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(Article begins on next page)

**Selective removal of contaminants of emerging concern (CECs) from urban water cycle via
Molecularly Imprinted Polymers (MIPs): potential of upscaling and enabling reclaimed water
reuse**

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Abstract

Contaminants of emerging concern (CECs) are one of the main barriers in the water cycle as they limit the water reuse due to their adverse effects on humans and the ecosystem. Natural and/or engineered ecosystems, such as conventional wastewater treatment processes, are not designed to remove CECs and contribute to the bioaccumulation in organisms considering high volumes of treated water discharges. The adoption of innovative solutions to upgrade urban water cycle facilities has gained relevance for the removal of these substances from final effluents. Molecularly imprinted polymers (MIPs) show promising selective removal toward a wide range of CECs. However, this solution is still limited to lab/bench scale and needs to be critically analyzed and assessed for possible scale-up in real environment. Therefore, in this review, an overview of the fate and occurrence of CECs in wastewater is initially reported together with the state-of-the-art in adsorption mechanisms to remove these compounds. In the central part of the paper, an evaluation of MIPs synthesis and their status in removing CECs from water matrix are presented. An upscaling pathway of MIPs column

from lab- to pilot-scale is given to be applied for enhanced CECs removal and safe water reuse in irrigation/fertigation. Finally, possible integrations of MIP columns to real wastewater treatment facilities is discussed and advantages and disadvantages of the potential solutions are addressed to enhance their sustainability.

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Keywords: adsorption; contaminants of emerging concern (CECs); molecularly imprinted polymer (MIP); tertiary wastewater treatment; upscaling; water reuse

34

1. Introduction

Agriculture practices, industrial discharges, and everyday activities play an important role in releasing pollutants via wastewater. These practices generate various organic contaminants which alter the water cycle causing a global concern linked to their eventual impact on wildlife and human health [1,2]. In recent years, many articles have appeared reporting the presence of new compounds, called “contaminants of emerging concern (CECs)”, in wastewater and aquatic environments. The United States Environmental Protection Agency (US EPA) defines CECs as new chemicals which impact on the environment and human health is poorly understood [3]. These CECs, natural or synthetic, can be found in water and wastewater treatment plants (WWTPs) in low concentrations, in the order of μg or ng per liter, but with the risk of contaminating and accumulating in the environment [4]. The ecotoxicological effects, fate, and behavior of CECs are not well understood, as they are not presently included in an international regular monitoring program [5,6]. The NORMAN project, established in 2005, is one of the largest world’s classified records of CECs occurring in the environment with over 1036 CECs together with their by-products and metabolites. These can be further categorized in 30 classes based on their origin and type such as pharmaceuticals, pesticides, plasticizers, hormones. All these compounds may generate high risks to human health due to their bioaccumulation in the fatty tissue, while biomagnification can give rise to undesirable long-term effects [3].

52 Most of these micropollutants are sent to conventional WWTPs where only a partial removal is
53 obtained by stripping, adsorption and/or biological degradation. This is mostly due to the complex
54 structure and chemical heterogeneity of the CECs as well as to the predicted no effect concentration
55 since conventional treatment units/processes are not designed to remove CECs, while even at very
56 low concentrations they are discharged in final effluents and accumulate in aquatic organisms and
57 adversely affect growth and reproduction [7]. Conventional secondary processes (i.e. activated sludge
58 and trickling filters) represent the most extensively used and studied processes in WWTPs. However,
59 these processes are not designed to remove CECs resulting in their discharge to receiving surface
60 waters [8]. Alternative treatment options must be considered for selective CECs removal such as
61 advanced oxidation processes, nanofiltration and reverse osmosis membranes [1,9]. However, most
62 of these methods require high investment and maintenance costs, complicated procedure for the
63 wastewater treatment and sometimes cause secondary pollution due to the formation of oxidation by-
64 products, which in some cases might be more toxic than the initial compound. Moreover,
65 physicochemical treatments such as coagulation and flocculation processes are generally unable to
66 remove endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products
67 (PPCPs). Conversely, adsorption processes do not add undesirable by-products and can be considered
68 superior to other techniques in wastewater treatment in terms of simplicity of design and operation
69 [10].

70 The demand for finding local solutions and using non-conventional water resources has been
71 increasing, especially in water-scarce areas like the Mediterranean Region where the lack of good
72 quality of irrigation water is already limiting the agriculture [11]. The greatest challenge in this
73 scenario is represented by the adoption of low-cost wastewater treatment technologies in these areas
74 and ensuring compliance with all health and safety standards regarding the reuse of treated
75 wastewater effluents. At this point, non-conventional adsorption technology based on molecularly
76 imprinted polymers (MIPs) represent a valid tool to remove selectively one or more specific target
77 molecules in the wastewater and surface water cycle. MIPs, obtained through a radical polymerization

78 synthesis, are characterized by highly selective sites or cavities with a specific affinity for a target
79 molecule, since they are capable to imitate the complex mechanisms typically occurring between
80 antibodies and biological receptors [12]. These polymers have high mechanical properties and can be
81 used in a wide range of applications and with different types of matrices such as biological fluids or
82 aqueous environmental solutions. The peculiar properties of MIPs, that will be discussed in Section
83 4, make them very interesting tools in different areas of application, including separation and
84 purification methods [13,14], sensors and biosensors [15,16], catalysis [17], and drug delivery [18–
85 20]. In the last decade, many studies reported the synthesis and the application of MIP technology to
86 the removal of a wide range of CECs such as diclofenac, ketoprofen and ibuprofen (non-steroidal
87 anti-inflammatory drugs, NSAIDs), ciprofloxacin and sulfamethazine (antibiotics), triclosan and
88 parabens (PCPs), bisphenol A (plasticizer) and atrazine (pesticide), from water and/or wastewater
89 with high removal performances [21,22]. Up to date, MIP columns have been successfully
90 implemented in the CECs removal from the water matrix, for pre-treatment analytical measurements
91 but only at the lab-scale [23–25], whereas its implementation in WWTPs has yet to be considered. If
92 MIPs features such as particles and pores size, possibility of regeneration for multiple times, high
93 affinity and mechanical and chemical resistance are considered, it is evident that MIP columns have
94 high potential to be integrated in urban water cycle facilities especially in small-scale decentralized
95 WWTPs designed for water reuse. In most cases, effluent water from these innovative wastewater
96 treatment configurations have such a high quality to comply with the minimum requirements for
97 irrigation; but the presence of CECs may strict its potential for reuse. At this point, adsorption
98 columns using MIPs as an advanced treatment may help to overcome this problem and thus to close
99 the water loop in the water-scarce regions by enabling reclaimed water reuse.

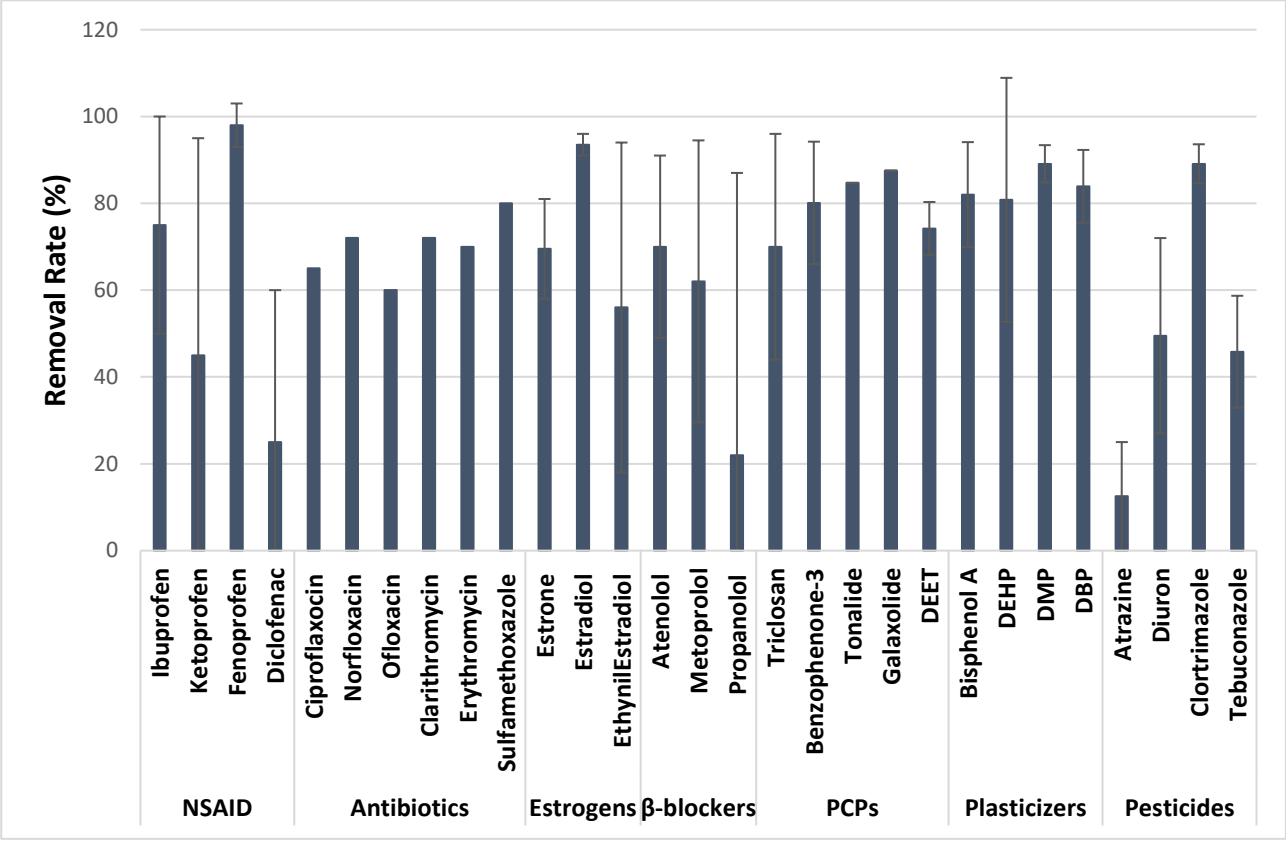
100 In this review paper, a detailed overview of the most common CECs found in wastewater and the
101 current status of their removal techniques from water matrix is initially provided. The adsorption
102 mechanisms of MIPs for enhanced CECs removal from water/wastewater are further presented with
103 their specific applications. Since the up-to-date applications of MIPs are limited to lab-scale, we

