, S. (2017). Computational design of molecularly imprinted polymer for direct detection of melamine in milk. *Separation Science and Technology (Philadelphia)*, *52*(8), 1441–1453.

Bayramoglu, G., & Arica, M. Y. (2011). Synthesis of Cr(VI)-imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) particles: Its adsorption propensity to Cr(VI). *Journal of Hazardous Materials*, *187*(1–3), 213–221.

Berber, A., Gürdal, M., & Bağırsakçı, K. (2021). Prediction of heat transfer in a circular tube with aluminum and Cr-Ni alloy pins using artificial neural network. *Experimental Heat Transfer*, *34*(6), 547–563.

Boysen, R. I., Schwarz, L. J., Nicolau, D. V., & Hearn, M. T. (2017). Molecularly imprinted polymer membranes and thin films for the separation and sensing of biomacromolecules. *Journal of Separation Science*, *40*(1), 314–335.

Cegłowski, M., Kurczewska, J., Ruszkowski, P., Liberska, J., & Schroeder, G. (2019). The influence of cross-linking agent onto adsorption properties, release behavior and cytotoxicity of doxorubicin-imprinted microparticles. *Colloids and Surfaces B: Biointerfaces*, *182*, 110379.

Chaemchuen, S., Heynderickx, P. M., & Verpoort, F. (2020). Kinetic modeling of oleic acid esterification with UiO-66: from intrinsic experimental data to kinetics via elementary reaction steps. *Chemical Engineering Journal*, *394*(February), 124816.

Chaudhary, V., & Sharma, S. (2019). Suspension polymerization technique: parameters affecting polymer properties and application in oxidation reactions. *Journal of Polymer Research*, *26*(5).

Che Lah, N. F., Ahmad, A. L., & Low, S. C. (2021). Molecular imprinted membrane biosensor for pesticide detection: Perspectives and challenges. *Polymers for Advanced Technologies*, *32*(1), 17–30.

Chen, G. N., Li, N., Luo, T., & Dong, Y. M. (2017). Enantiomers recognition of propranolol based on organic-inorganic hybrid open-tubular mips-cec column using 3-(trimethoxysilyl)propyl methacrylate as a cross-linking monomer. *Journal of Chromatographic Science*, *55*(4), 471–476.

Chen, L., Wang, X., Lu, W., Wu, X., & Li, J. (2016). Molecular imprinting:

Perspectives and applications. *Chemical Society Reviews*, *45*(8), 2137–2211.

Chen, W., Guo, Z., Ding, Q., Zhao, C., Yu, H., Zhu, X., Fu, M., & Liu, Q. (2021). Magnetic-graphene oxide based molecular imprinted polymers for selective extraction of glycoprotein at physiological pH. *Polymer*, *215*(October 2020), 123384.

Cheng, Z., Liu, X., Han, M., & Ma, W. (2010). Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution. *Journal of Hazardous Materials*, *182*(1–3), 408–415.

Ciardelli, G., Borrelli, C., Silvestri, D., Cristallini, C., Barbani, N., & Giusti, P. (2006). Supported imprinted nanospheres for the selective recognition of cholesterol. *Biosensors and Bioelectronics*, *21*(12), 2329–2338.

Corbin, D. A., & Miyake, G. M. (2022). Photoinduced organocatalyzed atom transfer radical polymerization (o-atrp): precision polymer synthesis using organic photoredox catalysis. *Chemical Reviews*, *122*(2), 1830–1874.

Corrales, J., Kristofco, L. A., Baylor Steele, W., Yates, B. S., Breed, C. S., Spencer Williams, E., & Brooks, B. W. (2015). Global assessment of bisphenol a in the environment: Review and analysis of its occurrence and bioaccumulation. *Dose-Response: An International Journa*, *13*(3), 1–29.

Cui, Y., He, Z., Xu, Y., Su, Y., Ding, L., & Li, Y. (2021). Fabrication of molecularly imprinted polymers with tunable adsorption capability based on solvent-responsive cross-linker. *Chemical Engineering Journal*, *405*.

Cydzik-Kwiatkowska, A., Bernat, K., Zielińska, M., Bułkowska, K., & Wojnowska-Baryła, I. (2017). Aerobic granular sludge for bisphenol A (BPA) removal from wastewater. *International Biodeterioration and Biodegradation*, *122*, 1–11.

Dąbrowski, A. (2001). Adsorption - From theory to practice. *Advances in Colloid and Interface Science*, *93*(1–3), 135–224.

Dai, C., Zhang, J., Zhang, Y., Zhou, X., & Liu, S. (2013). Application of molecularly imprinted polymers to selective removal of clofibric acid from water. *PloS One*, *8*(10).

Datta, J., & Włoch, M. (2019). Synthesis and polymerisation techniques of molecularly imprinted polymers. *Comprehensive Analytical Chemistry*, *86*, 17–40.

Derazshamshir, A., Yılmaz, F., & Denizli, A. (2015). Molecularly imprinted hydrophobic polymers as a tool for separation in capillary

electrochromatography. *Analytical Methods*, *7*(6), 2659–2669.

Dinu, A., & Apetrei, C. (2022). A review of sensors and biosensors modified with conducting polymers and molecularly imprinted polymers used in electrochemical detection of amino acids: phenylalanine, tyrosine, and tryptophan. *International Journal of Molecular Sciences*, *23*(3).

