# Emerging Tools for Recognition and/or Removal of Dyes from Polluted Sites: Molecularly Imprinted Membranes

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**Abstract:** Dyes are used in different industries as textile, paper, food processing, cosmetic, leather tanning, rubber, printing and so on. These chemical substances have negative effect on the quality of the water and food, causing human diseases and environmental problems. In view of these aspects, colorant have attracted the interest of the scientists in developing efficient routes for their detection and/or removal from the polluted sites. Although traditional technologies used for removal of dyes are efficient, there is the necessity of developing innovative systems both more cheaply and of easy performance. In this scenario, the integration of the membrane science with the molecular imprinting technology is an alternative way that present many advantages such us the removal or detection of a specific dye or a class of dyes and cost reduction processes. In fact, exploiting the benefits of these two technologies it is possible to develop molecularly imprinted membranes able to recognize a dye of interest in specific mode. This potential is promising for combatting the illegal use of dyes in food, drinks and aquaculture as well as for their removal. The main positive aspects of the imprinted membranes are their chemical stability, reusability, as well as the resistance to the pH and temperature. In addition, their preparation requires short operation time and it is not expensive. All these properties have an encouraging impact in dealing with the problem of dyes contamination.

This short review offers a description of the concept of molecular imprinting, starting from the approach of the synthesis of imprinted polymers until the description of the preparation of imprinted membranes. The application of imprinted polymers and membranes for the detection and/or removal of dyes from polluted sites will be also discussed.

**Keywords:** Specific recognition, molecular imprinting, molecularly imprinted membranes, dyes removal.

## INTRODUCTION

One of the more persistent environmental problems associated to some industrial processes is the removal of colors from effluents before to discharge them into the environment. Dyes are used in different industries as textile, paper, food processing, cosmetic, leather tanning, rubber, printing and so on. As example, textile wastewaters are highly colored and toxic and contain different molecules that belong to many different chemical classes. Colored wastewater is a consequence of batch processes both in the dye manufacturing industries and in the dye consuming industries. There are more than 10,000 commercial dyes with a production of over $7 \times 10^5$ tons per year. About 10-15% of the total production is lost during their synthesis and staining processes. In addition, almost 50% of the initial dyes load in staining industries is present in the dye bath effluents [1]. These pollutants affect the water quality and create human health and ecological problems due to the toxicity and durability of the dyes in wastewater [2]. In particular, colorants are carcinogenic and mutagenic for different fish species. In addition, they cause various damage to human beings as dysfunction of the kidney, liver, brain and central nervous system. Therefore, it is advantageous to develop technologies to remove them from polluted environments. In fact, wastewaters containing dyes and chemical residues need appropriate treatments in relation to the kind of reactive dye present in the effluents. In literature are present some reviews which deal with the different processes employed for the treatment of dyes [3-8]. They include physical, chemical and biological methods, such as flocculation, membrane-filtration, electrochemical techniques, ozonation, coagulation, precipitation, adsorption, fungal decolorization, adsorption and much more. However, the detection and/or removal of dyes by conventional methods result particularly difficult due to their stability to light and resistance to oxidizing agents [9] and operating costs. Owing to these weak points, there is the necessity of developing alternative strategies both more cheaply and of easy performance. In the last years, the development of molecular imprinting technology allowed to produce imprinted polymers and membranes for the selective detection and/or removal of dyes in alternative to the traditional methods. The main advantages of the imprinted membranes are their reusability, chemical stability, as well as the resistance

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to the pH and temperature. In addition, their preparation requires short operation time and it is not expensive. All these features have a positive impact in terms of environmental defense and economic costs.

Dickey *et al.* have highlighted the relation between dyes and molecular imprinting technology. Authors, that are believed to be the inventors of the first imprinted materials, produced imprinted adsorbents of silica gel in the presence of methyl orange (MO) or one of its structural homologues [10, 11]. Later, Wulff and Sarhan [12] and Klots and Takagishi [13], separately, applied this technology to develop imprinted organic network polymers. Since then, molecularly imprinted polymers (MIP) were used as synthetic materials capable to rebind analytes of interest. They were applied in numerous fields such as solid-phase extraction [14], drug delivery [15], sensors [16], chromatography [17], etc.

Generally, for the synthesis of an imprinted polymer three different steps are required. The first step concerns the formation of a complex (*via* covalent or non-covalent interactions) between a target analyte (also named template) and polymerizable functional monomers before polymerization. The second step is the polymerization process that allows to obtain a rigid polymer containing the template. The third step concerns the extraction of the template from the synthesized polymer with the consequent formation of recognition sites that are sterically and chemically complementary to the template.

Different polymerization techniques such as bulk polymerization [18], suspension polymerization [19], emulsion polymerization, two-step polymerization and precipitation polymerization [20] can be used to synthesize MIPs.

The imprinting technique was also applied by the scientists for the preparation of molecularly imprinted membranes (MIMs) [21-26] that can separate and purify a target molecule or selectively recognize an analyte from a mixture of similar compounds. Thanks to their high selective properties, imprinted membranes have potential applications in numerous fields [27-29]. In addition, compared to other processes, separations based on membranes do not require additives, and can be performed isothermally at low temperatures.

This short review provides a description of the concept of molecular imprinting, starting from the approach of the MIP synthesis until the description of

the methods used for the preparation of MIMs. The application of imprinted polymers and membranes for the recognition and removal of dyes from polluted environment will be also discussed.

## THE CONCEPT OF MOLECULAR IMPRINTING

Molecular imprinting technology is a method to introduce molecular recognition sites into synthetic materials reproducing natural recognition elements, such as biological receptors and antibodies [30, 31]. Imprinted materials are widely applied, they are used in drug delivery [32], in affinity separations [33, 34], in clinical diagnostic [35], in catalysis and sensors technologies [36, 37], for the detection of environmental contaminants [38] and much more. Compared with other biological systems imprinted materials are less expensive, stronger, resistant to elevated temperatures and pressures, and are chemically inert [39].

Dickey [10] introduced the concept of molecular imprinting. However, this technique has not received much attention until 1972 when Wulff and Sarhan [13] and Takagishi and Klotz [14] developed organic polymer networks with prearranged ligand selectivity.

The principle of the imprinting is detailed as follows: a polymerization of a monomer occurs in the presence of the target molecules. During the polymerization monomers are spatially positioned around the template with the aid of a cross-linker. The polymerizable monomers must have chemical complementarity with the template to interact with it and forming stable template-monomer complexes. This aspect is fundamental for the success of molecular recognition. The first step of the molecular imprinting process begins with the dissolution of template, functional monomers, cross-linking agent and initiator in a porogenic solvent. The subsequent polymerization step allows to obtain a macroporous polymeric matrix, that has incorporated the template. The removal of the template molecules from the polymer produces recognition sites that are complementary to the template in shape, size and chemical function. The resultant imprinted polymer is able to recognize and selectively bind the template separating it from a mixture of similar chemical compounds [39-42]. Figure **1** reports the scheme of the molecular imprinting process.

The process of molecular imprinting seems to be simple and easy to realize. Anyway, the application of

**Figure 1:** Representation of the molecular imprinting process.

this technique is intricate because of the number of parameters that must be taken into account to obtain a good imprinting effect. Some examples are the appropriate choice of the couple monomer-template and their ratio, the choice of the cross-linker and the ratio cross-linker/functional monomer, the type of solvent, the polymerization conditions and the adopted imprinting strategy. In fact, the homogeneity of the

recognition sites, as well as their spatial orientation, accessibility and stability are strictly related to the chemical and structural properties of the synthesized polymer.

Until now, a large number of templates were used to generate imprinted polymers. Anyway, not all the existing chemical compound are suitable to be



**Figure 2:** Some functional monomers used in MIP synthesis.

imprinted. The choice of the target molecule has a central role because its chemical structure influence the orientation of the functional monomer during the polymerization step. An important factor is the stability of the template, which must be ideally inert under the polymerization conditions, and not be involved into the reaction mechanism [40]. The chemical complementarity between the template and the functional monomer represent also a relevant aspect for achieving a good imprinting effect. In addition, the functional monomer must be in excess with respect to the template.

The chemical structure of the most common functional monomers is shown in Figure **2**.

The sufficient rigidity of a synthesized MIP is guaranteed by the presence of the cross-linker that freezes the nascent polymeric matrix in an appropriate configuration to interact with the template, and so, stabilizing the recognition sites [35, 43, 44]. Usually high cross-linker/functional monomer ratios (80%) are used to produce imprinted materials with satisfactory mechanical stability [45, 46]. However, an extreme excess of the cross-linker can hinder the binding sites because it might be problematic to totally remove the template. This is because of an exacerbate polymer rigidity, thus resulting in polymers with low binding capacity and/or template bleeding phenomenon during

the re-binding step [47, 48]. Moreover, at low cross-linker ratio, the stability of the recognition sites is not preserved owing to low degree of cross-linking of the synthesized MIP [49]. The performance of a MIP is also affected by the type of the cross-linker which should exhibits very few interactions with the template to minimize the formation of non-specific recognition sites [39, 50].

Figure **3** lists some of the most common cross-linkers used for imprinting process.

Ethylene glycol dimethacrylate (EDMA) and trimethalolpropane trimethacrylate (TRIM) are the most commonly used cross-linkers. However, TRIM is viewed to give more rigid and effective binding sites than EDMA [39, 51].