104 provide the basic but crucial steps to follow while considering to upscale MIP adsorption columns to
105 pilot scale. Furthermore, innovative ways to integrate MIP columns to real wastewater facilities are
106 introduced with possible demonstrative-scale proposals to ensure the safe reuse of treated effluent for
107 irrigation with respect to the minimum requirements for water reuse of the European Parliament and
108 of the Council [26]. Benefits and drawbacks of the application of MIPs to remove CECs from
109 wastewater are then discussed and possible solutions are presented to enhance the sustainability of
110 MIPs in water reuse systems. The highlights of this paper can support decisions towards further
111 development of MIPs in removing CECs from water environment.

112 **2. Contaminants of emerging concern**

113 CECs, also known as emerging compounds [27], are natural or synthetic chemicals together with
114 their transformation products, frequently detected in water bodies, which are not commonly or only
115 partially monitored in the environment. CECs may cause environmental damage and suspected
116 harmful effects on the ecosystem and human health [3]. The steady release of CECs to the
117 environment has been predicted to be occurring for a long time and through diverse sources [28] with
118 concentrations ranging from μg to ng per liter. The list of compounds and chemicals in the CECs
119 group are significantly large and ever-expanding with the introduction of new commercial chemicals,
120 changes in use, and disposal of chemicals currently in widespread use and further identification of
121 new molecules [29]. Since conventional WWTPs are not designed to remove this wide range of
122 molecules, many of these remain in considerable concentration in the effluents, and subsequently in
123 the surface waters [4]. As shown in **Fig. 1**, many CECs, such as atrazine (pesticides), diclofenac
124 (NSAIDs), propranolol (β -blockers), ethynilestradiol (estrogens), and ciprofloxacin (antibiotics), are
125 characterized by low removal rates in WWTPs and this fact underlines the importance of studying
126 these compounds in depth. However, as highlighted by Ben et al. [30], the type of treatment used in
127 the plant can be favorable for one or more categories of CECs with respect to the others. Moreover,
128 in some cases, by-products that are still harmful to the environment and human health can be formed

129 in these processes as in oxidative treatments. In this section, four main categories of CECs are
130 reviewed that received a particular interest for their frequent presence in water bodies.



131
132 **Fig. 1.** CECs removal rate in percentage by WWTPs [4,30–33].

133
134 **2.1. Pharmaceuticals**

135 Pharmaceuticals represent one of the most critical environmental issues for industrialized countries,
136 due to their widespread use in the treatment of diseases, injuries, or illnesses on humans and
137 veterinary [34,35]. Pharmaceutically active compounds, contained in drugs and medicine, are
138 complex molecules with different functionalities and physicochemical properties to have specific
139 biological activities. Due to their huge number, these compounds are classified in several subclasses,
140 but in this review, emphasis will be given to those categories which are most detected in urban water
141 and wastewater [33].

142 Non-steroidal anti-inflammatory drugs (NSAID) are the most used compounds for pain relief;
143 NSAID-type CECs are often detected in surface water and compounds like ketoprofen, ibuprofen,

144 naproxen, paracetamol, diclofenac, and mefenamic acid are particularly resistant to conventional
145 wastewater treatment methods which are not very effective in their removal [36]. Hormones and
146 estrogens are considered an important emerging contaminant due to their directly disrupt effects on
147 the endocrine systems and long-term persistence of living organisms [37]. Respect to other estrogens,
148 17α -ethinylestradiol is a common female oral contraceptive with endogenous activity [38,39], usually
149 present in wastewater and particularly difficult to remove. Antibiotics are complex organic molecules
150 used for the inhibition and elimination of pathogenic bacteria. The compounds most frequently
151 identified in the environments are amoxicillin, ciprofloxacin, erythromycin, and penicillin [40].

152 **2.2. Personal Care Products**

153 PCPs is a common term used to indicate several products, which can be found and bought without a
154 prescription in health, beauty and drug department stores. The most used CECs in PCPs are organic
155 UV-filters, preservatives and fragrances. The substances in PCPs are generally conjugated to other
156 drugs and pharmaceutical contaminants as in the case of antidandruff shampoo [41]. Among the most
157 detected PCPs in surface water [42], parabens has to be considered; they are chemicals used as
158 preservatives in cosmetics and pharmaceuticals [43]; also triclosan is another compound widely used
159 as an antimicrobial in soaps, deodorants, skin creams, toothpaste, and plastics [44] and commonly
160 detected in surface water [41,45]. Many of these pollutants can enter the organisms through direct
161 ingestion or by absorption through the skin where they can bioaccumulate thanks to their lipophilic
162 nature, are excreted through urine or simply removed by washing them off [46], and eventually end
163 up in aquatic and/or soil environments.

164 **2.3. Plasticizers**

165 Plasticizers consist of clear colorless, oily liquids of low molecular weight generally used as additives
166 to improve flexibility or distensibility to facilitate material handling in the processing and formulation
167 of finished products [47,48]. Based on their chemical structure, plasticizers can be divided into
168 diverse categories [49]; among them, phthalates received a lot of attention due to their wide use and
169 release in water bodies. They are esters of phthalic acid containing a benzene ring with two functional

170 ester groups such as in diethylhexyl phthalate (DEHP), diethyl phthalate (DEP), and dibutyl phthalate
171 (DBP) [50]. Due to their relatively low molecular weight, phthalates can easily migrate and spread
172 into the environment; moreover, because of their lipophilic nature, phthalates can pass through natural
173 barriers such as skin, lung and gut tissue of humans with the consequences of bioaccumulation and
174 biomagnification [51,52].

175 **2.4. Pesticides**

176 Pesticides constitute any mixture of substances that can prevent, destroy, repel, or mitigate a pest; in
177 which fungicides, herbicides, bactericides, and insecticides are the main categories [53] that can be
178 found as pesticides contamination through surface runoff from agricultural areas and wastewater in
179 urban areas [54]. Based on the chemical structure it possible to recognize many sub-classes [55], such
180 as organochlorines (including aldrin and DDT), organophosphates (diazinon and malathion),
181 carbamates (carbaryl and propoxur), triazines (atrazine), and chloroacetamides (metolachlor and
182 alachlor). Unfortunately, since pesticides are stable in the environment, as in the case of
183 organochlorines which have a long environmental half-life, they bioaccumulate in the food chain,
184 and the extensive use of these substances easily cause poisoning through various toxicity
185 mechanisms. Their application in the liquid form contaminates the environment more than their
186 application as a powder [56].

187 **3. Adsorption mechanism of CECs**

188 Advanced treatment technologies have been developed over time to reduce the adverse impacts of
189 pollutants in the environment, such as adsorption, biological, and oxidation processes. Adsorption
190 processes, capable of moving contaminants from one phase (liquid such as water) into another (as
191 solid), have been widely used in the removal of CECs [29,57]. The adsorbing material is called the
192 adsorbent or sorbent, while the substances being adsorbed are the adsorbates; their properties and the
193 interactions occurring between them are quite specific and depend on their composition and chemical
194 nature [58]. The adsorption mechanism involves intermolecular transfer of contaminants onto the
195 solid surface of the sorbent upon physical or chemical interactions. In the physical adsorption process,

different types of interactions such as electrostatic, hydrogen bonds, steric, π - π stacking, Van der Waals forces, and dipole induced dipole interactions are involved. Otherwise, during chemisorption processes, the pollutants are adsorbed through chemical covalent bonds established with the sorbent. Once adsorbed, contaminants are hardly removed from the sorbent which cannot be easily regenerated because of strong forces between them. Chemical adsorption commonly occurs between metallic ions and adsorbents that have several functional groups, whereas for organic contaminants, the main mechanism of interaction would be physical [59]. However, the two processes can occur alternatively but also simultaneously, depending on the type of technology used.