Dong, W., Yan, M., Liu, Z., Wu, G., & Li, Y. (2007). Effects of solvents on the adsorption selectivity of molecularly imprinted polymers: Molecular simulation and experimental validation. *Separation and Purification Technology*, *53*(2), 183–188.

D'Orazio, G., Asensio-Ramos, M., Fanali, C., Hernández-Borges, J., & Fanali, S. (2016). Capillary electrochromatography in food analysis. *TrAC - Trends in Analytical Chemistry*, *82*, 250–267.

Eslami, H., Esmaeili, A., Ehrampoush, M. H., Ebrahimi, A. A., Taghavi, M., & Khosravi, R. (2020). Simultaneous presence of poly titanium chloride and Fe2O3-Mn2O3 nanocomposite in the enhanced coagulation for high rate As(V) removal from contaminated water. *Journal of Water Process Engineering*, *36*, 101342.

Ezzati, R. (2020). Derivation of Pseudo-First-Order, Pseudo-Second-Order and modified Pseudo-First-Order rate equations from Langmuir and Freundlich isotherms for adsorption. *Chemical Engineering Journal*, *392*(September 2019), 123705.

Faheem, M., & Bhandari, R. K. (2021). Detrimental effects of bisphenol compounds on physiology and reproduction in fish: a literature review. *Environmental Toxicology and Pharmacology*, *81*, 103497.

Fan, X., Katuri, G. P., Caza, A. A., Rasmussen, P. E., & Kubwabo, C. (2021). Simultaneous measurement of 16 bisphenol A analogues in house dust and evaluation of two sampling techniques. *Emerging Contaminants*, *7*, 1–9.

Fapa-ms, S., Esi-ms, I. M. S., & Gu, M. (2019). Application of molecularly imprinted polymers (mip) and magnetic molecularly imprinted polymers (mag-mip) to selective analysis of quercetin. *Molecules*, *24(*13), 2364.

Fu, N., Li, L., Liu, X., Fu, N., Zhang, C., Hu, L., Li, D., Tang, B., & Zhu, T. (2017). Specific recognition of polyphenols by molecularly imprinted polymers based on a ternary deep eutectic solvent. *Journal of Chromatography A*, *1530*, 23–34.

G. Wulff, W. Vesper, R. Grobe-Einsler, and A. S. (1977). On the synthesis of polymers

containing chiral cavities and their use for the resolution of racemates. *Makromol. Chem.*, *178*, 2799–2816.

Galogahi, F. M., Zhu, Y., An, H., & Nguyen, N. T. (2020). Core-shell microparticles: generation approaches and applications. *Journal of Science: Advanced Materials and Devices*, *5*(4), 417–435.

Gao, M., Gao, Y., Chen, G., Huang, X., Xu, X., Lv, J., Wang, J., Xu, D., & Liu, G. (2020). Recent Advances and Future Trends in the Detection of Contaminants by Molecularly Imprinted Polymers in Food Samples. *Frontiers in Chemistry*, *8*, 1–20.

Golker, K., & Nicholls, I. A. (2017). The influence of a methyl substituent on molecularly imprinted polymer morphology and recognition – acrylic acid versus methacrylic acid. *European Polymer Journal*, *92*, 137–149.

Grecco, C. F., de Souza, I. D., & Queiroz, M. E. C. (2021). Novel materials as capillary coatings for in-tube solid-phase microextraction for bioanalysis. *Journal of Separation Science*, *44*(8), 1662–1693.

Günay, A., Arslankaya, E., & Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *146*(1–2), 362–371.

Guo, W., Hu, W., Pan, J., Zhou, H., Guan, W., Wang, X., Dai, J., & Xu, L. (2011). Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/Fe3O4 composites. *Chemical Engineering Journal*, *171*(2), 603–611.

Guo, Y., Wei, X., Gao, S., Yue, W., Li, Y., & Shen, G. (2021). Recent advances in carbon material-based multifunctional sensors and their applications in electronic skin systems. *Advanced Functional Materials*, *31*(40), 1–35.

Gurkan, B., Squire, H., & Pentzer, E. (2019). Metal-free deep eutectic solvents: preparation, physical properties and significance. *Journal of Physical Chemistry Letters*, *10*(24), 7956–7964.

Gutierrez-Climente, R., Gomez-Caballero, A., Guerreiro, A., Garcia-Mutio, D., Unceta, N., Goicolea, M. A., & Barrio, R. J. (2017). Molecularly imprinted nanoparticles grafted to porous silica as chiral selectors in liquid chromatography. *Journal of Chromatography A*, *1508*, 53–64.

Hasanah, A. N., Safitri, N., Zulfa, A., Neli, N., & Rahayu, D. (2021). Factors affecting preparation of molecularly imprinted polymer and methods on finding template-

monomer interaction as the key of selective properties of the materials. *Molecules*, *26*(18).

Hasanah, A. N., Soni, D., Pratiwi, R., Rahayu, D., Megantara, S., & Mutakin. (2020). Synthesis of Diazepam-Imprinted Polymers with Two Functional Monomers in Chloroform Using a Bulk Polymerization Method. *Journal of Chemistry*, *2020*.