The nature and the volume of the solvent are other two important elements because they influence the morphology and the pore volume of a MIP [44, 52]. In fact, the solvent exert the double function of solvent and pore forming agent. First, the solvent promotes the dissolution of the polymerization reagents and secondly it allows the formation of pores into the polymer network [40]. Referring to the polymer morphology, in the high-diluted polymerizations, the growing polymer occupies only a small part of the total available volume and more small particles/powders with higher surface
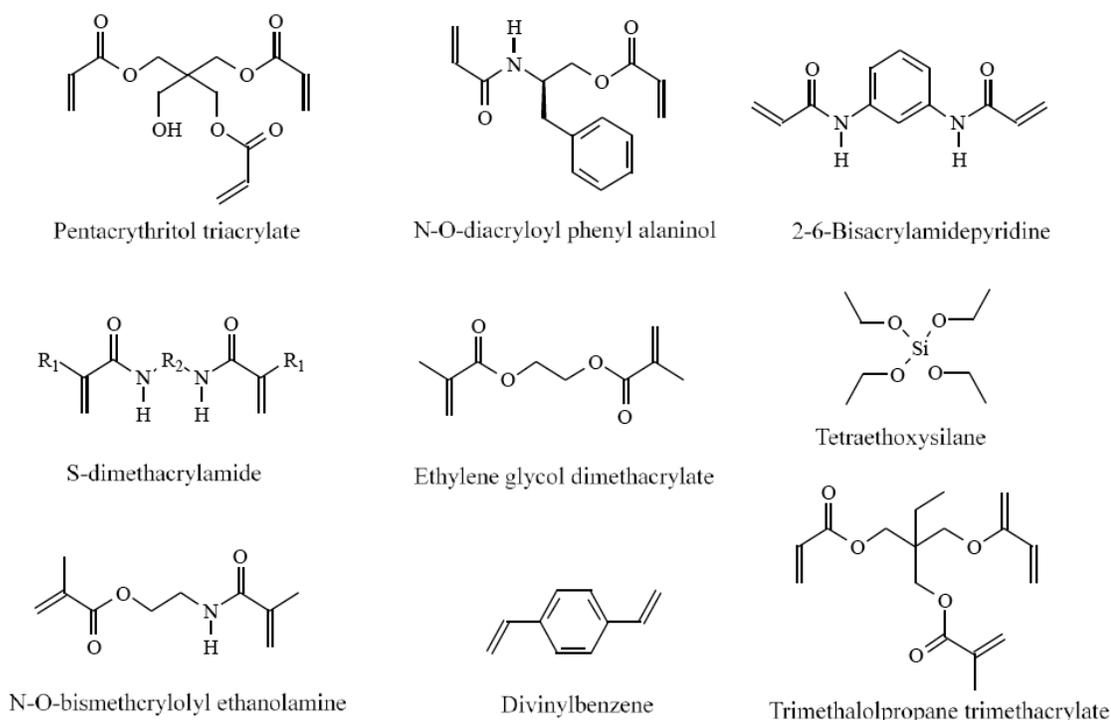


Pentacrythritol triacrylate

N-O-diacryloyl phenyl alaninol

2-6-Bisacrylamidepyridine

S-dimethacrylamide

Ethylene glycol dimethacrylate

Tetraethoxysilane

N-O-bismethcrylolyl ethanolamine

Divinylbenzene

Trimethalolpropane trimethacrylate

**Figure 3:** Classic cross-linkers used in MIP synthesis.

area are produced [44]. The solvent should also promote the template-monomer interactions without interfering with the formation of the pre-polymerization complex.

Molecular imprinting using simultaneously different types and ratios of functional monomers was inspected by Ramström' s group [53]. In this work, three types of terpolymers were prepared by varying the molar ratio of functional monomer to target molecule and using two differents monomeric functionalities in the polymerization mixture. Results of the recognition tests showed as the polymer made with the highest molar ratio of functional monomer to the template exhibited the best separation factor. In addition, the MIPs prepared by two different monomers had better recognition capacity than polymers synthesized using only one functional monomer. In a combination of theoretical and experimental studies, Golker *et al.* [54] correlated for the first time the extent of monomer-template complexation with the composition, the morphology and the recognition performance of the final imprinted polymer. Authors demonstrated that even slight modifications in stoichiometry determine changes in binding site affinity and heterogeneity in synthesized MIP [54].

Baggiani *et al.* [55] proposed an alternative view, which attributes the imprinting effect to the presence of template molecules that increase the pre-existing recognition properties of a non-imprinted polymer (NIP). In this context, authors experimentally confirmed that if a NIP possess recognition properties towards a template, the corresponding MIP will exhibit a substantial imprinting effect. Moreover, if a NIP does not show recognition properties towards the template, the corresponding MIP also will display a weak imprinting effect [55].

Many authors examined the influence of the initiator on the synthesis of imprinted polymers. Mijangos *et al.* synthesized different polymers changing the initiator and polymerization conditions. Results of their experiments revealed as MIPs synthesized at low temperature and quantities of initiators, as well as over a long polymerization time exhibited the best recognition properties [56]. Azonitriles are mostly used as initiators. The 1,1'-azo-bis-(cyclohexyl carbonitrile) (ABCHC) is a superior quality initiator at low temperatures due to its greater solubility in comparison to azo-isobutyronitrile (AIBN) which is the most used. Skudar *et al.* reported that this quality might be an advantage in photochemical initiation of a polymerization process [57].

The chemical structure of some initiators used in MIP synthesis is shown in Figure **4**.

The effect of polymerization temperature on the final performance of the nascent MIP is a parameter that must be also taken into account. Several studies were focused on this aspect [56, 58]. Results of these investigations have highlighted as MIPs synthesized at lower temperatures exhibited greater selectivity with respect to the same polymers prepared at higher temperatures.

Usually, low polymerization temperature allows to better stabilizing the template–monomer pre-polymerization complexes. Nevertheless, higher polymerization temperature promotes the completeness of the polymerization process, which for its part enhances the quantity and quality of the recognition sites [59]. However, an optimal polymerization temperature for each couple template-monomer can be established. Imprinting properties can be conferred to a polymeric material by means of two
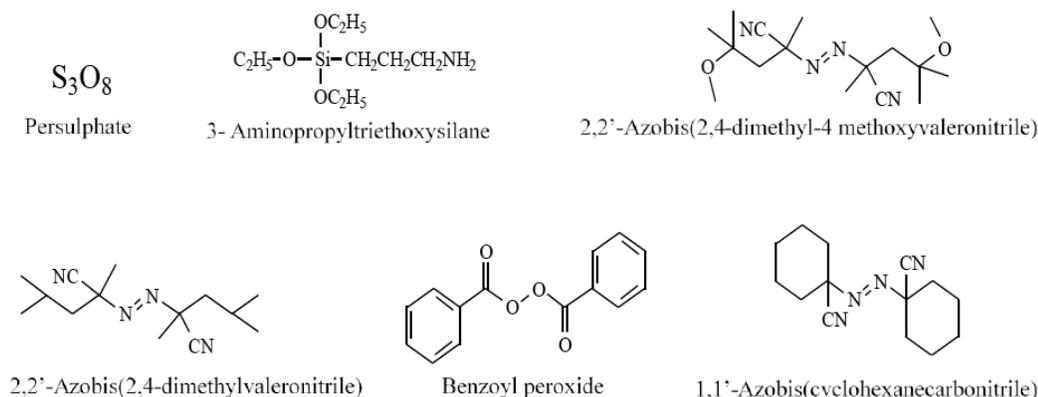


**Figure 4:** Some initiators used in MIP synthesis.

different kinds of interaction: the covalent bond firstly proposed by Wulff, [60] and the non-covalent interaction suggested by Mosbach [61]. The first involves the formation of a reversible covalent bond between the template and the functional monomer in the pre-polymerization mixture. There is then a subsequent chemical cleaving of this bond to remove the template from the polymeric matrix and promote the formation of the recognition sites. During the rebinding step, the template-monomer interactions also take place by means of the same covalent bond. Covalent imprinted polymers are highly stable and selective and favorites the formation of homogeneous recognition sites thanks to the possibility to control the stoichiometry of the process. The second type of interaction relies non-covalent self-assembly template-monomer bonds (*i.e.*, hydrogen, hydrophobic and Van der Waals interactions, metal chelation, *etc.*) before polymerization. After the polymerization step, the removal of the template allows to obtain an imprinted polymer with recognition sites able to re-bind the template *via* the same non-covalent interactions.

Actually, the non-covalent imprinting method is the most popular owing to its easy operation mode and the wide range of functional monomers, which complement every desired template molecule. In addition, this kind of interaction is the basis of the molecular recognition, which take place in living systems [14, 26, 62, 63]. A weakness of this approach is that the non-covalent interactions are less strong than covalent bonds and are ruled by an equilibrium process. Therefore, the functional monomer is used in excess compared to the template to shift the equilibrium versus the formation of the pre-polymerization complex. This can promote a random distribution of the free monomer into the polymer matrix letting the formation of a high number of non-specific recognition sites [64-66].

Problems related to covalent and non-covalent imprinting can be overcome endorsing a combination of the two different methods in a semi-covalent approach. This method, pioneered by Whitcombe [67], exploits the formation of covalent interactions during the imprinting process and the establishment of non-covalent binding during the recognition step.

MIPs are difficult to characterize owing to their insoluble nature. Anyway, some analytical techniques can help to perform chemical and morphological characterizations. They include solid-state magnetic nuclear resonance (NMR) [68], elemental micro-analysis (EDX) and Fourier-transform infrared spectroscopy (FT-IR) [69] which can be applied for the determination of the chemical composition of a polymer. As example, Annamma and co-workers [68] confirmed the incorporation of the crosslinking agent EGDMA and of the functional monomer 4-vynilpyridine in the polymer backbone of a prepared MIP by $^{13}$C NMR spectra.

More often, the presence of the functional monomer in the synthesized polymers is confirmed by FT-IR studies, which allow to compare the spectrum of a single functional monomer with that one of the polymer. In this case, it is possible to follow the shifting or the disappearance of some signals into the polymer with respect to the monomer as results of the polymerization process [62, 69, 70].

Pore size, pore size distribution and specific pore volumes are usually determined by means of morphological characterizations. In particular, the microscopy is used to assess the mechanical integrity of polymer particles and to ascertain the presence of macropores. Nitrogen sorption porosimetry allows determining surface area, pore size distribution and specific pore volume. The method consists in exposing a fixed amount of a dry polymer to a nitrogen at different pressures and constant temperature. The calculation of the adsorbed gas as a function of pressure permits to constructs sorption isotherms from which can be determined the parameters of interest. Mercury intrusion porosimetry gives the same information of the nitrogen sorption porosimetry but it is more sensitive. Literature well details both methods [71-76].

Solvent uptake measurements to determine the specific pore volume of MIPs are also performed. As example, Zhong *et al.* [77] synthesized a MIPs for recognition of levofloxacin. In this work, authors studied the morphology of the polymer particles using the above reported methods. In the same context, Lu and co-workers [78] carried out pore analysis and swelling measurements to investigate the effect of the polymerization temperature on the morphology of three different imprinted polymers. Spivak reviewed the morphological and physical characterization methods of MIPs [79]. Author reported the range of the values for the surface area of a MIP that is between 100 and 400 m$^2$/g. In addition, it was highlighted that the percentage of crosslinking monomer, the type and amount of porogen, and the reaction temperature have a large influence on the surface area and pore distribution.

Sellergren and Shea [80] have carried out a complete characterization of a series of L-phenylalanine anilide (L-PheNHPh) imprinted polymers synthesized by photo and thermal polymerization. The morphology of the polymers varied from gel-like non porous to macroporous. Thermal analysis showed that the first type of polymers resulted more stable than the corresponding macro porous materials. In addition, it was found that a porous polymer is not a prerequisite to obtain an efficient chromatographic imprinted material.