3.1. Definitions and models

In a solid-liquid system, adsorption results in the removal of contaminants from the solution and their accumulation on the solid surface until saturation of the adsorbates capacities; after a certain time of contact, a dynamic equilibrium between the analytes in solution and the analytes adsorbed on the solid phase is established [60]. The relationships between mass of adsorbate adsorbed per unit weight of adsorbent and liquid-phase equilibrium concentration of adsorbate are represented by adsorption isotherms. Several adsorption isotherms were developed and proposed to describe the specific interactions between them, such as Langmuir [61], Freundlich [62], Sips [63], Redlich-Petersen [64] and others. Among these, the most used models to describe adsorbents material in water and wastewater matrices are Langmuir and Freundlich; these isotherms are considered also for Molecularly Imprinted Polymers, even though the adsorption characteristics of these polymers are often estimated from the Scatchard equation [65]. In fact, the Scatchard plot analysis allows to have further information on the affinity of binding sites of MIPs toward each target molecules which can be selectively adsorbed (Eq. 1). The Langmuir adsorption model (Eq. 2) is the simplest one and can be applied when a single adsorbate is adsorbed by a series of energetically equivalent sites on the homogeneous surface of the solid, as in the case of chemisorption process. Otherwise, Freundlich isotherm (Eq. 3), is applicable to adsorption processes that occur on heterogenous surface [66]. The three isotherms model are reported below:

$$\frac{q_e}{C_e} = (q_m - q_e)K_d \quad (1)$$

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (2)$$

$$q_e = K_f C_e^{1/n} \quad (3)$$

where C_e (mg/L) is the concentration of the analyte at the equilibrium, q_e and q_m (mg/g) is the mass of adsorbate per unit mass of adsorbant material, at the equilibrium and at maximum adsorption, respectively; K_l is the Langumir consant (mg/g), K_f is the Freundlich costant (mg/g) and $1/n$ is the exponent of non-linearity; K_d is the Scatchard constant. The main characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor (R_L), Eq. (4):

$$R_L = \frac{1}{1 + K_l C_0} \quad (4)$$

where K_l is Langmuir constant (mg/g) and C_0 is initial concentration of adsorbate (mg/L). Depending on this value, the process is defined unfavorable (when $R_L > 1$), linear (when $R_L = 1$), favorable (when $0 < R_L < 1$), and irreversible (when $R_L = 0$).

A correct understanding and interpretation of the adsorption isotherms is fundamental for a correct interpretation of the relationship between the sorbent material and the adsorbates. The use of the adsorption models can provide a valuable tool to describe molecular recognition by MIPs. Such models may be critical in better understanding MIP behavior in complex systems where more than one adsorbate may simultaneously interact with the surface. In a recent study [67], four isotherm models (Langmuir, Freundlich, Langmuir-Freundlich, and Brunauer Emmet and Teller (BET)) were used to characterize the binding behavior of MIPs in the adsorption of five different phenolic compound: phenol (Ph), 2-methylphenol (2-MP), 3-methylphenol (3-MP), 2-chlorophenol (2-CP), and 4-teroctylphenol (4-OP). Even if MIPs tended to be nearly homogeneous and to have well defined binding sites, in this case the MIP has not only one type of binding site, but similar binding sites in

terms of shape and active functionality which are involved when interacting with a given adsorbate. In fact, the Langmuir and Langmuir-Freundlich models gave the best fitting statistics for Ph, 2-MP, 3-MP, and 2-CP, whereas the recognition of the bigger and more hydrophobic 4-OP was explained only by the BET model, which implies the formation of multilayers adsorption sites; in this latter model the adsorption is based on the assumption that the energy of interactions between the adsorbing species and the surface is strongest in the first layer and decreases for subsequent layers deeper in the polymer matrix.

3.2. Removal of CECs

Many factors affect the adsorption process in a specific real case: surface area, nature and initial concentration of the analytes, temperature, pH solution, nature and amount of adsorbate. In order to remove CECs commonly found in wastewater, tertiary treatments must be implemented with sorbent material of different types. Removal efficiency and adsorption capacity of most common sorbents are summarized in **Table 1**.

Activated carbon (AC) is the most popular and widely used adsorbent in WWTPs. AC, prepared from various sources (e.g. coal, coconut shells, lignite, wood, etc.), is a charcoal physically and chemically treated to increase its adsorptive properties. The inorganic contents, after the pyrolysis process of the organic matter with oxidizing gases, are efficiently extracted from the carbonized material to produce powder (PAC) or granular particles (GAC) with high surface area [68,69]. AC has been considered as an effective adsorbent for treating persistent/non-biodegradable organic compounds such as CECs. Biochar (BC) is a stable source of carbon obtained from biomass, by thermal or hydrothermal processes at high temperature with low or zero oxygen atmosphere, even if according to many authors it is difficult to distinguish BC from AC [70,71]. Similar to AC, BC can be further chemically activated through an acid or basic process which leads to the formation of new functionalities on the surface of the sorbent to enhance the interactions with the contaminants and to increase their adsorption [70,72].

269 Carbon nanotubes (CNTs) are carbon allotropes with a graphite-like structure which displays
270 different adsorption characteristics depending on the degree of coil, the generation of the original
271 sheet, diameter, internal geometry, physicochemical properties and the treatment process used for
272 synthesis [73].

273 Clay minerals are well known natural materials with plastic properties, particles less than two
274 micrometers composed mainly of hydrous-layer silicates of aluminum, though occasionally they may
275 contain magnesium and iron. Because of their low cost, high porosity, and abundance in the
276 environment, clays such as montmorillonite, mica, kaolinite, pyrophyllites (talc), bentonite, and
277 diatomite are good candidates as adsorbents [10]. Numerous other sorbents have also been reported
278 in the literature for removing CECs from water matrices including zeolites, metal oxide, graphene
279 oxide, and polymeric resins [65,74,75]. In this regard, MIPs can be a valuable alternative sorbent
280 thanks to their high selectivity to bind target molecule and their flexibility to couple with different
281 materials to exploit synergic properties, as in the case of MIPs having a core shell of TiO_2 particles,
282 obtained through a surface polymerization, used to remove and photocatalytically degrade the
283 fungicide orto-phenylphenol [76].

284 **Table 1.** Removal efficiency and adsorption capacity of different sorbents.

Matrix	Category	Adsorbent	Sorbent dose (mg/L)	Contaminant	Type of interaction	Isoterm models	Adsorption capacity (mg/g)	Removal (%)	Reference
Hospital Wastewater	Active Carbon	PAC	8, 23, 43	Diclofenac				96, 98, 99	[77]
				Carbamazepine				98, 99, 100	
				Propanolol				91, 94, 94	
				Ciprofloxacin				10, 99, 99	
				Sulfemathoxazole				0, 34, 40	
Acqueous Lab scale		PAC	10.04	Ibuprofen	van der Waals, π - π stacking and hydrogen bonding	Based on the Langmuir and Freundlich model isotherms	12.6	70	[78]
			19.20	Ketoprofen			24.7	88	
			19.78	Naproxen			39.5	90	
			19.28	Diclofenac			56.2	91	
		GAC	1000	Triclosan	Langmuir isotherm	41.5 – 18.5			
Acqueous Solution	Biochar	Acid rice husk	5000	Tetracycline	π - π stacking	Langmuir isotherm	12		[79]
		Alkali rice husk	5000	Tetracycline			29		
Acqueous Solution		N-biochar	2000	Diclofenac	π - π stacking	Langmuir isotherm	231		[80]
				Naproxen			155		
				Ibuprofen			25.3		
		O-biochar	2000	Diclofenac			124		
				Naproxen			147		
		Ibuprofen	14.6						
Acqueous Solution	Carbon Nanotube	MWCNT (O ₂ =2,0%)		Tetracycline		Langmuir isotherm	217.8		[81]
		MWCNT (O ₂ =3,2%)					269.25		

Acqueous Solution		MWCNT (O ₂ =4,7%)		Ciprofloxacin	Langmuir isotherm	217.56			[82]
		MWCNT (O ₂ =5,9%)				210.43			
		MWCNT (O ₂ =2,0%)				150.9			
		MWCNT (O ₂ =3,2%)				178.9			
		MWCNT (O ₂ =4,7%)				206			
		MWCNT (O ₂ =5,9%)				181.2			
Acqueous Solution		SWCNT	1000	Ibuprofene		231	100		[83]
		MWCNT	1000	Triclosan		81	100		
		O-MWCNT				19	97		
		SWCNT				558			
		MWCNT				434			
		O-MWCNT				105			
Acqueous Solution	Clay Mineral	Bentonite	30000	Amoxicilline	elctrostatic	Langmuir and Freundlich	20	88	[84]
Acqueous Solution		Montmorillonite		Trimethoprim	elctrostatic	Langmuir and Freundlich	60	-	[85]
Acqueous Solution		Kaolinite		Ciprofloxacin	elctrostatic			95	[40]
Acqueous Solution		Montmorillonite	1800	Sulfamidethoxine	elctrostatic	Freundelich		13	[86]
				Sulfemathoxazole				10	
				Tetracycline				99	
				Oxytetracycline				90	
Acqueous Solution	Others	Zeolite	20	Ciprofloxacin	dipole dipole and π - π stacking			51	[74]
Acqueous Solution		Fe/Mn	1000	Tetracycline				88	[75]
Acqueous Solution		Gaphene Oxide	181	Tetracycline	π - π stacking and cation- π bonding	Langmuir	313		[87]

Acqueous Solution	MIP	Diclofenac	hydrogen bonding	325	99	[65]
	NIP				15	

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300 4. **Molecularly imprinted polymers**

301 MIPs can be considered analogues of the natural antigen-antibody systems, constituted by synthetic
302 receptors able to retain specific target molecules according to their chemical functionalization. MIPs
303 potentially offer the specificity and selectivity of the biological receptors with the explicit advantages
304 of durability with respect to environmental conditions and low cost.