He, J. X., Pan, H. Y., Xu, L., & Tang, R. Y. (2021). Application of molecularly imprinted polymers for the separation and detection of aflatoxin. *Journal of Chemical Research*, *45*(5–6), 400–410.

He, S., Zhang, L., Bai, S., Yang, H., Cui, Z., Zhang, X., & Li, Y. (2021). Advances of molecularly imprinted polymers (MIP) and the application in drug delivery. *European Polymer Journal*, *143*, 110179.

Ho, Kyung, LI, X. (2017). Application of deep eutectic solvents in hybrid molecularly imprinted polymers and mesoporous siliceous material for solid-phase extraction of levofloxacin from green bean extract. *Analytical Sciences*, *33*(5), 611–617.

Ho, Y. S., & McKay, G. (1998). Kinetic models for the sorption of dye from aqueous solution by wood. *Process Safety and Environmental Protection*, *76*(2), 183–191.

Hu, T., Chen, R., Wang, Q., He, C., & Liu, S. (2021). Recent advances and applications of molecularly imprinted polymers in solid-phase extraction for real sample analysis. *Journal of Separation Science*, *44*(1), 274–309.

Huang, D. L., Wang, R. Z., Liu, Y. G., Zeng, G. M., Lai, C., Xu, P., Lu, B. A., Xu, J. J., Wang, C., & Huang, C. (2014). Application of molecularly imprinted polymers in wastewater treatment: a review. *Environmental Science and Pollution Research*, *22*(2), 963–977.

Huang, D., Tang, Z., Peng, Z., Lai, C., Zeng, G., Zhang, C., Xu, P., Cheng, M., Wan, J., & Wang, R. (2017). Fabrication of water-compatible molecularly imprinted polymer based on β-cyclodextrin modified magnetic chitosan and its application for selective removal of bisphenol A from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, *77*, 113–121.

Huang, Y. Q., Wong, C. K. C., Zheng, J. S., Bouwman, H., Barra, R., Wahlström, B., Neretin, L., & Wong, M. H. (2012). Bisphenol A (BPA) in China: A review of sources, environmental levels, and potential human health impacts. *Environment International*, *42*(1), 91–99.

Ikegami, T., Mukawa, T., Nariai, H., & Takeuchi, T. (2004). Bisphenol A-recognition polymers prepared by covalent molecular imprinting. *Analytica Chimica Acta*,

504(1), 131–135.

Ismail, N., Venault, A., Mikkola, J. P., Bouyer, D., Drioli, E., & Tavajohi Hassan Kiadeh, N. (2020). Investigating the potential of membranes formed by the vapor induced phase separation process. *Journal of Membrane Science*, *597*, 117601.

Jablonský, M., Majová, V., Šima, J., Hroboňová, K., & Lomenová, A. (2020). Involvement of deep eutectic solvents in extraction by molecularly imprinted polymers—a minireview. *Crystals*, *10*(3), 1–12.

Kavci, E. (2021). Malachite green adsorption onto modified pine cone: Isotherms, kinetics and thermodynamics mechanism. *Chemical Engineering Communications*, *208*(3), 318–327.

Khan, A., Qyyum, M. A., Saulat, H., Ahmad, R., Peng, X. S., & Lee, M. (2021). Metal–organic frameworks for biogas upgrading: Recent advancements, challenges, and future recommendations. *Applied Materials Today*, *22*, 100925.

Kouki, S., Jaoued-Grayaa, N., Anene, A., Beyou, E., Chevalier, Y., & Hbaieb, S. (2022). The enhanced adsorption properties of molecular imprinted polymer material prepared using nitroxide-mediated Radical Deactivation Reversible Polymerization. *Polymer*, *249*, 124841.

Krisanti, E., Terahadi, F., Fauzia, F., & Putri, S. (2015). Alcohol-based natural deep eutectic solvents (NADES) as green solvents for extraction of mangostins from Garcinia mangostana pericarp. *Planta Medica*, *81*(16).

Lamei, N., Ezoddin, M., & Abdi, K. (2016). Air assisted emulsification liquid-liquid microextraction based on deep eutectic solvent for preconcentration of methadone in water and biological samples. *Talanta*, *165*, 176–181.

Li, G., Wang, W., Wang, Q., & Zhu, T. (2015). Deep eutectic solvents modi fi ed molecular imprinted polymers for optimized puri fi cation of chlorogenic acid from honeysuckle. *Journal of Chromatographic Science*, *54*(2), 271–279.

Li, L., Liu, Y., Wang, Z., Yang, L., & Liu, H. (2020). Development and applications of deep eutectic solvent derived functional materials in chromatographic separation. *Journal of Separation Science*, 1–48.

Li, X., Dai, Y., & Row, K. H. (2019). Preparation of two-dimensional magnetic molecularly imprinted polymers based on boron nitride and a deep eutectic solvent for the selective recognition of flavonoids. *Analyst*, *144*(5), 1777–1788.

Li, X., & Row, K. H. (2016). Development of deep eutectic solvents applied in extraction and separation. *Journal of Separation Science*, *39*(18), 3505–3520.

Li, X., & Row, K. H. (2020). Preparation of levofloxacin-imprinted nanoparticles using designed deep eutectic solvents for the selective removal of: Levofloxacin pollutants from environmental waste water. *Analyst*, *145*(8), 2958–2965.