Combinatorial chemistry and theoretical studies were developed by many scientists to investigate the template/monomer complexes. The properties of MIPs were also evaluated and a rational design of these materials was performed. These approaches resulted advantageous, especially in terms of short time, lower cost and safety [81-85]. In this context, Lulińsk et al. [86] have reported the efficacy of the theoretical analysis of pre-polymerization complexes for the dopamine-MIPs. The calculation of the binding energies demonstrated that the complex formed between dopamine and methacrylic acid was more stable (-151.83 kJ/mol) than that formed with acrylonitrile (-49.51 kJ/mol) due to the participation of water molecules in hydrogen bounds [86].

Some publications deal with the application of the density functional theory (DFT) to evaluate the binding energy between monomer and template [87-91]. As an example, Donato et al. [91] performed DFT and ab-initio method of computational molecular modeling to calculate the binding energies of the hydrogen bonds between the template 4,4'-methylendianiline (MDA) and the monomer acrylic acid (AA). The results showed the importance of the solvent in the formation of pre-polymerization complexes and the H- bonds between MDA and AA was (-16.70 Kcal/mol).

Today, molecular imprinting technology is widely applied in many research fields, which have taken advantage of the high specifity and selectivity exhibited by the imprinted materials.

However a valid and realistic contribution to the development of innovative strategies of recognition at molecular level in requested. In this perspective, the preparation on advance functional membranes by means of the introduction of specific recognition sites into their matrix represent an easy route to prepare imprinted materials. In fact, imprinted polymers can be used to develop their special format represented by the molecularly imprinted membranes (MIMs). These latter, have the ability to distinguish between target molecule and other analytes. This property plays a significant part in the transport or retention of particular substances, thus improving the separation efficiency of the typical membrane processes.

## MOLECULARLY IMPRINTED MEMBRANES

The development of membrane technology goes back a long time ago the advent of the molecular imprinting technique and was very successful on a large scale, even on an industrial level [92-94]. A membrane is an interphase between two neighboring phases, which acts as selective barrier regulating the transport of chemical species phase to phase. It can be homogenous or heterogeneous, dense or porous, symmetric or asymmetric, neutral or charged, solid or liquid. The transport of a chemical specie across a membrane can occur by convection or diffusion: In addition, it can be induced by an electric field or by a concentration, pressure and temperature gradient [95]. Blood detoxification [96], waste water treatment [97], controlled drug release [98] enzymatic catalysis [99], food treatment [100] and many more [101-103], represent some examples about the application of membrane science.

The integration of the imprinting technique and of the membrane technology allowed the scientists to obtain molecularly imprinted membranes, with high specific molecular recognition capacity of targeted organic compounds [104-106]. MIMs-based processes can be performed in absence of additives and at low temperature, thus reducing the operating costs. In comparison with classical membranes, MIMs exhibit a better selectivity. In addition, compared to the traditional imprinted polymers, MIMs may operate in continuous processes [107].

The selective separation of a target molecule with a MIM can be obtained by means of two different transport mechanisms: the "facilitated permeation" and the "retarded permeation" of the target analyte. In the first case, a fast permeation of the template through the membrane is obtained thanks to a preferential pathway made via binding to and dissociating from the recognition sites in the membrane. Other solutes shall be submitted to a slower transport. Shan Ping and co-workers [108] gave an example of facilitated permeation. Authors developed composite imprinted membranes using levodropropizine (LDPZ) as the template. In competitive permeation studies the

selectivpity factor LDPZ/l-phenylpiperazine (a structural homologue) was 2.34.

In the case of the second type of transport mechanism slow or no template transport is observed. This phenomenon is due to template's binding affinity with the recognition sites of the membrane. Zhu and co-workers [109] that developed surface molecularly imprinted electrospun affinity membranes for separation of proteins gave an example of the retarded permeation.

Molecularly imprinted membranes can be prepared from organic polymers, as well as from inorganic materials (oxides, ceramics, and metals). They can have a dense or a porous structure and can have a flat-sheet or hollow fiber configuration [96]. Different strategies were exploited for the development of MIMs. Among them, the in-situ cross-linking polymerization was one of the firstly used. Piletsky and co-workers have applied this method to synthesize the first MIM [110]. Authors used the nucleotide adenosine monophosphate (AMP) as the template and acrylate functional monomers. In recognition tests, the template was preferentially permeated through the imprinted membranes. MIMs able to selectively transport L-phenylalanine were also prepared by Marx-Tibbon *et al.* [111]. Authors demonstrated that the value of the template flux was higher compared to other similar molecules such as tyrosine and tryptophan. First membranes produced by the in situ cross-linking polymerization method exhibited low permeability and mechanical stability. This problem was addressed by

Sergeyeva *et al.* [112] that improved mechanical stability and flexibility of MIMs by adding oligo-urethane-acrylate macro-monomer to the polymerization environment containing atrazine as the template. Others improved membrane permeability by adding a pore forming agent to the system. For example, Kimaro *et al.* [113] developed uranyl-ion imprinted membrane using styrene as the monomer and divinylbenzene as the cross-linker. The addition of polyester to the polymer composition promoted the formation of channels that facilitated the transport of ions across the imprinted sites.

The preparation of MIMs is achieved also by means of the phase inversion process, which is a widely used method for the preparation of polymeric membranes. This technique involves the polymer transition from a liquid phase to a solid state. The process can be accomplished by means of two different strategies: the "dry" and the "wet" method [44, 102, 114]. The first one is the simplest way. It consists in casting the polymer solution on an appropriate surface and subsequently to allow the solvent evaporation for obtaining a solid polymeric film. Figure **5** reports a graphic repre-sentation of this method.

This procedure leads to the formation of dense membranes, owing to an increase of the polymer concentration in the forming membrane because of solvent evaporation. The "wet" method is realized by immerging the polymer casted solution in a coagulation bath containing a non-solvent for the polymer. The formation of the membrane is due to a precipitation
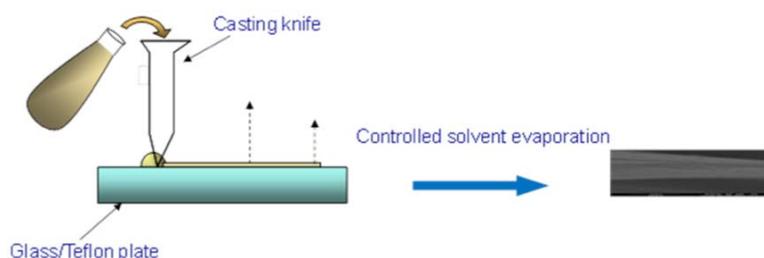


**Figure 5:** Representation of the "dry" phase inversion method used for membranes preparation.
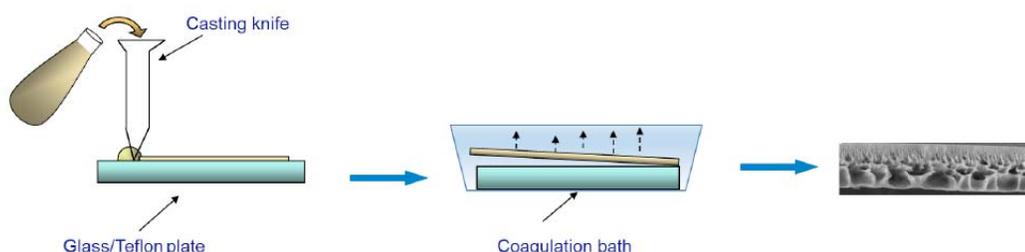


**Figure 6:** Representation of the "wet" phase inversion method used for membranes preparation.

provoked over the contact with the non-solvent. In fact, there is an exchange between the solvent and the non-solvent resulting by diffusion of the non-solvent from the coagulation bath to the cast film and an opposite diffusion of the solvent. Figure **6** shows the "wet" phase inversion process.

Generally, membranes prepared with this method present a porous structure [115].

Yoshikawa *et al.* firstly proposed the "dry" phase inversion for the preparation of MIMs. Authors applied this method for preparing MIMs containing acrylonitrile and styrene as the membrane-forming matrix for tetrapeptide recognition [44, 116-119]. To the other side, Kobayashi and co-workers introduced the "wet" phase inversion method for MIMs preparation. Authors prepared porous membranes using poly(acrylonitrile-co-acrylic acid) as membrane forming material and theophylline as the template [120]. The results of the permeation experiments showed that this membrane have a strong binding capacity towards theophylline. Trotta *et al.* [121], used the same copolymer to produce MIMs as tools for the recognition of the antibiotic tetracycline hydrochloride. Ramamoorthy and Ulbricht [122] used cellulose acetate (CA) and sulfonated polysulfone for the preparation of Rhodamine B-imprinted blend membranes. Silvestry *et al.* developed other MIMs, for clinical application [123]. In this case, Poly(ethylene-co-vinyl alcohol) was chosen as membrane forming material. The production process was carried out in the presence of different template species (phosphatidylcholine, α -amylase). Folic acid, a constituent of the vitamin B, was successfully removed from aqueous media with poly(AN-co-Aamide) imprinted membranes prepared by the phase inversion technique. The membranes exhibited a specific binding capacity of 5.3 $\mu mol/g_{membr.}$ [124]. Tasselli *et al.* [125] investigated the performance of MIMs based on different acrylic copolymers. In particular, poly(acrylonitrile) (PAN), poly(acrylonitrile-co-itaconic acid) P(AN-co-IA), poly(acrylonitrile-co-acrylic acid) P(AN-co-AA) and poly(acrylonitrile-co-Acrylamide) P(AN-co-AAm) were used as membrane forming polymers. The template was the flavonoid naringin. All the prepared membranes displayed good recognition towards naringin. Among them, P(AN-co-AAm)-based membranes exhibited the best overall (12.9 $\mu mol/g_{memb.}$) and specific binding capacity (9.0 $\mu mol/g_{memb}$).

Some other publications (and more) discussed the preparation of MIMs by using this technique [28, 29, 126-134].