305 4.1. **Polymerization synthesis**

306 MIPs synthesis is based on the formation of a complex between a target molecule (template) and a
307 monomer, in which one or more functional groups able to interact between them are involved. In the
308 presence of a large excess of a cross-linker, the initiator (in sub-stoichiometric amounts) promotes
309 the formation of radicals and consequently the propagation of the radical polymerization. As the
310 three-dimensional polymer network increases, the polymer loses the solvation by solvent and
311 precipitates in solid form on the bottom of the reaction vessel [88]. After the polymerization process,
312 the template is removed from the polymer through a washing procedure, which varies according to
313 the interactions established between the monomer and the template, leaving specific recognition sites
314 complementary in shape, size, and chemical functionality. Therefore, the resulting polymer
315 selectively recognizes and binds only molecules based on chemical properties similar to the template
316 molecule. Intermolecular interactions, between the target molecule and the functional groups present
317 in the polymer matrix, guide the phenomena of molecular recognition. Similarly, Non-Imprinted
318 Polymers (NIPs) are synthesized in the same way without using the target molecule during the pre-
319 polymerization step and are used as a control to evaluate the efficacy of the polymerization obtained.
320 The occurrence of intramolecular interactions between the monomer and the template before the
321 polymerization process represents a preliminary essential condition for obtaining specific binding
322 sites for the target molecule. We illustrated two main routes (**Fig. 2**) followed for the polymerization
323 which depends on the nature of the pre-polymerization interactions between template and monomer
324 [89]. MIPs can be formed by non-covalent intermolecular interactions, such as hydrogen bonding,
325 ion coupling or dipole interactions, between the target molecule and the monomer, even if non-

specific binding sites can derive from an incorrect stoichiometric relationship between the template molecule and the monomers, thus leading to a reduction in the selectivity and in the efficiency of the synthesized polymer [90].

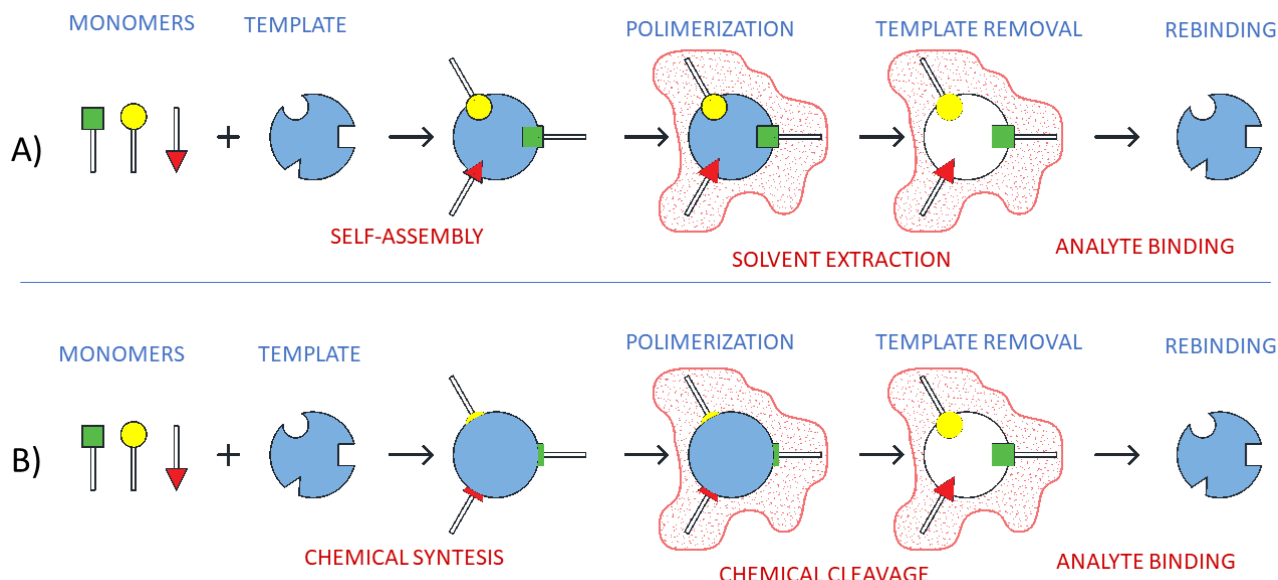


Fig. 2. Polymerization steps of MIPs through **a)** non-covalent **b)** covalent (adapted from [89]).

In the other case, covalent bonds with a defined 1:1 stoichiometry between monomer and template molecules are formed in the pre-polymerization phase. At the end of polymerization, the main issue is represented by the cleavage of the bond and the removal of the template molecules. Therefore, covalently imprinted MIPs must have reversible bonds that can be easily broken, without perturbing their geometry and chemistry which make them appropriate also in real matrices [91].

4.2. Type of synthesis

The main challenge of MIPs technology consists in the synthesis of a suitable polymer for a particular application field, without the disadvantages caused by temperature, pH, interferes and other parameters present in the solution of real matrices. In these last few years, many articles have appeared in the literature about different types of synthesis. Among these, bulk polymerization is the most common and simplest procedure with the reaction carried out in a small amount of solvent to have the precipitation of the polymer as a monolith, which is subsequently crushed and sieved [92].

344 However, this procedure has a low reproducibility, with partial destruction of the selective binding
345 sites during the crushing and the additional risk of losing the most volatile fraction of the polymer or
346 obtaining unwanted particle sizes [93]. A development of the previous method is represented by the
347 precipitation polymerization which requires the use of larger volumes of porogenic solvents [94].
348 Once the critical mass is reached, the polymer is no longer solubilized and precipitates as spherical
349 particles. In this way, the size and the porosity of the spherical particles are easily controlled by
350 choosing the appropriate reaction mixture [95], but with the possibility that the monomer and the
351 template could be irreversibly solubilized causing a partial loss of the reagents and hence a decrease
352 of the polymerization yield [96]. Another option is represented by the emulsion polymerization in
353 which two immiscible solvents are used in the presence of a stabilizing surfactant to obtain small
354 droplets (micelles) inside which the polymerization reaction takes place [97]. A similar procedure,
355 even though more complex, is represented by the Pickering emulsion polymerization [98], where
356 solid particles are used to stabilize the small droplets formed in the mixture of two immiscible liquids,
357 thus eliminating or reducing the dependence on surfactant emulsifiers and making the procedures
358 cheaper. At the end of the polymerization, solid particles must be removed by an additional washing
359 with an appropriate solvent, as in the case of hydrofluoric acid to leach silica nanoparticles [99].
360 Finally, the most innovative type of synthesis can be represented by the surface polymerization which
361 involves the formation of a thin layer of the polymeric material, with its high molecular affinity, on
362 the surface of different types of substrate. In this way, it is possible to exploit also the properties of
363 the physical support; for example carbonanotubes (CNTs) can be used to increase the contact surface
364 [100], Fe_3O_4 to create magnetic microparticles easy to separate [101], TiO_2 to combine photocatalytic
365 processes [76] and SiO_2 to enhance a rapid mass transfer and faster binding kinetics [102,103].
366 Benefits and drawbacks for each type of polymerization useful to MIPs synthesis are summarized in
367 **Table 2.**

368

369 **Table 2.** Benefits and drawbacks of different types of polymerization used to synthesize MIPs.

Type of synthesis	Benefits	Drawbacks
Bulk polymerization	• Simplicity of method makes it possible to perform in any laboratory • Do not require particular skills or sophisticated instrumentation	• Tedious procedures of grinding and sieving • Wastage of useful polymer fraction, irregularly sized particles
Precipitation polymerization	• Nanoparticles size with easy separation. • High surface area	• Low yield of synthesis • Partial loss of the template during the synthesis • High solvent consumption
Emulsion polymerization	• Allows to predetermine the polymer particle size • Formation of spherical particles	• Complicated processes and use of stabilizers and surfactants can contaminate the MIPs • Stabilizers and surfactants are difficult to remove from the resulting MIPs and may generally interfere with the imprinting procedure
Surface polymerization	• Spherical particles, highly reproducible results • Applicable to most imprinting systems, particle size can be adjusted • Features of particles joined to the selectivity of the final polymer	• Complicated procedures and reaction conditions • Substrates can be synthesized too • Bigger particles size