Li, Z., Li, Z., Li, D., Gao, H., Chen, X., Cao, L., Hou, Y., & Li, S. (2015). Molecularly imprinted polymer-based chemiluminescence imaging assay for the determination of ethopabate residues in chicken muscle. *Analytical Methods*, *7*(21), 9295–9303.

Liu, K., Song, Y., Song, D., & Liang, R. (2020). Plasticizer-free polymer membrane potentiometric sensors based on molecularly imprinted polymers for determination of neutral phenols. *Analytica Chimica Acta*, *1121*, 50–56.

Liu, Q., Yang, J., Li, H., Ye, J., Fei, Z., Chen, X., Zhang, Z., Tang, J., Cui, M., & Qiao, X. (2021). Activated carbon prepared from catechol distillation residue for efficient adsorption of aromatic organic compounds from aqueous solution. *Chemosphere*, *269*, 128750.

Liu, R., & Poma, A. (2021). Advances in molecularly imprinted polymers as drug delivery systems. *Molecules*, *26*(12).

Liu, X., Wu, F., Au, C., Tao, Q., Pi, M., & Zhang, W. (2019). Synthesis of molecularly imprinted polymer by suspension polymerization for selective extraction of p-hydroxybenzoic acid from water. *Journal of Applied Polymer Science*, *136*(3), 1–8.

Liu, Z., Wang, Y., Xu, F., Wei, X., Chen, J., Li, H., He, X., & Zhou, Y. (2020). A new magnetic molecularly imprinted polymer based on deep eutectic solvents as functional monomer and cross-linker for specific recognition of bovine hemoglobin. *Analytica Chimica Acta*, *1129*, 49–59.

Ma, J., Yan, M., Feng, G., Ying, Y., Chen, G., Shao, Y., She, Y., Wang, M., Sun, J., Zheng, L., Wang, J., & Abd El-Aty, A. M. (2021). An overview on molecular imprinted polymers combined with surface-enhanced Raman spectroscopy chemical sensors toward analytical applications. *Talanta*, *225*(December 2020), 122031.

Ma, Y., Liu, H., Wu, J., Yuan, L., Wang, Y., Du, X., Wang, R., Marwa, P. W., Petlulu, P., Chen, X., & Zhang, H. (2019). The adverse health effects of bisphenol A and related toxicity mechanisms. *Environmental Research*, *176*(7).

Madikizela, L. M., Tavengwa, N. T., & Chimuka, L. (2017). Applications of molecularly imprinted polymers for solid-phase extraction of non-steroidal anti-

inflammatory drugs and analgesics from environmental waters and biological samples. *Journal of Pharmaceutical and Biomedical Analysis*, *147*, 624–633.

Madikizela, L., Tavengwa, N., & Pakade, V. (2018). molecularly imprinted polymers for pharmaceutical compounds: synthetic procedures and analytical applications. *Recent Research in Polymerization*, 47–67.

Malik, M. I., Shaikh, H., Mustafa, G., & Bhanger, M. I. (2019). Recent Applications of Molecularly Imprinted Polymers in Analytical Chemistry. *Separation and Purification Reviews*, *48*(3), 179–219.

Mamman, S., Suah, F. B. M., Raaov, M., Mehamod, F. S., Asman, S., & Zain, N. N. M. (2021). Removal of bisphenol A from aqueous media using a highly selective adsorbent of hybridization cyclodextrin with magnetic molecularly imprinted polymer. *Royal Society Open Science*, *8*(3).

Marfà, J., Pupin, R. R., Sotomayor, M., & Pividori, M. I. (2021). Magnetic-molecularly imprinted polymers in electrochemical sensors and biosensors. *Analytical and Bioanalytical Chemistry*, *413*(24), 6141–6157.

Martín-Esteban, A. (2016). Recent molecularly imprinted polymer-based sample preparation techniques in environmental analysis. *Trends in Environmental Analytical Chemistry*, *9*, 8–14.

Mobasherpour, I., Salahi, E., & Ebrahimi, M. (2014). Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto multi-walled carbon nanotubes. *Journal of Saudi Chemical Society*, *18*(6), 792–801.

Mohajeri, S. A., & Ebrahimi, S. A. (2008). Preparation and characterization of a lamotrigine imprinted polymer and its application for drug assay in human serum. *Journal of Separation Science*, *31*(20), 3595–3602.

Mohamed Idris, Z., Hameed, B. H., Ye, L., Hajizadeh, S., Mattiasson, B., & Mohd Din, A. T. (2020). Amino-functionalised silica-grafted molecularly imprinted polymers for chloramphenicol adsorption. *Journal of Environmental Chemical Engineering*, *8*(5).

Mohebali, A., Abdouss, M., Kazemi, Y., & Daneshnia, S. (2021). Fabrication and characterization of pH-responsive poly (methacrylic acid)-based molecularly imprinted polymers nanosphere for controlled release of amitriptyline hydrochloride. *Polymers for Advanced Technologies*, *32*(11), 4386–4396.

Ndunda, E. N. (2020). Molecularly imprinted polymers—A closer look at the control polymer used in determining the imprinting effect: A mini review. *Journal of*

Molecular Recognition, *33*(11), 1–11.