The phase inversion process was recently applied for developing MIMs exhibiting both, size exclusion properties and molecular recognition ability during nanofiltration processes [135]. This technique was also exploited to produce hybrid-imprinted membranes. The adopted strategy involves the mixing of a cross-linked imprinted polymer with a supporting polymer that forms the membrane structure during the phase inversion step. Several works deal with the development of this kind of membranes. Takeda and Kobayashi [136] developed four different type of membranes using polystyrene (PS), polysulfone (PSf), nylon 66 (Ny) and cellulose acetate (CA) as polymer matrix. SEM analysis of the resulting hybrid membranes showed that the cross-linked polymers were well embedded into the porous polymeric matrices. Takeda *et al.* also prepared imprinted membranes by hybridization of indole-3-ethanol (IE) imprinted polymer with polysulfone as membrane forming matrix [137]. Divinylbenzene (DVB) was used as the cross-linker. It was observed that the alone imprinted polymer showed non-selective binding towards the template. Conversely, the polymer hybridized with the polysulfone exhibited selective recognition of IE with respect to the structural analogues indole, pyrrole and 8-hydroxyquinoline [137]. Silvestri *et al.* develop polymeric devices containing imprinted nanosphere as a novel approach to improve the recognition of molecules of clinical interest in water [138]. Faizal *et al.* prepared tocopherol-imprinted membranes using polysulfone (PS), cellulose acetate (CA), and nylon (Ny) as scaffold polymers. The investigated membranes showed selective binding and good retention of α-tocopherol with respect to its derivative [139]. More recently, Borrelli and co-workers removed the riboflavin from beer using membranes incorporating imprinted polymer particles [140]. Two different hybrid membranes were also prepared by dispersing in a poly(vinylchloride) (PVC) matrix a MIP synthesized using methacrylic acid or 2-vinylpyridine as functional monomer. Membranes acted as ionophores in a charged carrier mechanism [141]. Similar membranes were produced as new sensing materials for detection of antibiotics [142, 143].

Donato *et al.* [91], hybridized a 4, 4'-methylene-dianiline-imprinted polymer with poly(vinylidene fluoride) (PVDF) for the recognition of this genotoxin in organic medium. MIMs showed high binding capacity (7.5 μmol/g membrane) and exhibited a selectivity factor of 1.82 towards the structural omologue 4,4'-ethylendianiline. Hybrid MIMs were also applied in enantiomeric separation [144], catalysis [145],

separation of flavonoids [146], environment pollution [147] and sensor technology [44].

Many authors used both the photo and the thermal polymerization methods to produce composite imprinted membranes [44]. This type of membranes seems to be attractive particularly in terms of high permeability and good flexibility. Composite MIMs were firstly prepared by Wang *et al.* [148] *via* the UV surface imprinting of a polyacrylonitrile membrane (containing a photosensitive dithiocarbamate group) in the presence of theophylline as the target molecule.

Ulbricht *et al.* [149] produced a composite MIM for recognition of the herbicide desmetryn, using photo-initiated copolymerization of 2-acrylamido-2-methyl1-propane sulphonic acid and N, N′-methylene-bis-acrylamide. They deposited a thin layer of MIP on the surface of PVDF membranes. These membranes exhibited a strong selective binding of desmetryn from aqueous mixtures of herbicides. Others also reported the preparation of composite imprinted membranes for recognizing herbicides [150-153]. Composite MIMs imprinted with S-naproxen were prepared by Donato *et al.* by photo-copolymerization of polypropylene with the functional monomer 4-vinylpiridine [154]. More recently, Wang and co-workers produced S-naproxen-imprinted hollow fibres using PVDF as membrane forming matrix [155]. Authors applied the thermal polymerization. Polyvinylidene substrate was also used for developing composite MIMs towards theophylline [156]. Membranes imprinted with the same molecule were prepared very recently by Ye *et al.* [157]. The MIP was synthesized by thermal polymerization of the monomer methacrylic acid (MAA), the cross-linker ethylene glycol dimethacrylate (EDMA), and 2, 2′-azobisisobutyronitrile (AIBN) as the free-radical initiator. The synthesized MIP was deposited on the surface of α-Al2O3 ceramic microporous hollow fiber membranes. Morphological characterizations of the thin imprinted layer showed a thickness of 1 μm. The membranes allowed to preferentially permeate theophylline rather than the similar compound theobromine. The selectivity factor was 2.63 [157].

In another approach, Tonglairoum *et al.* produced imprinted composite electrospun nanofiber membranes using propranolol as target molecule [158]. In this work, authors imprinted microspheres prepared *via* oil/water polymerization and then incorporated in Eudragit-RS100 nanofibers until up 50% (*w/w*). Methyl methacrylate (MMA) and divinylbenzene (DVB) were chosen as functional monomer and cross-linker,

respectively. Composite MIMs were also developed for the recognition of lovastatin [159], magnolol [160], adenosine 3′,5′-cyclic monophosphate [161], for the detection of water contaminants [42, 44] and many other target molecules [162, 163].

Molecularly imprinted membranes have not only a polymeric nature but in some cases they were manufactured by polymerizing thin polymeric films on the surface of inorganic supports [164, 165]. In this perspective, Kunitake and Lee reviewed the preparation of ultrathins titania gel films obtained *via* the sol-gel imprinting process [166]. During MIMs preparation some drawbacks concern the incomplete availability of the imprinted sites due to their random distribution in the membrane. Moreover, an imprinted membrane having a high number of recognition site and a pore structure suitable for an efficient performance in terms of permeability and separation is difficult to obtain. Despite these weaknesses, imprinted membranes represent the most profitable separation tools at molecular level and possess versatility of application. This short review only reports some examples of a wide variety of MIMs application and it is focused on the development of imprinted polymers and membranes for dyes recognition. However, readers interested in deepening their knowledge on the development and application of the molecular imprinting technique for membranes preparation can refer to suitable literature [39, 42, 44, 92-95, 114, 167].

## DYES

Dyes have attracted many interests recently because of increasingly stringent limitations on the organic content of industrial e*ffl*uents [168]. Over 100,000 commercially dyes are available and more than $7 \times 10^5$ tons of dyes are produced every year [169]. These compounds are present in traces in industrial wastewater but their presence is very dangerous due to their toxic and also carcinogenic effects [170]. Today, they are widely used in the textile, paper, plastic, food and cosmetic industries [171]. Dye molecules depending on their charge are classified in anionic (direct, acid, reactive), cationic (basic) and nonionic (disperse) [172]. Based on their structure, azo-andanthraquinonic-dyes represent the two major classes and together are the 90% of all organic colorants [173]. The color of the dyes is due to the presence of chromophores [174]. A chromophore presents conjugated double bonds giving a configuration of electrons that have the possibility to

absorb certain wavelengths of visible light and transmits or reflects others.

The detection and/or removal of these compounds from industrial effluents include adsorption with organic or inorganic matrices, ionic exchange coagulation, enzymatic decomposition, photocatalysis, and membrane technologies [175].

Organic materials as polysaccharides present very interesting properties as organic adsorbents being low-cost polymers, abundant in nature and renewable resources. However, chitosan and chitin are soluble in acidic media and so cannot be used in this conditions and so physical or chemical modifications are necessary [173]. Chiou and co-workers studied the adsorption capacity of cross-linked chitosan beads of four reactive dyes (RB2, RR2, RY2, RY86), one direct dye (DXR81) and three acid dyes (AO12, AR14, AO7) from aqueous solution [176]. The authors found that the adsorption capacity are affected considerably by the colorant initial concentration, pH and adsorbent dosage. Besides, the cross-linked chitosan, compared to the commercial activated carbon, revealed excellent performance for the anionic dyes. The removal of two dyes Remazol Yellow Gelb 3RS and basic yellow 37 from aqueous solutions were studied by Kyzas and Lozaridis using cross-linked (grafted with carboxyl and amide groups) chitosan as powder o beads [177]. The experimental results indicated as better systems the powder than thee beads. In addition, chitosan grafted with amide groups exhibited superior properties at acid pH, while that grafted with carboxyl groups showed better adsorbent properties at basic pH.

The most popular adsorbent system is an inorganic species: the activated carbon [178]. However, the used is limited for its high cost [179]. The adsorption with these organic and inorganic adsorbents is not selective and so the binding capacity of the supports is reduced [175]. Considering the limitations about the cost, different research groups tried to prepare the activated carbon using cheaper materials. As an example, recently, Sun *et al.* [180] investigated the adsorption of three reactive dyes (reactive red 23, reactive blue 171 and reactive blu 4) on activated carbon prepared from a green alga (Enteromorphas prolifera), which is available in different parts of the world. This study showed as the adsorption of the reactive dyes is pH-dependent and with the maximum of the removal in the pH range of 4.5-6.0. Clay materials are low costs inorganic adsorbents [181]. They exhibited high affinity with cationic and anionic dyes. About these materials, a

problem is that the sorption capacity is pH dependent. Coagulation and flocculation processes are extensively used as pretreatments to remove fine particles and colorants prior the biological treatment being simple and economic [182]. Coagulation is obtained lowering the zeta potential at the surface of the particles and then the interaction of the particles gives agglomerates formation [183]. Various cationic, anionic and non-ionic polymers as coagulants are used. However, different are the problems presents in this process. First, the recycle of the chemicals used during the coagulation. The generation of colored coagulated solid waste, that requires ways and means of legislative disposal [184]. As an example, poly(dimethyl-diallyl ammonium chloride) was mixed with poly(ferric chloride) and used for removing CI disperse blues 79, obtaining 98 % of removal [185].

Physical and chemical treatment methods as for example adsorption and coagulation present some drawbacks as cost, time and release of residues [186]. An alternative to these techniques is the use of enzymes as biochemical route for wastewater treatment [187]. The enzymes degrade the target pollutant without effect on other components. In addition, their environmental impact is very low because of they are biodegradable [188]. The principal enzymes used in this area are: azo-reductases, laccases and peroxidases. Azo reductase catalyze the reaction only in the presence of reducing equivalents as FADH and NADH [189]. It is very important to evidence as in presence of oxygen the reduction is inhibited [186].

Laccases were widely studied for the degradation of azo dyes [190, 191]. In particular, they decolorize these dyes through a non-specific free radical mechanism and at the same time is avoided the formation of toxic compounds [192, 193].

Peroxidases are hemoproteins that catalyze reactions in the presence of hydrogen peroxide [194]. Horseradish peroxidase was used for degrading azo dyes [195]. The experimental results showed as the degradation was dependent on the pH.

Lignin (LiP) and manganese peroxidase (MnP) exhibit similar reaction mechanism. Recently, Zucca and co-workers [196] demonstrated as two immobilized metallo-porphirine (structurally similar to the ligninolytic peroxidase) to bleach six different dyes. The two different enzymes effectively bleached all tested dyes working in mild operating conditions (standard

pressure, room temperature and neutral pH, using no organic solvents).