4.3. Solvents, monomers and water compatibility

MIPs represent useful tools which can be exploited for different kind of applications through the control of the polymerization reaction conditions. Among them, the solvent reaction is one of the most important parameters in MIPs synthesis. First of all, it has to solubilize the reagents to favor the polymerization process but without forming strong intermolecular interactions with the monomer and target molecules which could interfere in the pre-polymerization process [104]; for this reason, aprotic solvents (acetonitrile, toluene) are generally used. Moreover, the chosen solvents should be porogenic to favor the formation of larger pores, thus enhancing the contact surface of the obtained polymer. At the same time, the solvent should have chemical properties similar to the matrices in which the polymer will be used, to guarantee a coherent microenvironment that facilitates the retention of the target molecule [105]. The choice of the solvent is also determined from the fact that MIPs have to be used in water matrices but, because of their hydrophobic nature, they have problems

of water compatibility. The use of water mixtures with porogenic solvents during the polymerization [106], of more hydrophilic monomer such as 2-hydroxyethyl methacrylate (HEMA) [107], or the coating of surface nanoparticles with a broad range of functionalities to enhance its hydrophilicity [101] can be useful remedies to this problem. In addition to the factors affecting the solubility of the monomers and templates in the chosen solvent, also the selectivity of the monomers towards the CECs has to be taken into account. For example, methacrylic acid [95] and 2-vinyl pyridine [65] were used in similar synthesis, through precipitation polymerization, for the selective removal of diclofenac but, due to the different chemical interactions between the monomers and the diclofenac, the two obtained polymers exhibited different adsorption efficiencies, around 65 mg/g and 350 mg/g, respectively. Another example is given by Huang et al. [108], who described the synthesis of two different MIPs for the selective extraction of quercetin, through bulk polymerization using two monomers, 4-vinylpyridine (MIP-4VP) and acrylamide (MIP-AM). In this study, two SPE cartridges were filled with the two polymers and sequentially used to increase the selective removal of quercetin from a mixture with other analogue compounds. The adsorption behavior of the two polymers was also investigated and was found that MIP-4VP had a higher adsorption capacity than MIP-AM, 0.4 mg/g and 0.3 mg/g, respectively. With this method it is possible to take advantage not only from the different adsorption ability but also from the adsorption mechanisms of the two MIPs and a different extraction order may influence the binding affinity for quercetin. Considering the above, it is evident that this technology is rather complex but at the same time it has the advantage of being versatile and flexible and by choosing the appropriate reaction conditions it is possible to enhance the affinity and the selective removal for a specific molecule.

4.4. Enhanced removal of CECs via MIPs

The possibility to design micro and nanoparticles with predetermined features has favored the use of MIPs in many applications for the control and removal of CECs. For example, MIPs are widely used in detection and analysis of CECs, as well as sensing [15], sample pretreatment [109], and chromatographic fields [110]. In particular, in the analytical field, these polymers have seen a

409 significant step forward in the samples' pretreatment, which is enriched and eluted in a new solution,
410 avoiding the effects of the real matrix [111]. In this way, MIPs opportunely synthesized can be filled
411 in SPE cartridges (Solid Phase Extraction), called MISPE [112], which can selectively retain specific
412 molecules and subsequently release them after a washing with a different solution for the analysis. In
413 the literature, several examples of MIPs application as adsorbent for CECs in a wide variety of
414 matrices are reported which show that CECs are selectively adsorbed by these MISPE cartridges due
415 to the different binding affinity as reported in **Table 3**. Generally, MIPs' performances are measured
416 in terms of adsorption capacity and selectivity toward a particular target molecule. For the adsorption
417 efficiency, batch tests are usually carried out by using different concentrations of the target molecule
418 with MIPs as well as with NIPs to find the imprinting factor (IF) value, the main indicator of the
419 selectivity properties of the polymer obtained in the synthesis [109]. The selectivity of a polymer
420 toward a particular CEC is usually determined in batch tests performed in the presence of other CECs,
421 as in the case of a polymer for diclofenac removal which was assayed also together with indomethacin
422 and ibuprofen, and was found to have a removal rate of 100% for diclofenac, 57% and 0% for the
423 other two drugs, respectively [93]. In another work by Cantarella and co-workers [92], MIP
424 adsorption specificity toward diclofenac was compared with those toward other compounds as
425 acetylsalicylic acid, trimethoprim and methyl orange and, despite similar physicochemical properties
426 between all the compounds, MIP was able to adsorb 90 % of diclofenac and only less than 20% of
427 the other compounds.

428 Although in MIPs syntheses one specific template molecule is generally used, the sites created in the
429 polymer pores may have a cross affinity also for others compounds with physicochemical properties
430 similar to those of the template. This is a crucial point for many polymers which are produced for the
431 selective binding of a specific molecule but which are able to adsorb in the same binding site also
432 other compounds with a similar chemical structure. In the study of Geng et al. [21], a proprazine-
433 MIP was synthesized by a surface molecular imprinting technique on nano-TiO₂ particles and was
434 found to efficiently adsorb proprazine with an imprinting factor of 16.04. Moreover, this polymer

435 was also able to adsorb simazine and atrazine even if with a lower affinity. In a similar way, Vicario
436 et al. [25] reported a surface polymerization on silica particles to obtain a MIP for the recognition of
437 parabens (PCPs) in swimming pool water. Amount of 25 mg of MIP used with a time contact of 15
438 minutes, it was able to adsorb benzyl paraben with a removal percentage of 85% and, at the same
439 time, also metylparaben and propylparaben with 65% removal in both cases. These results are
440 consistent with the fact that methyl and propyl parabens have similar substituents and hence similar
441 affinity for MIPs particles, while the benzyl groups have higher affinity for MIPs' binding sites.

442 MIPs use for the removal of CECs from real matrices may have some problems and difficult operating
443 conditions. In fact, wastewater is one of the most complicated matrices which can be subjected to
444 MIPs due to the presence of many interferences (i.e. solid particles, high ions concentrations)
445 depending on the prior treatment configuration. MIPs particles may exhibit multiple sorption
446 mechanisms, especially in complex real matrices, due to the coexistence of hydrophobic and
447 hydrophilic structures within the polymer. The hydrophilicity of the binding sites in the core of the
448 particles provides the selective interactions with the target molecule, meanwhile the outer layer can
449 interact with other compounds via hydrophobic interactions and this could induce problems of surface
450 contamination and cause a decrease in the selectivity of the polymer [112]. The need to detect and
451 quantify CECs in wastewater matrices led to the development of new MISPE cartridges with high
452 selectivity for specific class of molecules, rather than for a sole compound. In fact, as said above,
453 similar compounds can access to the same binding sites, even if with different affinities. As reported
454 in the study of Prieto et al. [113], a precipitation polymerization, starting from methacrylic acid
455 (MAA) and ethylene glycol dimethacrylate (EGDMA) as the monomer and crosslinker, and using
456 ciprofloxacin as the template molecule, was carried out to obtain MIPs able to remove selectivity
457 ciprofloxacin, norfloxacin and ofloxacin. In other synthesis, fenopufen [114] and ketopufen [115]
458 were used as the template molecules in bulk polymerizations to obtain MIPs sorbent for SPE able to
459 retain also ibuprofen, in addition to the other two anti-inflammatory drugs. The prepared MISPE
460 could be reused several times through regeneration with an appropriate washing solution.

One of the most important parameters to consider when dealing with aqueous matrices is the pH of the solution, since it substantially modifies the sorbent's adsorption capacity. In fact, pH modifies all the ionizable functional groups present on the adsorbent as well as on the structure of the molecules dissolved in the solution. In this way, the chemical interactions between MIPs and the various CECs may be strengthened or weakened by a change in the pH and hence also the affinity of the binding sites toward the target molecule. For example, in the work of Samah et al. [93], MIPs, produced by bulk polymerization with diclofenac as the target molecule, have a decreased removal efficiency at pH above 3. However, it is not possible to establish a predicted trend for MIPs adsorption capacity toward target molecules with increasing or decreasing pH, as it depends on the most favorable chemical environment in which they are involved. Indeed, Bakhtiar et al. [116] found a decrease in MIPs adsorption capacity of 20% toward 2-phenilphenol when the pH was different from 7. Again, Dai and Cortalezzi [117] reported an increase in the adsorption capacity of a MIPs sensor toward 2,4 di-nitrotoluene as the pH value increased. Other parameters may influence MIPs' adsorption efficiency, even if to a lesser extent than pH, as the ionic strength and the organic matter present in the wastewater. The ionic strength affects has a similar effect to that of pH, in fact it may increase or decrease the adsorption affinity in the binding sites according to the chemical species and to the interactions involved. On the other hand, organic matter acts as interferes on the hydrophilic surface of the polymers reducing their affinity for a target molecule with a decrease in the adsorption efficiency; this type of behavior are reported in several papers where the MIPs are tested with different concentration of humic acid in batch test, where are evaluated their adsorption capacities [117,118].

In addition to the efficiency and selectivity illustrated above, another fundamental point to take in consideration when using MIPS is the possibility of regenerating the absorbent material and reusing it several times, attractive not only to save the material but also in terms of production sustainability. In fact, MIPs can effectively be recycled and used again without losing their performance. In the regeneration step, the molecules adsorbed on the polymer matrix are dissolved and removed by a

487 solvent mixture, able to specifically solubilize the target molecules and to favor their elution.
488 Generally, adsorption and regeneration are performed several times on the same polymer and the
489 adsorption capacities during the cycles are evaluated. As shown by Vicario et al. [25], MISPE
490 cartridges can be reused at least five times with a proper washing step using a solvent mixture of
491 ethanol and acetic acid for the selective extractions of parabens; otherwise a mixture of acetonitrile
492 and acetic acid was used to elute three different NSAIDs, as in the study of Madikizela et al. [24]. In
493 another case, MIPs exhibited an excellent adsorption affinity for five different acidic pharmaceutical
494 compounds used as template molecules, without loss of performance for fifteen regeneration cycles,
495 by the use of methanol and acetic acid with a 9:1 ratio [118].