Ng, H. M., Saidi, N. M., Omar, F. S., Ramesh, K., Ramesh, S., & Bashir, S. (2018). Thermogravimetric Analysis of Polymers. *Encyclopedia of Polymer Science and Technology*, *13*, 1–29.

Niu, M., Pham-huy, C., & He, H. (2016). Core-shell nanoparticles coated with molecularly imprinted polymers : a review. *Microchimica Acta*, *183*(10), 2677–2695.

Omidi, M., Fatehinya, A., Farahani, M., Akbari, Z., Shahmoradi, S., Yazdian, F., Tahriri, M., Moharamzadeh, K., Tayebi, L., & Vashaee, D. (2017). Characterization of biomaterials. In *Biomaterials for Oral and Dental Tissue Engineering*. Elsevier Ltd.

Orimi, S. M. H., Khavarpour, M., & Kazemi, S. (2020). Removal of bisphenol a from water solution using molecularly imprinted nanopolymers: Isotherm and kinetic studies. *Journal of Water and Environmental Nanotechnology*, *5*(1), 56–67.

Özcan, A., Öncü, E. M., & Özcan, A. S. (2006). Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *277*(1–3), 90–97.

Pardeshi, P. M., & Mungray, A. A. (2019). Photo-polymerization as a new approach to fabricate the active layer of forward osmosis membrane. *Scientific Reports*, *9*(1), 1–13.

Pardeshi, S., & Singh, S. K. (2016). Precipitation polymerization: A versatile tool for preparing molecularly imprinted polymer beads for chromatography applications. *RSC Advances*, *6*(28), 23525–23536.

Parisi, O. I., Ruffo, M., & Puoci, F. (2019). Molecularly imprinted polymers for selective recognition in regenerative medicine. In *Nanostructured Biomaterials for Regenerative Medicine*. Elsevier Ltd.

Pazhoor, M. T., Gautam, P. K., Samanta, S., Suman, Bangotra, P., & Banerjee, S. (2021). Performance assessment of Zn–Sn bimetal oxides for the removal of inorganic arsenic in groundwater. *Groundwater for Sustainable Development*, *14*(April), 100600.

Pelch, K., Wignall, J. A., Goldstone, A. E., Ross, P. K., Blain, R. B., Shapiro, A. J., Holmgren, S. D., Hsieh, J. H., Svoboda, D., Auerbach, S. S., Parham, F. M., Masten, S. A., Walker, V., Rooney, A., & Thayer, K. A. (2019). A scoping review

of the health and toxicological activity of bisphenol A (BPA) structural analogues and functional alternatives. *Toxicology*, *424*(May), 152235.

Piletsky, S. A., Piletskaya, E. V., Yano, K., Kugimiya, A., Elgersma, A. V., Levi, R., Kahlow, U., Takeuchi, T., Karube, I., Panasyuk, T. I., & El'skaya, A. V. (1996). A biomimetic receptor system for sialic acid based on molecular imprinting. *Analytical Letters*, *29*(2), 157–170.

Poliwoda, A., Mościpan, M., & Wieczorek, P. P. (2016a). Application of molecular imprinted polymers for selective solid phase extraction of bisphenol a. *ecological Chemistry and Engineering S*, *23*(4), 651–664.

Pratiwi, R., Megantara, S., Rahayu, D., Pitaloka, I., & Hasanah, A. N. (2018). Comparison of bulk and precipitation polymerization method of synthesis molecular imprinted solid phase extraction for atenolol using methacrylic acid. *Journal of Young Pharmacists*, *11*(1), 12–16.

Qin, H., Hu, X., Wang, J., Cheng, H., Chen, L., & Qi, Z. (2019). Overview of acidic deep eutectic solvents on synthesis, properties and applications. *Green Energy and Environment*, *5*(1), 8–21.

Qwane, S. N., Mdluli, P. S., & Madikizela, L. M. (2020). Synthesis, characterization and application of a molecularly imprinted polymer in selective adsorption of abacavir from polluted water. *South African Journal of Chemistry*, *73*(July), 84–91.

Revellame, E. D., Fortela, D. L., Sharp, W., Hernandez, R., & Zappi, M. E. (2020). Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. *Cleaner Engineering and Technology*, *1*(October), 100032. https://doi.org/10.1016/j.clet.2020.100032

Rojas, G., Silva, J., Flores, J. A., Rodriguez, A., Ly, M., & Maldonado, H. (2005). Adsorption of chromium onto cross-linked chitosan. *Separation and Purification Technology*, *44*(1), 31–36.

Sajini, T., Gigimol, M. G., & Mathew, B. (2019). A brief overview of molecularly imprinted polymers supported on titanium dioxide matrices. *Materials Today Chemistry*, *11*, 283–295.

Saraji, M., & Alijani, S. (2021). A molecularly imprinted polymer on chromium (III) oxide nanoparticles for spectrofluorometric detection of bisphenol A. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, *255*, 119711.

Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P. R., & Reshma, B. (2021). Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere*, *280*, 130595.

Şenol, Z. M., Gül, Ü. D., & Gürkan, R. (2020). Bio-sorption of bisphenol a by the dried- and inactivated-lichen (Pseudoevernia furfuracea) biomass from aqueous solutions. *Journal of Environmental Health Science and Engineering*, *18*(2), 853–864.