Hydrogen peroxide ($H_2O_2$) is commonly used to bleach dyes. This process can effectively carried out when $H_2O_2$ is used the presence of Fe (II) [197]. However, direct photolysis and advanced oxidation process such as UV/ $H_2O_2$, UV/Fenton and UV/$O_3$ were also used for the degradation of colorants [198]. Recently, Thomas *et al.* [199] used advanced oxidation processes (as Fenton reaction, $H_2O_2$ photolysis and so on) to degrade the Acid Red 1 (AR1, azo dyes). They demonstrated as the destruction of the AR1 is very efficient but simultaneously it is time consuming. Optimized operating conditions (dye concentration, pH and oxidant dose) were determined for different advance oxidative processes (UV, $O_3$, $H_2O_2$/UV, $O_3$/UV, $H_2O_2$/$O_3$/UV) for the degradation of the Red C1-5B [200]. The experimental results indicated $H_2O_2$/UV process as suitable for the removal of the dye (almost 100 %) in a very short time.

Among the different wastewater treatment technologies, the photo-catalytic oxidation to degrade various dyes and pollutant seems to be an effective treatment technique [201]. The presence of the catalyst increases the rate decomposition [175]. Different research groups studied the photo-catalytic-degradation of different dyes using as catalyst the titanium dioxide ($TiO_2$) [202-205]. This catalyst is used being resistant to chemical and photo corrosion and for its low cost [206]. In addition, it can be recycled [207] and is more active than other semiconductor materials [207]. In recent times, Gupta and co-workers [208] demonstrated as the Amaranth ca be completely degraded by $TiO_2$ sensitized photo-oxidation process using UV radiation. Besides, it was also found the best reaction dosage of titanium oxide (about 0.16 $gL^{-1}$). To improve the catalytic activity efficiency of the $TiO_2$ were added nanoparticles of $SiO_2$ because they created new catalytic active sites [209]. In particular, the photo-catalytic experiments were carried out on aqueous solution of acid red 88 using $TiO_2$ and $TiO_2$-$SiO_2$ nanoparticles irradiating the system for four hours. The results evidenced a dye decomposition of 94% and 97% with $TiO_2$ and $TiO_2$-$SiO_2$ nanoparticles, respectively.

Among the different membranes processes ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are suitable for the treatment of wastewater. In particular, for the removal of dyes RO [210] and NF [211, 212] are considered useful. The use of NF for the removal of different colorants (CI Reactive RED 2, CI Reactive Orange 12, CI Reactive Blue 19, CI Reactive Black 5) was demonstrated [213, 214]. Recently, some researchers studied the treatment of dyes (acid basic and reactive dyes) by applying individual coagulation/flocculation (CF) and nanofiltration (NF) and their combination (CF-NF) [215]. The CF process achieved about 90 % of dye removal. Moreover, for the treatment of multiple dyes wastewater poly(aluminum chloride) is the best coagulant and poly(diallyldimthyl ammonium chloride) the best flocculant. The positively charged NF membranes exhibited a removal of 100 % for anionic and cationic dyes. The combination of CF and NF overcome the limits of individual process. In this last case, the fouling of the membrane is abated and the flux is higher. Reverse osmosis process was also used for the removal of dyes. As an example Mustafa and Nakib [216] demonstrated the possibility to remove two different colorants (direct blue 6 and direct yellow). The maximum of the rejection is 98.89 % and 98.30 % for direct blue 6 and direct yellow, respectively. However, the major disadvantages of NF and RO is the flux decline in the permeate owing to the concentration polarization and fouling. On the other side, the ultrafiltration technique due to the very large pores of the used membranes is suitable only for the removal of high molecular weight and insoluble dyes (as for example indigo) [184]. An interesting route is the combination of the ultrafiltration with the complexation ability of the water-soluble polymer (PAUF). In this year, the recovery of the methylene blue by means of PAU was proved. The experiments showed a high retention (98 %) [217].

## IMPRINTED POLYMERS VS IMPRINTED MEM-BRANES FOR DYES RECOGNITION

Although the above-mentioned technologies used for the detection and removal of dyes are effective, some disadvantageous determine a restriction of their employment. As example, biological treatments present restricted flexibility in design and operation time.

Other drawbacks are the high costs of active carbon and other technologies like electrochemical destruction, ozonation, and photo-catalysis. In the last few years, molecular imprinted polymers and membranes as alternative sorbents for selective detection and/or removal of dyes from polluted environments were proposed. In this scenario, particularly interesting is the possibility of employing molecularly imprinted membranes and/or polymers for the detection of illegal dyes in food and beverages as well as in water used in agricultural field.

The main advantages of the imprinted materials are the reusability, chemical and storage stability, as well as the resistance at temperature and pH. Furthermore, their preparation is low cost and requires short operation time. These properties have a positive impact in terms of economic costs and environment protection. Literature data reported more papers in which MIPs are used for the dyes removal rather than examples of MIMs. This indicates that significant efforts must be done to be able to apply them on large scale in this field. This is because different are the advantages of the membrane technology as the possibility to work in a continuous way and to perform in a single stage separation and removal. Food treatment, aquaculture, textile industry as well as biology and water detoxification represent the most popular fields in which can be envisaged a potential employment of dyes-imprinted materials.

Gong *et al.* [218] employed the imprinting technology to prepare dye-molecular-imprinted microsphere poly(siloxanes) by means of the sol-gel method using disperse red, disperse blue or water-soluble dyes as the template. During absorption studies the imprinted poly(siloxanes) showed high selective recognition properties with respect to the corresponding non-imprinted materials. Later, Yan and co-workers [219] prepared Malachite green-imprinted polymers (MG-MIPS) by the precipitation polymerization method. Methacrylic acid, ethylene glycol dimethacrylate, azobisisobutyronitrile, were used as functional monomer, cross-linker, initiator and porogen, respectively. Malachite green is a dye largely used in aquaculture and dye industries and it has a carcinogen action on rodent liver [220, 221]. Equilibrium sorption experiments performed with MG-MIPS and their corresponding non-imprinted polymers showed that these materials could be used for analytical applications such as separation, determination of traces of MG in water, in soil matrices or in seafood.

Ramamoorthy and Ulbricht [222] applied the imprinting technique to produce polymeric membranes imprinted with the fluorescent dye Rhodamine B, widely used in biotechnology and food areas, exhibiting harmful effects to skin, eyes and brain of humans [223, 224]. The membranes were prepared *via* the phase inversion technique using cellulose acetate-sulfonated polysulfone (CA-SPS) polymer blends. The experimental results showed as cellulose acetate and CA-SPS membranes exhibited high recognition capacity with respect to blank membranes the blank

membranes. The authors stated that the SPS changes the template rebinding capacity.

In 2012, Liu *et al.* prepared imprinted membranes towards the same molecule *via* the electrospinning technique, using polyethylene terephthalate (PET) as membrane forming polymer [225]. Electrospinning technology is a useful method to prepare ultrathin fibers with diameters ranging from a few nanometers to a few micrometers. Owing to their small pore size, high permeability and surface area are good candidate for filtration or adsorption devices [226]. The introduction of specific recognition sites on the surface of electrospun nanofiber membranes offers the possibility to use them as adsorbent materials and separation of a sample from complex mixture solutions. Very recent papers deal with the development of core-shell magnetic imprinted polymers extraction and determination of Rhodamine B residues in food [227, 228].

Refererring to the textile industry, reactive dyes-imprinted polymers were successfully developed by Okutucu *et al.* [229]. Authors, synthesized molecularly imprinted polymers able for selectively recognize of three different dyes: Cibacron Orange P-4R (CR), Cibacron Red P-4B (CO) and Cibacron Black PSG (CB). Batch-rebinding studies allowed to evaluating the adsorption properties of the synthesized materials towards template molecules. The dye-imprinted polymers were used as a solid phase. The adsorption data of the colorants are the following: 45 % for CR, 72% for CO and 65% for CB.

Al-Degs and co-workers [230] prepared Cibacron Reactive Red imprinted polymer and its efficiency was compared with Cibacron Reactive Blu and Cibacron Reactive Yellow structural analogues of the template molecule. The selectivity coefficients (Red dye/dye) were 13.9 and 17.1, compared to Yellow and Blu dyes, respectively. The effect of the imprint was evident for the adsorption of the red dye, which is increased from 24.0 to 79.3 mg g$^{-1}$ after imprinting.

Kyzas *et al.* [231] synthesized two different imprinted polymers for the selective removal of Reactive Red (RR) and Basic Red (BR) from textile waste water. The BR-MIP in organic medium and RR-MIP in aqueous medium were synthesized. The methacrylic acid (functional monomer) and N, N-methylene-bis-acrylamide (cross-linker) were used for the preparation of the RR-MIP, while acrylamide and ethylene glycol di-methacrylate were used for the

**Table 1:  Binding Capacity and Selective Factors of CA-MB-Imprinted and PSf-MB-Imprinted Membranes (Adapted from 231)**

| Membrane | Binding Capacity | | | Selective Factor | |
|---|---|---|---|---|---|
| | MB | MO | FG | MB/MO | MB/FG |
| CA-MB-imprinted | $3.2 \times 10^{-2}$ | $5.43 \times 10^{-3}$ | $2.08 \times 10^{-3}$ | 5.9 | 15.4 |
| PSf-MB-imprinted | $1.5 \times 10^{-2}$ | $4.39 \times 10^{-3}$ | $1.88 \times 10^{-3}$ | 3.41 | 8.0 |

synthesis of BR-MIP. After using in four adsorption-desorption subsequent cycles, MIPs maintained the 90% of their initial adsorption capacity ($\leq 15$ mg/gpol). The experimental data evidenced that pH had effect on the process. In fact, for the BR-MIP the adsorption was better in basic conditions and the high removal (69 %) was performed at pH 10. On the contrary, RR-MIP adsorbed in a better way (90%) at pH 2. In addition, eelectivity studies with simulated and diluted real effluents MIPs displayed high separation factors (40-75) over competitive dyes. These results point out that the synthesized MIPS could be concretely applied [231].

In order to increase the absorption amount of these dyes, the same authors recently prepared two novel MIPs based on β-cyclodextrin (CD-MIPs) and chitosan (CH-MIPs) [231]. The effect of the polymerization conditions on the adsorption capacity and selectivity of the synthesized polymers was evaluated varying polymerization parameters such as the amount of initiator, of functional monomer and of cross-linker. Besides, CD-MIPs exhibited higher binding capacity with respect to CHI-MIPs, for both kind of materials the dye rebinding was up to 35 mg/g$_{pol}$ [232].