496 More recently, many articles have appeared in the literature describing a new MIPs' type of synthesis,
497 called Multi-Template, in which several target molecules are used as templates. In this way, it is
498 possible to extract, separate, and detect simultaneously different classes of chemical species, thus
499 increasing MIPs utility and expanding their potential application. In particular, multi-template MIPs
500 are highly desirable for a sustainable development of the processes. An example for NSAIDs multi-
501 template MIPs was reported by Madikizela and Chimuka [24], who used a mixture of naproxen
502 (NAP), ibuprofen (IBU) and diclofenac (DCF) in a 1:1:1 molar stoichiometry: an efficient adsorption
503 was achieved only after 10 minutes, with also good values of IF as 1.25 (NAP), 1.42 (IBU) and 2.01
504 (DCF) while the recovery rates were 38% for NAP, 69% for IBU and 87% for DCF. Another study
505 reported by Dai et al. [118], described a multi-template MIP synthesized by precipitation
506 polymerization for the selective removal of five acidic pharmaceuticals from wastewater. The
507 adsorption of the five compounds was rapid and the binding equilibrium was achieved within 30 min.
508 A decrease in the removal efficiency of five acidic pharmaceuticals by MIP was found in the pH
509 range of 8–10, while with increasing ionic strength from 0 to 30 mmol/L the removal rate increased.
510 For the treatment of large volumes of real matrices and, in particular, of wastewater significant
511 amounts of polymers are needed. It follows that the implementation from the lab scale to the pilot
512 scale is a crucial step which has to consider not only the adsorption capacities of the polymers but

513 also practical and economic issues. In the study of Cantarella et al. [92], a bulk polymerization using
514 methacrylic acid as the monomer was described for an efficient removal of diclofenac from
515 wastewater. Despite the lower adsorption capacity and the reuse cycles seen in previous studies
516 [65,95], 5 mg of MIP were able to remove in 10 minutes ~90% of diclofenac with an initial
517 concentration of 32 mg/L from an aqueous solution, with an adsorption capacity of ~33mg/g. If
518 compared with other type of synthesis, such as emulsion or surface polymerization, synthetic pathway
519 represents a valuable strategy to obtain MIP materials being less time and solvent consuming. The
520 adsorption performances for the selective removal of diclofenac from water suggested that MIPs
521 might be successfully applied for water treatment even on a large-scale application.

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535 **Table 3.** Experimental conditions in CECs recovery/removal from water matrices using MIPs.

Matrix	CECs (Category)	Polymerization reaction condition	Washing method	MIPs evaluation	SPE condition	Regeneration (n)	Concentration of analyte (µg/L)	Ref.
Water and Soil samples	(Pesticides) Propazine Simazine Atrazine	Surface Polymerization Support: APTS-TiO ₂ ; Reagents: Propazine/MAA/EGDMA ; AIBN; Solvent: Toluene 50ml; Conditions: 1°step 50°C, 6h; 2°step 60°C, 12h	Soxhlet extraction: (12h) MeOH:HAc (7:1) Washing: MeOH. Dried: under vacuum 80°C	Time contact: 8h; Film thickness: 25-37µm Adsorption Capacity: 6.8 mg/g Imprinting Factor: 16.04	Sorbent: 200 mg Conditioning: MeOH (5 ml), H ₂ O (5ml); Sample: 20ml Washing: 2ml ACN:H ₂ O (1:4). Elution: 2ml MeOH;	-	Linear Adsorption range: 0-11 mg/L. Recovery %: 91.6–103.3	[21]
Aqueous samples	(Preservants, PCPs) Methylparaben Propylparaben Benzylparaben	Surface Polymerization Support: Silica Particles; Reagents: Benzylparaben/MAA/EGDMA; Benzoyl Peroxide; Solvent: Toluene; Conditions: 60°C, 4h	Repeated Washing: MeOH:HAc (9:1) for 8 times Centrifugation: 5000rpm 15min Final Washing: MeOH	Time Contact: 15min Imprinitig Factor: 1.77;	Sorbent: 25mg Sample: 10ml (flow rate 1 ml/min); Washing: 2ml H ₂ O Ultrapure; Elution: 0.5ml EtOH/HAc (8:2); Cycles: 5 (times)	-	Range: 0.01 to 2.5mg/L; Recovery %: 0.59 (MP), 11.0 (PP), 85.5 (BP);	[25]
Lake Water	(Antibiotics) Sulfadiazine (SDZ) Sulfathiazole (STZ) Sulfamerazine (SMT) Sulfamethazine (SMM) Sulfamethoxazol (SMX) Sulfadoxine (SDX)	Multi-Templates Surface Polymerization Support: VTTS-MGO@mSiO ₂ ; Reagents: Templates/MAA/EGDM A; AIBN; Solvent: Toluene 50ml; Conditions: 1°step 50°C, 12h; 2°step 50°C, 2h	Repeated Washing: MeOH:HAc (9:1) Final Washing: MeOH and dried o.n.;	Time Contact: 15min Imprinitig Factor: 2.47 (SDZ); 2.64 (STZ); 2.32 (SMT); 2.47 (SMM) 2.68 (SMX); 2.40 (SDX);	Sorbent: 20mg Sample stirring: 50ml for 10min; Elution: 2ml MeOH in 6min; Cycles: 5 (times)	-	Conc.: 0.82 (SDZ), 1.11 (STZ), 0.59 (SMT), 1.01 (SMM), 0.87 (SMX), 1.12 (SDX);	[23]
Tap Water	(Plasticizers) Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP) diethyl phthalate (DEP) Dimethyl phthalate (DMP)	Precipitation Polymerization Reagents: DBP/MAA/EGDMA (1:4:20); AIBN; Solvent: ACN (20ml); Conditions: Temp (60°C)	Repeated Washing: MeOH:HAc (9:1) Final Washing: MeOH and dried 4h at 50°C.;	Time Contact: 45min Adsorption Capacity: 22mg/g;	Sorbent: 200mg Conditioning: MeOH (15ml), H ₂ O (15ml); Sample: 15ml Washing: 1ml ACN:MeOH(1:1). Elution: 2ml MeOH;	-	Recovery %: 96 BBP, 94 DEP, 96 DBP, 94 DMP; Conc.: 0.82 (SDZ), 1.11 (STZ), 0.59 (SMT), 1.01 (SMM), 0.87 (SMX), 1.12 (SDX);	[119]

River Water	(Plasticizer) Diethyl hexyl phthalates	Emulsion Polymerization Reagents: DEHP/methacrylamide /N,N_-methylene-bis- acrylamide (2.56/14.1/5.188); Solvents: DMF and H ₂ O (2:8) 10ml and Oil mineral 20ml; Conditions: Temp. (50°C); Time (6h)	Soxhlet: (12h) MeOH Washing: Acetone Dried: Air flow	Surface Area: Time Contact: 5min; Adsorption Capacity: 49.83mg/g; Imprintig Factor: 12.86;	Sorbent: 5 mg (25-38µm) Conditioning: H ₂ O (5ml) Sample: 5.0 ml Elution: CH ₂ Cl ₂ (1ml)	Sorbent: 20 mg Sonication: CH ₂ Cl ₂ (20ml) Time: 30 min Cycles: 6 (times)	Concentration range: 0.035 to 3.0	[120]
Wastewater	(Antibiotics) Ciprofloxacin Norfloxacin Ofloxacin	Precipitation Polymerization Reagents: Ciprofloxacin/MAA/EGD MA (0.11/0.88/2.2); AIBN; Solvent: MeOH (12 ml); Conditions: Temp (60°C)	Ultrasound bath: (12h) MeOH Vacuum Filtered: (8h) MeOH:HAC (1:1) and acetone	-	Sorbent: 100 mg (25-38µm) Conditioning: MeOH /Hac (10ml) 1:1; MeOH (10ml) and H ₂ O (10ml) Sample: 1.6ml Washing: MeOH (ml), H ₂ O (1ml) Elution: MeOH:Hac (1:1, v/v)	-	Influent: 0.697, 1.121, 0.925; Effluent: 2.433, 0.741, 0.567;	[113]
Wastewater	(NSADs) Fenoprofen	Bulk Polymerization Reagents: Fenoprofen/2- VP/EGDMA; CAN; Solvent: DMF and DMSO Conditions: Co ²⁺ as Pivot	Soxhlet extraction: MeOH/HAc (9:1) Washing: MeOH	Surface Area: 1607m ² /g Adsorption Capacity: 38.8 mg/g; Imprintig Factor: 1.86;	Sorbent: 50mg (25-50µm) Conditioning: 3 ml MeOH, 5 ml H ₂ O (pH 5); Sample: 50-200 ml Washing: TEA/H ₂ O Elution: MeOH/EtOH/ACN (1-5ml)	Sorbent: 10mg Elution: TEA/Water Cycles: 5 (times) Water spiked: 50mg/L	Influent: 0.08-0.068 Effluent: 0.47-0.040	[114]
Wastewater	(NSADs) Ketoprofen	Bulk Polymerization Reagents: Fenoprofen/2- VP/EGDMA; CAN; Solvent: ACN/Toluene (1:9) Conditions: 1°step 60°C, 16h; 2°step 80°C, 24h	Repeated Elution: ACN:HAc (9:1) Final Washing: ACN	Surface Area: 207m ² /g Time Contact: 45min Adsorption Capacity: 8.24mg/g	Sorbent: 14mg (25-50m) Conditioning: 1ml MeOH, 1ml H ₂ O; Sample: 50ml (pH 5 flow rate 1ml/min), dried 10min; Washing: 1ml TEA/H ₂ O (5%) Elution: 1ml MeOH	Sorbent: 10mg Elution: 3ml Water and 3ml MeOH; Water spiked: 5µg/L	Influent: 22.5- 34mg/L; Effluent: 1.14- 5.33mg/L	[115]