Shah, S. A. H., Mohamad, S., Md Saleh, N., Yih, B. S., Rahim, N. Y., Miskam, M., & Asman, S. (2022). A Review of Molecular Imprinting Polymer for Separation of Bisphenol-A and its Analogues: Synthesis and Application. *Current Analytical Chemistry*, *18*(8), 867–891.

Shamhari, A. 'Afifah, Hamid, Z. A., Budin, S. B., Shamsudin, N. J., & Taib, I. S. (2021). Bisphenol a and its analogues deteriorate the hormones physiological function of the male reproductive system: A mini-review. *Biomedicines*, *9*(11).

Sharma, G., & Kandasubramanian, B. (2020). Molecularly Imprinted Polymers for Selective Recognition and Extraction of Heavy Metal Ions and Toxic Dyes. *Journal of Chemical & Engineering Data*, *65*(2), 396–418.

Sirot, V., Rivière, G., Leconte, S., Leblanc, J. C., Kolf-Clauw, M., Vasseur, P., Cravedi, J. P., & Hulin, M. (2021). Infant total diet study in France: Exposure to substances migrating from food contact materials. *Environment International*, *149*.

Surikumaran, H., Mohamad, S., & Sarih, N. M. (2014). Molecular imprinted polymer of methacrylic acid functionalised β-Cyclodextrin for selective removal of 2,4-dichlorophenol. *International Journal of Molecular Sciences*, *15*(4), 6111–6136.

Susanti, I., & Hasanah, A. N. (2021). How to develop molecularly imprinted mesoporous silica for selective recognition of analytes in pharmaceutical, environmental, and food samples. *Polymers for Advanced Technologies*, *32*(5), 1965–1980.

Székely, G., Bandarra, J., Heggie, W., Ferreira, F. C., & Sellergren, B. (2012). Design, preparation and characterization of novel molecularly imprinted polymers for removal of potentially genotoxic 1,3-diisopropylurea from API solutions. *Separation and Purification Technology*, *86*, 190–198.

Tan, L., Zhou, L. Di, Jiang, Z. F., Ma, R. R., He, J. Y., Xia, Z. N., Zhang, Q. H., Wang,

C. Z., & Yuan, C. S. (2021). Selective separation and inexpensive purification of paclitaxel based on molecularly imprinted polymers modified with ternary deep eutectic solvents. *Journal of Pharmaceutical and Biomedical Analysis*, *192*, 113661.

Terzopoulou, Z., Papageorgiou, M., Kyzas, G. Z., Bikiaris, D. N., & Lambropoulou, D. A. (2016). Preparation of molecularly imprinted solid-phase microextraction fiber for the selective removal and extraction of the antiviral drug abacavir in environmental and biological matrices. *Analytica Chimica Acta*, *913*, 63–75.

Thach, U. D., Thi, H. H. N., Pham, T. D., Mai, H. D., & Nhu-Trang, T. T. (2021). Synergetic effect of dual functional monomers in molecularly imprinted polymer preparation for selective solid phase extraction of ciprofloxacin. *Polymers*, *13*(16).

Tian, Y., Wang, Y., Wu, S., Sun, Z., & Gong, B. (2018). Preparation of Ampicillin Surface Molecularly Imprinted Polymers for Its Selective Recognition of Ampicillin in Eggs Samples. *International Journal of Analytical Chemistry*, *11*.

Tomé, L. I. N., Baião, V., da Silva, W., & Brett, C. M. A. (2018). Deep eutectic solvents for the production and application of new materials. *Applied Materials Today*, *10*, 30–50.

Torres-Cartas, S., Catalá-Icardo, M., Meseguer-Lloret, S., Simó-Alfonso, E. F., & Herrero-Martínez, J. M. (2020). Recent advances in molecularly imprinted membranes for sample treatment and separation. *Separations*, *7*(4), 1–28.

Trotta, F., Baggiani, C., Luda, M. P., Drioli, E., & Massari, T. (2005). A molecular imprinted membrane for molecular discrimination of tetracycline hydrochloride. *Journal of Membrane Science*, *254*(1–2), 13–19.

Ungureanu, E., Mustățea, G., & Popa, M. E. (2020). *Safety aspects related to the Bisphenol A migration process in packed meat and milk products – a review*. *26*(4), 380–385.

Ünlü, A. E., Arlkaya, A., & Takaç, S. (2019). Use of deep eutectic solvents as catalyst: A mini-review. *Green Processing and Synthesis*, *8*(1), 355–372.

Unnithan, A. R., Gnanasekaran, G., Sathishkumar, Y., Lee, Y. S., & Kim, C. S. (2014). Electrospun antibacterial polyurethane-cellulose acetate-zein composite mats for wound dressing. *Carbohydrate Polymers*, *102*(1), 884–892. https://doi.org/10.1016/j.carbpol.2013.10.070

Uzun, L., & Turner, A. P. F. (2016). Molecularly-imprinted polymer sensors:

Realising their potential. *Biosensors and Bioelectronics*, *76*, 131–144.

van der Merwe, D., Gehring, R., & Buur, J. L. (2018). Toxicokinetics in Veterinary Toxicology. In *Veterinary Toxicology: Basic and Clinical Principles: Third Edition* (Third Edit). Elsevier Inc.