Hybrid MIMs was another type of imprinted materials recently prepared by Asman *et al.* [233] for the selective recognition of Methylene Blue (MB) which is widely used in the textile industry as well as in aquaculture and in biology as stain. Membranes were prepared *via* the phase inversion process hybridizing MB-MIP powders into a polymer membrane cellulose acetate (CA) and polysulfone (PSf) as membrane forming materials. Sorption studies evidenced that MB-imprinted membranes were able to remove MB rapidly from contamined solutions (in 60 minutes). Besides, the CA-MB-imprinted membranes exhibited higher binding capacity with respect to PSf-MB-imprinted membranes. All of them were selective toward the structural analogues fast green (FG) and methyl orange (MO). Table **1** reports the binding capacity and the selectivity factor of both kind of membranes.

Aiming to the photo-catalytic degradation of MO present in waste waters, Zhao *et al.* [234] developed imprinted composite membranes using TiO2/calcium alginate hydrogel as supporting matrix. Ethylenetri(β-methoxy) ethyoxysilane (KH-570) and γ-amido-propyl-tri-ethyl-oxysilane (KH-550) were used as functional monomers and methyl orange (MO) as the template. The imprinted membrane adsorbed more dye than the NIP one. In addition, the adsorption rate was very fast. In the same work, imprinting and photo-degradation technologies were coupled to study the degradation of MO and using the methyl red (MT) as competitive molecule. Results demonstrated that the adsorption of MO on imprinted membranes was fast and membranes showed a good selective photo-degradation of MO with respect to the MR. This work demonstrated as the combination of imprinting technology and photo-catalysis can make the water treatment a simple, fast and effective process.

Luo and co-workers also gave an example of water purification using imprinting technology in 2011 [235]. Authors prepared novel hydrophilic molecularly imprinted polymers (mag-MIPs) by an inverse emulsion–suspension polymerization. The 1-(α-methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br) was used as a new functional monomer and MIPs were used for removing five kinds of water-soluble acid dyes from wastewater and soft drink. Compared with traditional solid-phase extraction techniques and their corresponding blanks, MIPs showed higher removal efficiency and selectivity [235]. Results of this work indicated that imprinted materials represent also an efficient way to recycle the water-soluble acid dyes in water media. Imprinted materials aiming the removal of alizarin [236] and carcinogenic polycyclic aromatic hydrocarbons [237] from contaminated waters were also developed.

Another field where the colorants are used is that of the food. However, the use of industrial dyes in food packaging is very dangerous because their biotransformation products are toxic for human body. Therefore, it is extremely important to develop

detection tools for the determination of dyes traces in food. As example, it is very interesting to detect the presence of Sudan I in which is a dye used in the past as food additive but the European Union for its carcinogen action banned it. In this context, Puoci and coworkers [238] synthesized Sudan I-imprinted polymers to discover the illegal use of this compound as an alternative strategy to the traditional and expensive detection methods. In the same perspective and few years later, Baggiani et al. [239] prepared MIPs beads exhibiting selectivity toward Sudan dyes. To avoid the interference of residual template molecules during the rebinding step, a template analogue like 1-(4-chlorophenyl)azonaphthalen-2-ol (chloro-Sudan, 1) was used during the imprinting process. The possibility to detect and quantify traces of Sudan dyes in food matrices was evaluated by extracting some hot chilly pepper samples spiked with different amounts of Sudan I. Results indicated that the analyte recovery rate was more than 80%. In addition, it was possible to measure amounts of dyes lower that to 0.75 µgg-1 in food matrices.

Xu et al. [240] developed MIPs-based surface plasma resonance (SPR) sensor for the detection of the same dye. Authors combined a nanofilm (75 ± 5 nm thick) of molecularly imprinted polymer (MIP) with a SPR. The MIP-SPR sensor exhibited high adsorption capacity and high selectivity versus the dye. In particular, the system showed a linear response for the Sudan I in the range 50-400 ng mL$^{-1}$ with a detection limit of 30 ng mL$^{-1}$ [240].

Sudan dyes were also detected through MIP-coated micro extraction fibers prepared by surface reversible addition–fragmentation chain transfer polymerization [241]. MIP coated fibers revealed enhanced selectivity coefficients (3.0-6.5) for the Sudan I-IV dyes. In addition, coupling the fibers with liquid chromatography and mass spectrometry detection it was possible to reach a limit of 21-55 ng mL$^{-1}$ for the four dyes. Some other publications discussed the removal of Sudan dyes [242-247].

In 2013 Zhan [248] and coworkers synthesized molecularly imprinted polymeric particles (by means of the semi-covalent method) which were used for a fast detection of the azo dye Acid Orange II in food and environmental samples. The produced MIPS were applied for an online solid-phase extraction and a magnetic imprinted solid-phase extraction procedure. For both methods, the recovery rate was more than

70%. Li et al. used another approach, for the preparation of imprinted polymers aiming the detection of Basic Orange II in foods [249]. Modified rosin was used as the cross-linker. Compared with the polymers synthesized using traditional cross-linkers, these new materials exhibited a higher binding capacity and selectivity properties. In samples with a spiked level of 5–11 mg kg$^{-1}$, the average recovery rate of the dyes was in the range of 68–80% with a standard deviation below 1.2%.

Seven water soluble azo-dyes were also recognized and discriminated by Long et al. [250] by means of a multi-channel molecularly imprinted polymer sensor array. The system discriminated each analyte at 100% of accuracy. Furthermore, recognition texts performed on two real samples like spiked chrysoidin in smoked bean curd extract and fanta lime soda (containing tartrazine), the sensor successfully identified the two azo-dyes.

Wang et al. [251] using as the template curcumin, (the principal active components of the Chinese traditional herb Curcuma longa) developed novel composite imprinted membranes. Curcumin has a bright-yellow color and may be used as a food coloring or additive owing to its anti-cancer and anti-oxidation action. Static binding experiments demonstrated that curcumin-imprinted membranes were selective towards the template with respect to the similar compounds dimethoxy-curcumin and bis-dimethoxy-curcumin. Therefore, these membranes might be used as separation tools for curcumin enrichment in food.

An imprinted membranes-based on an electrochemical sensor made-up by magnetic field induced self-assembly of reduced oxide graphene-based composites with $Fe_3O_4$ ($Fe_3O_4$@rGO) was also employed for the detection of amaranth. This work is an example of the creation of electrochemical and biological sensing membrane. The detection of the targeted dye (which is used to confer red color to drinks, syrups and sweets) was attained over the redox probe $K_3[Fe(CN)_6]$ by hindering the recognition sites, thus avoiding the interferences of oxidation products and of structural analogues of amaranth [252].

## CONCLUSIONS

In the last decades, the advent of molecular imprinting technology, endorsed the production of imprinted materials for the selective removal of dyes from polluted sites. In fact, these materials, proposed as specific recognition systems, could be an innovative

and more efficient route with respect to the traditional methods. Dyes are largely used at industrial level, but their content in industrial wastewater is rigorously limited due to the toxic and carcinogen action that they exert on human body.

Although the traditional technologies used for the removal of dyes are proficient, some drawbacks limit their application. For instance, coagulation and flocculation remove dyes from wastewater but the increase of concentrated sludge produced a disposal problem. On their side, biological treatments present limited elasticity in design and operation and require long operation time and large surface area. Other weaknesses are the high costs of active carbon and other technologies like electrochemical destruction, ozonation, and photo-catalysis. In this scenario, the employment of imprinted materials for dyes removal (and/or destruction) results advantageous in solving these kind of problems. Most encouraging characteristic of imprinted materials are the resistance to temperature and pH, the high stability and selectivity as well as their reusability. Furthermore, their preparation requires short operation time and it is not expensive.

Up to now, imprinted materials were applied in different fields, such us drug release, catalysis, blood detoxification, purification of active pharmaceutical compounds an much more. Referring to specific recognition of dyes, imprinted materials were developed for removal of dyes from contaminated food, industrial effluents, aquaculture and other.

Although these innovative tools have widespread potential, a lot of work for optimizing their production and achieving a substantial reduction of this type of pollutants must still be done. Nevertheless, the results so far achieved suggest that the integration of the different knowledge in the development of such systems will ensure a real benefit to humanity.

## REFERENCES

[1]   Maulin PS. On Site Application of Pseudomonas aeruginosa ETL-1942 and bacillus cereus ETL-1949 in decolorization and degradation of remazol black. Int J Environ Biorem Biodeg 2014; 2: 139-45.

[2]   Jadhav JP, Parshetti GK, Kalme SD, Govindwar SP. Decolourization of azo dye methyl red by *Saccharomyces Cerevisiae* MTCC 463. Chemosphere 2007; 68: 394-00. http://dx.doi.org/10.1016/j.chemosphere.2006.12.087

[3]   Banat IM, Nigam P, Singh D, Marchant R. Microbial decolorization of textile-dye-containing effluents: a review. Bioresour Technol 1996; 58: 217-27. http://dx.doi.org/10.1016/S0960-8524(96)00113-7

[4]   Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 2001; 77: 247-55. http://dx.doi.org/10.1016/S0960-8524(00)00080-8

[5]   Fu Y, Viraraghavan T. Fungal decolorization of dye wastewaters: a review. Bioresour Technol 2001; 1979: 251-62.

[6]   Slokar YM, Majcen Le Marechal A. Methods of decolouration of textile wastewaters. Dyes Pigments 1997; 37: 335-356. http://dx.doi.org/10.1016/S0143-7208(97)00075-2

[7]   Pearce CI, Lloyd JR, Guthrie JT. The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes Pigments 2003; 58: 179-96. http://dx.doi.org/10.1016/S0143-7208(03)00064-0

[8]   Sanghi R, Bhattacharya B. Review on decolourisation of aqueous dye solutions by low cost adsorbents. Color Technol 2002; 118: 256-69. http://dx.doi.org/10.1111/j.1478-4408.2002.tb00109.x

[9]   Ramesh B, Parande AK, Raghu S, Kumar TP. Textile Technology. Cotton textile pressing: Waste generation and effluent treatment. J Cotton Sci 2007; 11: 141-151.

[10]  Dickey FH. Specific adsorption. J Phys Chem 1955; 59: 695-07. http://dx.doi.org/10.1021/j150530a006

[11]  Mayes AG. A brief history of the New EraII of molecular imprinting. In Molecularly Imprinted Materials. 1$^{st}$ ed.; Yan N, Ramström O, Eds. Marcel Dekker: New York, NY, USA, 2005; pp. 13-23.

[12]  Wulff, G, Sarhan A. Über die Anwendung von enzymanalog gebauten polymeren zur Racemattrennung. Angew Chem 1972; 84: 364. http://dx.doi.org/10.1002/ange.19720840838

[13]  Takagishi T, Klotz I. Macromolecule-small molecule interactions; introduction of additional binding sites in polyethyleneimine by disulfide cross-linkages. Biopolymers 1972; 11: 483-91. http://dx.doi.org/10.1002/bip.1972.360110213

[14]  Widstrand C, Boyd B, Billing J, Rees A. Efficient extraction of toxic compounds from complex matrices using molecularly imprinted polymers. Am Lab 2007; 39: 23-24.