Wastewater	(NSADs) Naproxen Ibuprofen Diclofenac	<u>Multi-Template Bulk Polymerization</u> <u>Reagents:</u> Multi-Templates/MAA/EGDM A; CAN; <u>Solvent:</u> Toluene (50 + 25ml); <u>Conditions:</u> 1°step 70°C, 8h; 2°step 70°C, 16h	<u>Repeated Elution:</u> ACN:HAc (9:1) <u>Final Washing:</u> ACN	<u>Surface Area:</u> <u>Time Contact:</u> 10min; <u>Adsorption Capacity:</u> 4.47 (NAP), 3.60 (IBU), 5.45 mg/g (DCF); <u>Imprinitig Factor:</u> 1.25 (NAP), 1.42 (IBU), 2.01 (DCF);	<u>Sorbent:</u> 50mg (25-50µm) <u>Sample stirring:</u> 10ml for 10min (pH 2.5); <u>Vacuum Filtration:</u> 2ml MeOH:H ₂ O (1:9). <u>Elution:</u> 2ml ACN:HAc (8:2);	<u>Sorbent:</u> 50mg <u>Elution:</u> 2ml ACN:HAc (8:2); <u>Cycles:</u> 5 (times)	Influent wastewater spiked with 50µg/L per Templates; Recovery % 38 (NAP), 69 (IBU), 87 (DCF);	[24]
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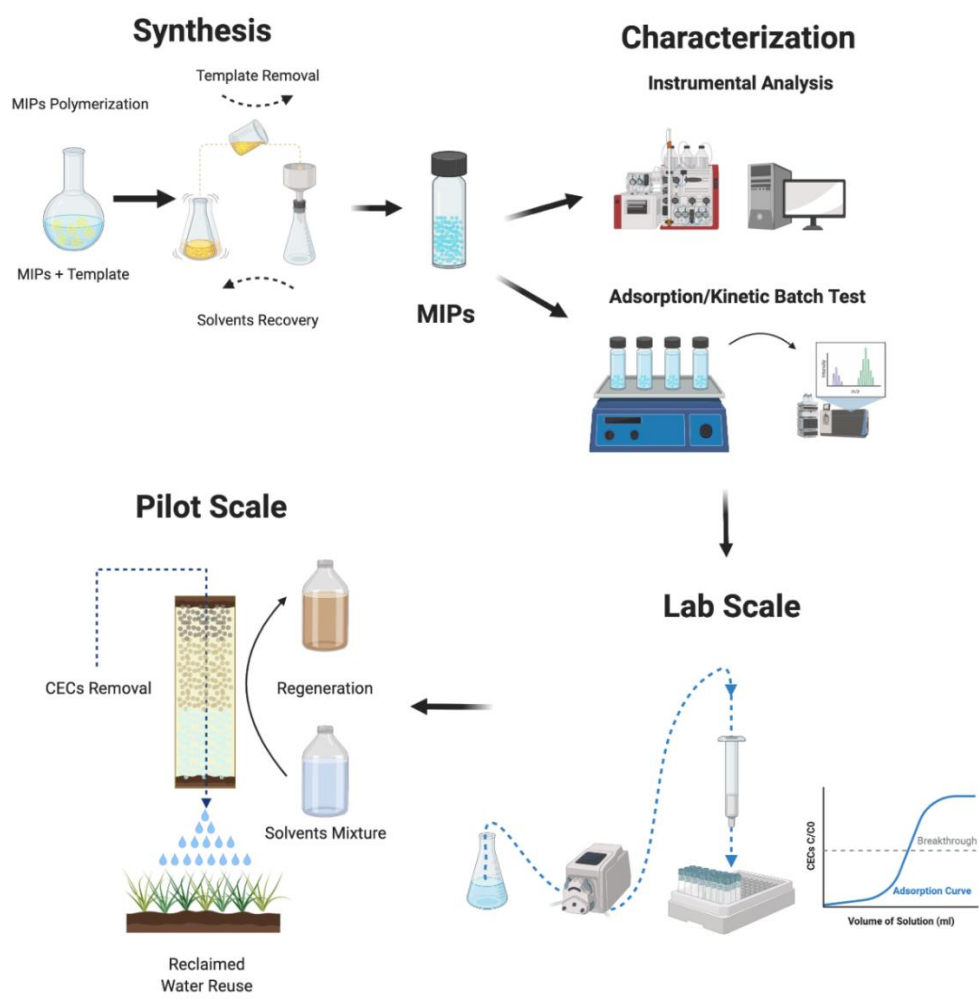
4.5. Upscaling MIP columns: from lab- to pilot-scale

Given their specific selectivity for one or more class of compounds, MIPs are excellent candidates to be implemented in tertiary treatment for the targeted CECs removal. The potential applicability of MIPs on a large scale was highlighted by Cantarella and colleagues [92] based on the extreme selectivity of the adsorption process and the reusability of the material by easy and efficient adsorption/regeneration cycles. Whereas the upscaling behavior of GAC adsorption columns for removing CECs has been tested [121], to the best of our knowledge, no pilot or demonstrative-scale of MIP columns in water and/or wastewater treatment has been done so far and related studies have been limited to lab-scale up to date. Therefore, we provide a basic necessary pathway to follow while upscaling MIPs particles in adsorption columns in real environment. In **Fig. 3**, the scale up route is divided into four main phases. The synthesis and vast production of polymers needs a further scaled-up step to control reaction yields and MIPs property, which must be reproducible and constant. One of the most crucial point is the removal of the template molecule by using large amount of organic solvents (see **Table 3**) per unit mass of polymer produced. Therefore, it is fundamental to find a proper side process to recover these solvents to minimize the environmental impact and to limit the production cost for the overall process sustainability. About this aspect, different methods can be applied to recover solvents: distillation is the most common and well-established technique used to separate solvents from aqueous or other organic mixtures. Due to the high boiling point of many CECs used as templates, the waste solvent can be distilled by heating and recondensation to leave CECs in a small fraction and to recover the recycled solvent. Alternatively, adsorption processes can be used to remove contaminants from the solvent but these procedures are not so feasible with organic matrices mainly constituted by methanol and high concentration of CECs as those obtained from template removal with other adsorbent materials. Finally, membrane processes can be a valuable solution compared to the others due to their inherent simplicity and energy efficiency, avoiding undesirable phase change, as in case of distillation. In the study of Cseri et al. [122], the three processes are compared for the methanol recovery in terms of carbon footprint. The distillation

process has a linear production of CO₂ higher than the adsorption one up to 70% of solvent recovery due to the high energy consumption, above 70% the adsorption process requires excessive amounts of adsorbent because of the highly concentrated solution. Membrane filtrations can be considered the greenest process but, it may be affected by high implementation and maintenance costs which have been considered in the entire MIPs process life cycle assessment. The MIPs' characterization can be done through instrumental analysis and experimental laboratory test. In the first case, chemical information obtained through FTIR and NMR analysis may not give a certain presence or absence of a specific organic compound in a polymer, as well as the orientation in space of the essential functional groups in the pre-polymerization phase. Conversely, Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) and Thermogravimetric Analysis (TGA), provide data on physical properties of the MIPs synthesized, such as surface area and size of pores and particles [111]. In the second step, lab-scale experimental batch tests are conducted to determine the adsorption affinity to different CECs through isotherms analysis and kinetic studies [95]. Successively, continuous flow tests in column are further conducted to verify the best configuration to implement in pilot-scale and to determine the MIPs' properties, when the flow passes through the column. Similarly of GAC or other sorbents material [57,123,124], empty bed contact time (EBCT) is a fundamental parameter to replicate the laboratory conditions on a pilot scale, which represents the time it takes for the flow to pass through the column at given reactor volume and flow rate. Once the optimal conditions are set, the experimental data collected in lab scale must be confirmed through installation of the column, commissioning and long-term validation.

Finally, MIPs adsorption behavior must be verified through the monitoring of CECs concentration in the effluent and evaluate the MIPs regeneration necessity and frequency. Due to the different CECs concentration in the influent and also due the diverse effluent requirements for the discharging or the safe reuse, is not easy to establish a common regeneration procedure. Given the maximum adsorption capacity and designed the best process condition, it is possible to estimate the treatable volume and predict when the break and breakthrough of the column could happen. However, a straight and

590 continuous monitoring of the effluent is necessary to detect the CECs concentration removed by the
 591 treatment. The economic aspects of the technology must be considered, and clearly the MIPs are more
 592 expensive than GAC sorbents concerning the synthesis, while the MIPs are easily regenerated
 593 maintaining their removal performance.
 594 An interesting study by Razali et al. [125], compared seven different adsorption materials for the
 595 treatment of wastewater contaminated by N-methyl-2-pyrrolidone (NMP) and N,N-
 596 dimethylformamide (DMF). Most of the tested adsorbents showed good performances, in particular
 597 MIP, functionalized with phenylboronic acid, showed superior performance being able to adsorb 677
 598 and 502 mmol DMF and NMP per kg adsorbent, respectively. Most of the compared adsorbent were
 599 regenerated up to 10 times without any loss of performance.