Wackerlig, J., & Schirhagl, R. (2016). Applications of Molecularly Imprinted Polymer Nanoparticles and Their Advances toward Industrial Use: A Review. *Analytical Chemistry*, *88*(1), 250–261.

Walshe, M., Garcia, E., Howarth, J., Smyth, M. R., & Kelly, M. T. (1997). Separation of the enantiomers of propranolol by incorporation of molecularly imprinted polymer particles as chiral selectors in capillary electrophoresis. *Analytical Communications*, *34*(4), 119–122.

Wang, B., Song, Z., & Sun, L. (2021). A review: Comparison of multi-air-pollutant removal by advanced oxidation processes – Industrial implementation for catalytic oxidation processes. *Chemical Engineering Journal*, *409*, 128136.

Wang, D., Liu, Y., Xu, Z., Zhao, D., Liu, Y., & Liu, Z. (2020). Multitemplate molecularly imprinted polymeric solid-phase microextraction fiber coupled with HPLC for endocrine disruptor analysis in water samples. *Microchemical Journal*, *155*, 104802.

Wang, J., & Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, *390*(January), 122156.

Wang, J., Zhou, Y., Wang, M., Bi, W., Li, H., Da, D., & Chen, Y. (2018). High throughput analysis for artemisinins with deep eutectic solvents mechanochemical extraction and direct analysis in real time mass spectrometry High throughput analysis for artemisinins with deep eutectic solvents mechanochemical extraction and direct. *Analytical Chemistry*, *90*(5), 3109–3117.

Wang, X., Li, G., & Row, K. H. (2018). Magnetic molecularly imprinted polymers based on silica modified by deep eutectic solvents for the rapid simultaneous magnetic-based solid-phase extraction of salvia miltiorrhiza bunge , glycine max (linn .) merr and green tea. *Electrophoresis*, *39*(8), 1111-1118.

Wang, Y., Tian, M., Yu, K., Li, L., Zhang, Z., & Li, L. (2019). A versatile strategy to fabricate magnetic ENG molecularly imprinted mesoporous silica particles for specific magnetic separation of bisphenol A. *New Journal of Chemistry*, *43*(8), 3400–3408.

Wassenaar, P. N. H., Rorije, E., Vijver, M. G., & Peijnenburg, W. J. G. M. (2021). Evaluating chemical similarity as a measure to identify potential substances of very high concern. *Regulatory Toxicology and Pharmacology*, *119*(October 2020), 104834.

Weber, T. W., & Chakravorti, R. K. (1974). Pore and solid diffusion models for fixed-bed adsorbers. *AIChE Journal*, *20*(2), 228–238.

Wilkes, J. S., Levisky, J. A., Wilson, R. A., & Hussey, C. L. (2014). Dialkylimidazolium. *Encyclopedia of Lubricants and Lubrication*, *237*(1980), 374–374. https://doi.org/10.1007/978-3-642-22647-2_100172

Wsoo, M. A., Shahir, S., Mohd Bohari, S. P., Nayan, N. H. M., & Razak, S. I. A. (2020). A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. *Carbohydrate Research*, *491*(February), 107978.

Wu, X., Du, J., Li, M., Wu, L., Han, C., & Su, F. (2018). Recent advances in green reagents for molecularly imprinted polymers. *RSC Advances*, *8*(1), 311–327.

Wu, Y. T., Zhang, Y. H., Zhang, M., Liu, F., Wan, Y. C., Huang, Z., Ye, L., Zhou, Q., Shi, Y., & Lu, B. (2014). Selective and simultaneous determination of trace bisphenol A and tebuconazole in vegetable and juice samples by membrane-based molecularly imprinted solid-phase extraction and HPLC. *Food Chemistry*, *164*, 527–535.

Xie, L., Xiao, N., Li, L., Xie, X., & Li, Y. (2020). Theoretical insight into the interaction between chloramphenicol and functional monomer (Methacrylic acid) in molecularly imprinted polymers. *International Journal of Molecular Sciences*, *21*(11), 1–14.

Xie, Q., Xia, M., Lu, H., Shi, H., Sun, D., Hou, B., Jia, L., & Li, D. (2020). Deep eutectic solvent-based liquid-liquid microextraction for the HPLC-DAD analysis of bisphenol A in edible oils. *Journal of Molecular Liquids*, *306*, 112881.

Xu, K., Wang, Y., Wei, X., Chen, J., Xu, P., & Zhou, Y. (2018). Preparation of magnetic molecularly imprinted polymers based on a deep eutectic solvent as the functional monomer for specific recognition of lysozyme. *Microchimica Acta*, *185*(2).

Yang, G., Liu, H., Wang, M., Liu, S., & Chen, Y. (2006). Chromatographic characterization and solid-phase extraction on diniconazole-imprinted polymers stationary phase. *Reactive and Functional Polymers*, *66*(5), 579–583.

Yang, J., Li, Y., Wang, J., Sun, X., Cao, R., Sun, H., Huang, C., & Chen, J. (2015). Molecularly imprinted polymer microspheres prepared by Pickering emulsion polymerization for selective solid-phase extraction of eight bisphenols from human urine samples. *Analytica Chimica Acta*, *872*, 35–45.

Yang, S., Wang, Y., Jiang, Y., Li, S., & Liu, W. (2016). Molecularly imprinted polymers for the identification and separation of chiral drugs and biomolecules. *Polymers*, *8*(6), 216.