[15]  Alvarez-Lorenzo C, Concheiro A. Molecularly imprinted polymers for drug delivery. J Chromatogr B 2004; 804: 231–45. http://dx.doi.org/10.1016/j.jchromb.2003.12.032

[16]  Lavignac N, Allender CJ, Brain KR. Current status of molecularly imprinted polymers as alternatives to antibodies in sorbent assays. Anal Chim Acta 2004; 510:139-45. http://dx.doi.org/10.1016/j.aca.2003.12.066

[17]  Nilsson J, Spégel P, Nilsson S. Molecularly imprinted polymer formats for capillary electrochromatography. *J* Chromatog. B 2004; 804: 3-12.

[18]  Milojkovic SS, Dusan K, Comor JJ, Nedeljkovic JM. Radiation induced synthesis of molecularly imprinted polymers. Polymer 1997; 38 (11): 2853-5. http://dx.doi.org/10.1016/S0032-3861(97)85624-8

[19]  Zhang LY, Chend GX, Fu C. Synthesis and characteristics of tyrosine imprinted beads *via* suspension polymerization. React Funct Polym 2003; 56: 167-73. http://dx.doi.org/10.1016/S1381-5148(03)00054-3

[20]  Perez-Moral N, Mayes AG. Comparative study of imprinted polymer particles prepared by different polymerization methods. Anal Chim Acta 2004; 504: 15-21. http://dx.doi.org/10.1016/S0003-2670(03)00533-6

[21]  Piletsky SA, Panasyuk TL, Piletskay EV, Nicholls IA, Ulbricht M. Receptor and transport properties of imprinted polymer membranes, a review. J Membr Sci 1999; 157: 263-78. http://dx.doi.org/10.1016/S0376-7388(99)00007-1

[22] Yoshikawa, M. Molecularly imprinted polymeric membranes. Bioseparation 2002; 10: 277-86.
http://dx.doi.org/10.1023/A:1021537602663

[23] Donato L, Figoli A, Drioli E. Novel composite poly (4vinylpiridine)/polypropylene membranes with recognition properties for (S)-naproxen. J Pharmaceut Biomed Anal 2005; 37: 1003-1008.
http://dx.doi.org/10.1016/j.jpba.2004.09.020

[24] Suedee R, Bodhibukkana N, Tangthong N, Amnuaikit C, Kaewnopparat S, Srichana T. Development of a reservoir-type transdermal enantioselective controlled delivery system for racemic propanolol using a molecularly imprinted polymer composite membrane. J Control Release 2008; 129: 170-78.
http://dx.doi.org/10.1016/j.jconrel.2008.05.001

[25] Donato L, Mazzei R, Algieri C, Piacentini E, Poerio T, Giorno L. Molecular Recognition-driven. Membrane. Processes. In Smart Membranes and Sensors: Synthesis, Characterization, and Applications. Ed Annarosa Gugliuzza, Scrivener Publishing L.L.C. 2014; pp. 269-300.
http://dx.doi.org/10.1002/9781119028642.ch10

[26] Wang JY, Liu F, Xu ZL, Li K. Theophylline molecular imprint composite membranes prepared from poly (vinylidene fluoride) (PVDF) substrate. Chem Eng Sci 2010; 65: 3322-30.
http://dx.doi.org/10.1016/j.ces.2010.02.024

[27] Zayats M, Lahav M, Kharitonov AB, Willner I. Imprinting of specific molecular recognition sites in inorganic and organic thin layer membranes associated with ion-sensitive field-effect transistors. Tetrahedron 2002; 58: 815-24.
http://dx.doi.org/10.1016/S0040-4020(01)01112-7

[28] Donato L, Greco MC, Drioli E. Preparation of molecularly imprinted membranes and evaluation of their performance in the selective recognition of dimethoate. Desalin Water Treat 2011; 30: 171-77.
http://dx.doi.org/10.5004/dwt.2011.1960

[29] Garcia Del Blanco S, Donato L, Drioli E. Development of molecularly imprinted membranes for selective recognition of primary amines in organic medium. Sep Purif Technol 2012; 87: 40-6.
http://dx.doi.org/10.1016/j.seppur.2011.11.018

[30] Ye L, Mosbach K. Molecular imprinting synthetic materials as substitutes for biological antibodies and receptors. Chem Mater 2008; 20: 859-68.
http://dx.doi.org/10.1021/cm703190w

[31] Longo L, Vasapollo G. Molecularly imprinted polymers as nucleotide receptors. Mini-Rev Org Chem 2008; 5: 163-70.
http://dx.doi.org/10.2174/157019308785161620

[32] Puoci F, Iemma F, Picci N. Stimuli-responsive molecularly imprinted polymers for drug delivery: A review. Curr Drug Deliv 2008; 5: 85-96.
http://dx.doi.org/10.2174/156720108783954888

[33] Haginaka J. Monodispersed, molecularly imprinted polymers as affinity-based chromatography media. J Chromatogr B 2008; 66: 3-13.
http://dx.doi.org/10.1016/j.jchromb.2007.07.019

[34] Wei S, Mizaikoff B. Recent advances on noncovalent molecular imprints for affinity separations. J Sep Sci 2007; 30: 1794-05.
http://dx.doi.org/10.1002/jssc.200700166

[35] Piletsky SA, Turner NW, Laitenberger P. Molecularly imprinted polymers in clinical diagnostics-future potential and existing problems. Med Eng Phys 2006; 28: 971-977.
http://dx.doi.org/10.1016/j.medengphy.2006.05.004

[36] Li W, Li S. Molecular imprinting A versatile tool for separation, sensors and catalysis. Adv Polym Sci 2007; 206: 191-10.
http://dx.doi.org/10.1007/12_2006_105

[37] Morelli I, Chiono V, Vozzi G, Ciardelli G, Silvestri D, Giusti P. Molecularly imprinted submicronspheres for applications in a novel model biosensor-film. Sens Actuators B 2010; 150: 394-01.
http://dx.doi.org/10.1016/j.snb.2010.06.046

[38] Pichon V, Chapuis-Hugon F. Role of molecularly imprinted polymers for selective determination of environmental pollutants-A review. Anal Chim Acta 2008; 622: 48-61.
http://dx.doi.org/10.1016/j.aca.2008.05.057

[39] Vasapollo, G. Del Sole, R, Mergola, L, Lazzoi MR, Scardino A. Molecularly imprinted polymers: Present and future prospective. Int J Mol Sci 2011; 12: 5908-5945.
http://dx.doi.org/10.3390/ijms12095908

[40] Cormack PAG, Elorza AZ. Molecularly imprinted polymers: synthesis and characterization. J Chromatogr B 2004;m 804: 173-82.

[41] Shelke CR, Kawtikwar PS, Sakarkar DM, Kulkarni Nikhil P. Synthesis and characterization of MIPs-a viable commercial venture. Pharmaceutically. Review, 6(5), (http://www.pharmainfo.net/reviews/synthesis-and-characterization-m,ips-viable-commercial-venture) (Accessed on Jan 2010).

[42] Trotta F, Biasizzo M, Caldera F. Molecularly Imprinted Membranes. Membranes 2012; 2: 440-77.
http://dx.doi.org/10.3390/membranes2030440

[43] Yan H, Row KH. Characteristic and Synthetic Approach of Molecularly Imprinted Polymer. Int J Mol Sci. 2006; 7: 155-78.
http://dx.doi.org/10.3390/i7050155

[44] Algieri C, Drioli E, Guzzo L, Donato L. Bio-Mimetic Sensors Based on Molecularly Imprinted Membranes. Sensors 2014; 14: 13863-13912.
http://dx.doi.org/10.3390/s140813863

[45] Yungerman I, Srebnik S. Factors Contributing to Binding-Site Imperfections in Imprinted Polymers. Chem Mater 2006; 18: 657-63.
http://dx.doi.org/10.1021/cm050598f

[46] Li J, Wei G, Zhang, Y. Molecularly imprinted polymers as recognition elements in sensors. In Molecularly Imprinted Sensors: Overview and Applications. Li S, Ge Y, Piletsky, SAA, Lunec J, Eds. Elsevier: Amsterdam (Netherlands) 2012; pp. 35-55.
http://dx.doi.org/10.1016/B978-0-444-56331-6.00002-5

[47] Toufaili, FAE, Brüggemann VA. Screening combinatorial libraries of molecularly imprinted polymer films casted on membranes in single-use membrane modules. J Chromatogr B 2004; 840: 135-39.
http://dx.doi.org/10.1016/j.jchromb.2004.02.016

[48] Hilal N, Kochkodan V, Busca G, Kochkodan O, Atkin BP. Thin layer compositemolecularly imprinted membranes for selective separation of cAMP. Sep Purif Tec 2003; 31: 281-89.
http://dx.doi.org/10.1016/S1383-5866(02)00205-8

[49] Chen L, Xu S, Li J. Recent advances in molecular imprinting technology: current status, challenges and highlighted applications. Chem Soc Rev 2011; 40: 2922-42.
http://dx.doi.org/10.1039/c0cs00084a

[50] Yoshimatsu K, Reimhult K, Krozer A, Mosbach K, Sode K, Ye L. Uniform molecularly imprinted microspheres and nanoparticles prepared by precipitation polymerization: The control of particle size suitable for different analytical applications. Anal Chim Acta 2007; 584: 112-21.
http://dx.doi.org/10.1016/j.aca.2006.11.004

[51] Kandimalla, VB, Ju H. Molecular imprinting a dynamique technique for diverse applications in analytical chemistry. Anal. Bioanal. Chem. 2004, 380, 587-605.
http://dx.doi.org/10.1007/s00216-004-2793-9

[52] Kobaiashi MA, Tate M, Rix C, Jakubov TS, Mainwaring DE. The effect of molecular imprinting on the pore size distribution of polymers. Adsorption 2007; 13: 315-21.
http://dx.doi.org/10.1007/s10450-007-9062-0

[53]    Ramström O, Andersson LI, Mosbach K. Recognition sites incorporating both pyridinyl and carboxy functionalities prepared by molecular imprinting. J Org Chem 1993; 58: 7562-64.
http://dx.doi.org/10.1021/jo00078a041

[54]    Golker K, Karlsson BCG, Olsson GD, Rosengren AM, Nicholls IA. Influence of Composition and Morphology on Template Recognition in Molecularly Imprinted Polymers, Macromolecules 2013; 46: 1408-14.
http://dx.doi.org/10.1021/ma3024238