600
 601 **Fig. 3.** A possible upscaling pathway for MIPs application to wastewater treatment for enhanced
 602 CECs removal and safe water reuse in irrigation/fertigation.

603 5. Integration of MIP columns to urban water cycle facilities

604 The application of conventional adsorption columns to remove CECs from water has been
605 successfully tested using GAC at pilot-scale [126] and even at full-scale [127]. However, MIPs are
606 more advantageous for treatment of trace contaminants because they can be specifically designed to
607 remove one or a group of target compounds. This is an advantage over nonspecific conventional
608 adsorption technologies such as AC, which may be consumed removing large amounts of non-trace
609 contaminants from the water [7]. As already discussed in previous sections, the degradation/removal
610 of CECs is more likely to be applied using coupled treatment systems which can bridge the
611 deficiencies in a single technology for the removal of these complex contaminants present in the
612 water environment [29]. Various configurations can be developed to integrate MIP columns in urban
613 water cycle facilities for enhanced removal of CECs. One possible configuration for municipal
614 wastewater treatment is proposed in **Fig. 4**, that is currently being developed under the
615 PRIMA/H2020 Project “FIT4REUSE” (fit4reuse.org), to produce a treated effluent that is suitable
616 for reuse in irrigation according to required standards. A MIP column can be easily coupled after the
617 up-flow anaerobic sludge blanket (UASB) and anaerobic membrane bioreactor (AnMBR). The
618 UASB + AnMBR has been an innovative solution for municipal wastewater treatment especially in
619 small-scale decentralized facilities where several advantages such as less energy cost, less fouling,
620 and higher operating organic loading rate (OLR) can be achieved [128]. After a pre-treatment unit
621 followed by a high-rate anaerobic treatment via UASB, AnMBR functions as post-treatment
622 (polishing step) and even guarantees disinfection thanks to microfiltration [129]. The permeate of the
623 AnMBR has often high quality and falls into Class A according to the European Regulation on
624 minimum requirements for water reuse of the European Parliament and of the Council [26] since it is
625 free from suspended solids and pathogens, while its nutrient-rich matrix allows a potential reuse in
626 fertigation [130]. At this point, CECs can be the limiting factor for water reuse and the integration of
627 MIP columns can be a promising solution based on the results obtained from lab-scale studies. The
628 permeate can be introduced to MIP column as an advanced treatment step to enhance the removal of

target CECs. The critical point here is that operating parameters of MIP columns is completely different than that of in other high-rate reactors. For instance, hydraulic retention time (HRT) is typically maintained in the range of 6-18h in UASB [131] and 4-16h AnMBR [132]; whereas, HRT/contact time is usually much lower in a MIP column (3-6min) [13,133]. The reactor volume required for MIPs is therefore very limited compared to others due to much lower contact time needed. In addition to operating conditions, the target CECs can vary with respect to local conditions. For instance, pesticides can be the dominant CECs in rural areas. Accordingly, the needs and characteristics of the pilot area must be clearly defined before the design and implementation of such treatment configuration. An additional disinfection unit (i.e. UV) can be also coupled at the end of the UASB + AnMBR + MIP configuration for a possible post-contamination in the MIP column.

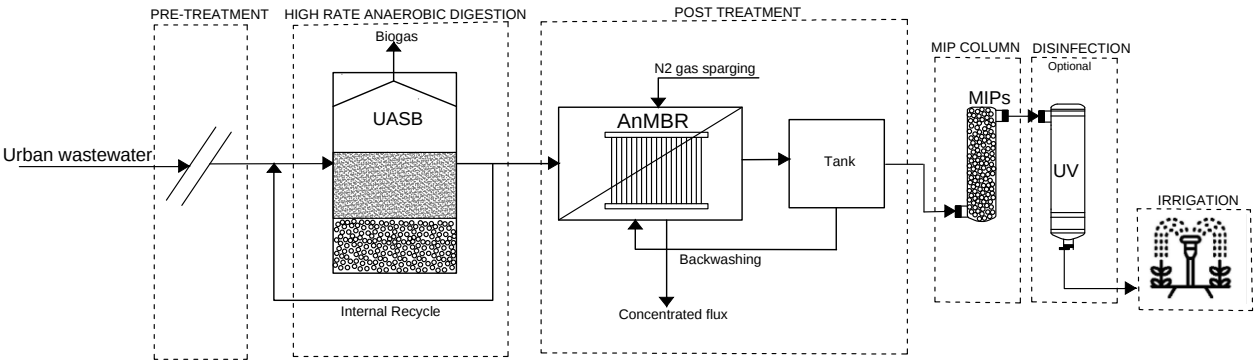


Fig. 4. A possible configuration for integrating MIP columns to urban water cycle facilities for enhanced CECs removal and enabling safe water reuse in irrigation/fertigation. This configuration is currently being developed under the PRIMA/H2020 Project “FIT4REUSE” (fit4reuse.org).

Although MIP columns offer promising applications for advanced wastewater treatment to remove CECs, they have certain limitations for up-scaling regarding cost and applicability. These limitations must be addressed with engineering solutions and at least partially eliminated in order to develop a sustainable urban water cycle framework as discussed in the next section.

650 **6. Sustainability of MIPs in water reuse systems**

651 Next generation wastewater treatment processes must be the best economically, environmentally and
652 socially, so their selection and implementation can be adequate. When developing processes for
653 solving a certain environmental issue, one must be aware that the use of resources and energy by
654 these processes will result in additional environmental burdens [134]. Adsorption columns using
655 MIPs can be a promising technology with elevated removal efficiencies of CECs and without the
656 transformation of products (by-products). However, such adsorption-based processes do not provide
657 a permanent solution since the target pollutants only change phase, so the treatment of the sorbent is
658 also necessary after application. In addition, although having relatively lower cost of preparation
659 compared to membrane technologies, the vast production of MIPs can be quite expensive and difficult
660 which makes their fabrication quite challenging. At this point, NIPs can be favored [7]. Meanwhile,
661 regeneration and subsequent reuse of MIPs/NIPs following their use for water and wastewater
662 treatment can reduce the overall costs of treatment. A life cycle assessment (LCA) and life cycle cost
663 analysis (LCC) should be applied to help with decision making and to provide a detailed overview of
664 the environmental sustainability of these technologies, which is currently lacking in the literature.
665 A possible solution to ease the reproduction of MIPs at demonstrative and/or full-scale can be
666 partially filling the adsorption columns with other materials in addition to NIPs/MIPs. Conventional
667 adsorbents such as PAC or GAC can be used as co-adsorbent; whereas a competitive adsorption and
668 selectivity may occur in the column for the target compounds. Then, MIPs can be saved by using
669 inert materials (such as sand, glass beads, ceramic balls) in the adsorption column, and the efficiency
670 of the adsorption process needs a further optimization of the mixing ratio of the materials.
671 Another point is that since the occurrence of CECs in wastewater is highly variable, a continuous
672 operation of any single unit for the removal of CECs may not be necessary in a treatment
673 configuration. Eventually, the adaptation of contamination sensors can be reasonable since recent
674 developments in sensor technology promise faster screening approaches coupled with effective
675 determination of target contaminants [135]. These systems can be integrated with early warning

676 systems for CECs [136], and thus enable to operate if only the target compound is above a certain
677 threshold concentration. When the concentration of a target CEC is high, these early warning sensor
678 systems can activate the circulation of effluent through the MIP column. Nevertheless, the choice of
679 the most appropriate technology or combination of different technologies vary based on the quality
680 requirements and potential application of the reclaimed water. Considering that most of the total water
681 demand is represented by irrigation (50% to 90%), there is no doubt that these innovative measures
682 can help to address the water scarcity problem in the regions like Mediterranean that face severe water
683 stress in the near future due to climate change.

684 **7. Final remarks and conclusions**

685 With this review paper, we highlight the potential of MIPs to be integrated to urban water cycle
686 facilities to ensure water safety in case the CECs create barriers in practice. Several advantages such
687 as no generation of oxidation or degradation byproducts and high regeneration potential make them
688 promising candidates for future water applications. Up to date, MIPs have been used to recover and/or
689 remove CECs from aqueous solution only at the lab-scale. Thus far, no studies have considered up-
690 scaled application of MIPs in real operative environment. The high selectivity and strong affinity of
691 MIPs to target compounds can replace conventional GAC/PAC based adsorption columns in
692 wastewater treatment. However, the optimization of synthesis steps is crucial to establish vast
693 production of MIPs in a high performance of CECs removal process. In any case when a MIP column
694 is designed to be upscaled and integrated to a wastewater treatment scheme, their sustainability must
695 be ensured. At this point, implementing LCA and LCC of MIPs in a relevant environment is highly
696 recommended, which is currently lacking in the literature since these systems are highly innovative
697 and further research is required.

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