Yang, Y., Meng, X., & Xiao, Z. (2018). Synthesis of a surface molecular imprinting polymer based on silica and its application in the identification of nitrocellulose. *RSC Advances*, *8*(18), 9802–9811.

Yang, Z., Zhang, Y., Zhu, W., Zan, X., Zhang, L., & Liu, Y. (2020). Effective oxidative degradation of coal gasification wastewater by ozonation: A process study. *Chemosphere*, *255*, 126963.

Yanti, Nurhayati, T., Royani, I., Widayani, & Khairurrijal. (2016). Synthesis and characterization of MAA-based molecularly-imprinted polymer (MIP) with D-glucose template. *Journal of Physics: Conference Series*, *739*(1).

Yates, J., Deeney, M., Rolker, H. B., White, H., Kalamatianou, S., & Kadiyala, S. (2021). A systematic scoping review of environmental, food security and health impacts of food system plastics. *Nature Food*, *2*(2), 80–87.

Yi, L. X., Fang, R., & Chen, G. H. (2013). Molecularly imprinted solid-phase extraction in the analysis of agrochemicals. *Journal of Chromatographic Science*, *51*(7), 608–618.

Yuan, X., Liu, T., Gao, L., Xing, L., Zhu, Y., & Li, S. (2018). A convenient separation method for di(2-ethylhexyl)phthalate by novel superparamagnetic molecularly imprinted polymers. *RSC Advances*, *8*(63), 36191–36199.

Yusof, N. A., Rahman, S. K. A., Hussein, M. Z., & Ibrahim, N. A. (2013). Preparation and characterization of molecularly imprinted polymer as SPE sorbent for melamine isolation. *Polymers*, *5*(4), 1215–1228.

Yusof, N. A., Zakaria, N. D., Maamor, N. A. M., Abdullah, A. H., & Haron, M. J. (2013). Synthesis and characterization of molecularly imprinted polymer membrane for the removal of 2,4-dinitrophenol. *International Journal of Molecular Sciences*, *14*(2), 3993–4004.

Zaafouri, Z., Batôt, G., Nieto-Draghi, C., Coasne, B., & Bauer, D. (2022). Impact of adsorption kinetics on pollutant dispersion in water flowing in nanopores: A

Lattice Boltzmann approach to stationary and transient conditions. *Advances in Water Resources*, *162*, 104143.

Zhang, C., Zhong, S., & Yang, Z. (2008). Cellulose acetate-based molecularly imprinted polymeric membrane for separation of vanillin and o-vanillin. *Brazilian Journal of Chemical Engineering*, *25*(2), 365–373.

Zhang, H., Song, H., Tian, X., Wang, Y., Hao, Y., Wang, W., Gao, R., Yang, W., Ke, Y. S., & Tang, Y. (2021). Magnetic imprinted nanoparticles with synergistic tailoring of covalent and non-covalent interactions for purification and detection of procyanidin B2. *Microchimica Acta*, *188*(1).

Zhang, L., Luo, K., Li, D., Zhang, Y., Zeng, Y., & Li, J. (2020). Chiral molecular imprinted sensor for highly selective determination of D-carnitine in enantiomers via dsDNA-assisted conformation immobilization. *Analytica Chimica Acta*, *1136*, 82–90.

Zhang, N., Scarsella, J. B., & Hartman, T. G. (2020). Identification and quantitation studies of migrants from bpa alternative food-contact metal can coatings. *Polymers*, *12*(12), 1–13.

Zhao, G., Liu, J., Liu, M., Han, X., Peng, Y., Tian, X., Liu, J., & Zhang, S. (2020). Synthesis of molecularly imprinted polymer via emulsion polymerization for application in solanesol separation. *Applied Sciences (Switzerland)*, *10*(8).

Zhao, W., Li, B., Xu, S., Huang, X., Luo, J., Zhu, Y., & Liu, X. (2019). Electrochemical protein recognition based on macromolecular self-assembly of molecularly imprinted polymer: A new strategy to mimic antibody for label-free biosensing. *Journal of Materials Chemistry B*, *7*(14), 2311–2319.

Zhao, X., Cheng, Y., Xu, H., Hao, Y., Lv, Y., & Li, X. (2020). Design and Preparation of Molecularly Imprinted Membranes for Selective Separation of Acteoside. *Frontiers in Chemistry*, *8*(September), 1–11.

Zhou, T., Zhang, K., Kamra, T., Bülow, L., & Ye, L. (2015). Preparation of protein imprinted polymer beads by Pickering emulsion polymerization. *Journal of Materials Chemistry B*, *3*(7), 1254–1260. https://doi.org/10.1039/c4tb01605j

Z.M., S., S.U., I., & D., A. (2019). Recovery of Crude Oil from Aqueous Medium by Optimised Styrene/Kenaf Shive Graft-Based Sorbent Via Regeneration Method: Study of the Equilibrium, Kinetics and Activation Energy. *World Journal of Innovative Research*, *6*(2).

Zunngu, S. S., Madikizela, L. M., Chimuka, L., & Mdluli, P. S. (2017). Synthesis and

application of a molecularly imprinted polymer in the solid-phase extraction of ketoprofen from wastewater. *Comptes Rendus Chimie*, *20*(5), 585–591.

VITA

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