[55]    Baggiani C, Giovannoli C, Anfossi L, Passini C, Baravalle P, Giraudi G. A Connection between the Binding Properties of Imprinted and Non imprinted Polymers: A Change of Perspective in Molecular Imprinting, J Am Chem Soc 2012; 134: 1513-18.
http://dx.doi.org/10.1021/ja205632t

[56]    Mijangos I, Navarro-Villoslada F, Guerreiro A, Piletska E, Chianella I, Karim K, Turner A, Piletsky S. The Influence of Initiator and Different Polymerisation Conditions on the Performance of Molecularly Imprinted Polymer, Biosens Bioelectron 2006; 22: 381-87.
http://dx.doi.org/10.1016/j.bios.2006.05.012

[57]    Skudar K, Bruggemann O, Wittelsberger A, Ramstrom O. Selective recognition and separation of β-lactam antibiotics using molecularly imprinted polymers. Anal Comm 1999; 36: 327-31.
http://dx.doi.org/10.1039/a905151a

[58]    Piletsky S.A, Mijangos I, Guerriro A, Piletska EV, Chianella I, Karim K, Turner APF. Macromolecules 2005; 38: 1410-14.
http://dx.doi.org/10.1021/ma048021r

[59]    Lu Y, Li C, Wang X, Sun P, Xing X. Influence of polymerization temperature on the molecular recognition of imprinted polymers. J Chromatogr B 2004; 804: 53-9.
http://dx.doi.org/10.1016/j.jchromb.2003.10.013

[60]    Wulf G. Molecular inprinting in cross-linked materials with the aid of molecular template-A way towards artificial antibodies. Angew Chem Int. Ed. Engl 1995; 34: 1812-32.
http://dx.doi.org/10.1002/anie.199518121

[61]    Mosbach K. Molecular imprinting. Trends Biochem Sci 1994; 19: 9-14.
http://dx.doi.org/10.1016/0968-0004(94)90166-X

[62]    Tasselli F, Donato L, Drioli E. Evaluation of molecularly imprinted membranes based on different acrylic copolymers. J Membr Sci 2008; 320: 167-72.
http://dx.doi.org/10.1016/j.memsci.2008.03.071

[63]    Chen L, Xuand S, Li J. Recent advances in molecular imprinting technology: current status, challenges and highlighted applications. Chem Soc Rev 2011; 40: 2922-42.
http://dx.doi.org/10.1039/c0cs00084a

[64]    Piletska EV, Guerriero AR, Whitcombe MJ, Piletsky SA. Influence of the polymerization conditions on the performance of molecularly imprinted polymers. Macromolecules 2009; 42: 4921-928.
http://dx.doi.org/10.1021/ma900432z

[65]    Wang CC, Lee W.C. Chromatographic characteristics of cholesterol-imprinted polymers prepared by covalent and non-covalent imprinting methods. J Chromatogr A 2002; 962: 69-78.
http://dx.doi.org/10.1016/S0021-9673(02)00559-9

[66]    Garcia R, Cabrita MJ, Costa Freitas AM. Application of Molecularly Imprinted Polymers for the Analysis of Pesticide Residues in Food-A Highly Selective and Innovative Approach. Am J Anal Chem 2011; 2: 16-25.
http://dx.doi.org/10.4236/ajac.2011.228119

[67]    Whitcombe MJ, Rodriguez ME, Villar P, Vulfson EN. A new method for the introduction of recognition site into polymers prepared by molecular imprinting: synthesis and characterization of polymer receptors for cholesterol. J Am Chem Soc 1995; 117: 7105-111.
http://dx.doi.org/10.1021/ja00132a010

[68]    Annamma KM, Mathew B. Design of 2,4-dichlorophenoxy acetic acid imprinted polymer with high specificity and selectivity. Mater Sci Appl 2011; 2: 131-40.

[69]    Del Sole R, De Luca A, Catalano M, Mele G, Vasapollo G. Non covalent imprinted microsphere: Preparation, evaluation and selectivity of DBU template. J Appl Polym Sci 2007; 105: 2190-197.
http://dx.doi.org/10.1002/app.26208

[70]    Nor AY, Siti K, Rahman A, Hussein MZ, Nor AI. Preparation and Characterization of Molecularly Imprinted Polymer as SPE Sorbent for Melamine Isolation, Polymers 2013; 5: 1215-1228.
http://dx.doi.org/10.3390/polym5041215

[71]    Westermarck S. Use of mercury porosimetry and nitrogen adsorption in characterisation of the pore structure of mannitol and microcrystalline cellulose powders, granules and tablets: thesis (2000) University of Helsinki Finland.

[72]    Allen T. Particle size measurement, 5Th Ed. Chapman & Hall New York (USA) 1997 p. 251.

[73]    Carli F, Motta A. Particle size and surface area distributions of pharmaceutical powders by microcomputerized mercury porosimetry. J Pharm Sci 1984; 73: 197-03.
http://dx.doi.org/10.1002/jps.2600730213

[74]    Brown SM, Lard EW. A comparison of nitrogen and mercury pore size distributions of silicas of varying pore volume. Powder Technol 1974; 9: 187-90.
http://dx.doi.org/10.1016/0032-5910(74)80031-8

[75]    Conner WC, Cevallos-Candau, JF, Weist EL, Pajares J, Mendioroz S, Cortés A. Characterization of pore structure: Porosimetry and sorption. Langmuir 1986; 2: 151-54.
http://dx.doi.org/10.1021/la00068a006

[76]    Webb PA, Orr C. Analytical methods in fine particle technology. Micromeritics Instrument Corp. Norcross, GA (USA) 1997; p. 301.

[77]    Zhong DD, Liu X, Pang QQ, Huang YP, Liu ZS. Rapid preparation of molecularly imprinted polymer by frontal polymerization. Anal Bioanal Chem 2013; 405: 3205-214.
http://dx.doi.org/10.1007/s00216-013-6722-7

[78]    Lu Y, Li C, Wang X, Sun P, Xing X. Influence of polymerization temperature on the molecular recognition of imprinted polymers. J Chromatography B 2004; 804: 53-59.
http://dx.doi.org/10.1016/j.jchromb.2003.10.013

[79]    Spivak DA. Optimization, evaluation, and characterization of molecularly imprinted polymers. Adv Drug Deliver Rev 2005; 57: 1779-794.
http://dx.doi.org/10.1016/j.addr.2005.07.012

[80]    Sellergren B, Shea KJ. Influence of polymer morphology on the ability of imprinted network polymers to resolve enantiomers J Chromatography 1993; 635: 31-49.
http://dx.doi.org/10.1016/0021-9673(93)83112-6

[81]    Liu Y, Wang F, Tan T, Lei M. Study of the properties of molecularly imprinted polymers by computational and conformational analysis. Anal Chim Acta 2007; 581: 137-46.
http://dx.doi.org/10.1016/j.aca.2006.08.015

[82]    Dineiro Y, Menendez I, Blanco-Lopez MC, Lobo-Castanon MJ, Miranda-Ordieres AJ, Tunon-Blanco P. Computational predictions and experimental affinity distributions for a homovanillic acid amolecularly imprinted polymer. Biosens. Bioelectron 2006; 22: 364-371.
http://dx.doi.org/10.1016/j.bios.2006.03.027

[83]    Piletska EV, Turner NW, Turner APF, Piletsky SA. Controlled release of the herbicide simazine from computationally designed molecularly imprinted polymers. J Control Release 2005; 108: 132-39.
http://dx.doi.org/10.1016/j.jconrel.2005.07.016

[84]    Wie S, Jakusch M, Mizaikoff, B. Capturing molecules with templated materials-Analysis and rational design of molecularly imprinted polymers. Anal Chim Acta 2006; 578; 50-58.
http://dx.doi.org/10.1016/j.aca.2006.06.077

[85]  Riah S, Eynollahi S, Ganjali MR, P. Norouzi. Computational Approach to Investigation of Template/Monomer Complex in Imprinted Polymers; Dinitrobenzene Sensor. Int J Electrochem Sci 2010; 5: 509-16.

[86]  Lulińsk P, Maciejewska D, Bamburowicz-Klimkowska M, Szutowski M. Dopamine-Imprinted Polymers: Template-Monomer Interactions, Analysis of Template Removal and Application to Solid Phase Extraction. Molecules 2007; 12: 2434-449.
http://dx.doi.org/10.3390/12112434

[87]  De Luca, G, Donato L, García Del Blanco S, Tasselli F, Drioli E. On the cause of controlling affinity to small molecules of imprinted polymeric membranes prepared by noncovalent approach: A computational and experimental investigation. J Phys Chem B 2011; 115: 9345-351.
http://dx.doi.org/10.1021/jp2006638

[88]  Pietrzyk A, Kutner W, Chitt R, Zandler ME, D'Souza F, Sannicolò F, Mussini PR. Melamine acoustic chemosensor based on molecularly imprinted polymer film. Anal Chem 2009; 81: 10061-070.
http://dx.doi.org/10.1021/ac9020352

[89]  Lattach Y, Archirel P, Remita S. Influence of the chemical functionalities of a molecularly imprinted conducting polymer on its sensing properties: Electrochemical measurements and semiempirical DFT calculations. J Phys Chem B 2012; 116: 1467-481.
http://dx.doi.org/10.1021/jp2071524

[90]  Prasad BB, Rai G. Study on monomer suitability toward the template in molecularly imprinted polymer. An ab initio approach. Spectrochim Acta Part A-Mol Biomol Spectros 2012; 88: 82-89.
http://dx.doi.org/10.1016/j.saa.2011.11.061

[91]  Donato L, Tasselli F, De Luca G, Garcia Del Blanco S, Drioli E. Novel hybrid molecularly imprinted membranes for targeted 4,4'-methylendianiline. Sep Purif Technol 2013; 116: 184-91.
http://dx.doi.org/10.1016/j.seppur.2013.05.027

[92]  Ho WSW, Sirkar K. Membrane Handbook, Kluwer Academic Publishers, Dordrecht 1992.
http://dx.doi.org/10.1007/978-1-4615-3548-5

[93]  Ulbricht M. Membrane separations using molecularly imprinted polymers. Review. J Chromatography B 2004; 804: 113-25.
http://dx.doi.org/10.1016/j.jchromb.2004.02.007

[94]  Charcosset C. Membrane processes in biotechnology: An overview. Biotech Adv 2006; 24: 482-92.
http://dx.doi.org/10.1016/j.biotechadv.2006.03.002

[95]  Baker RW. Overview of Membrane Science and Technology, Membrane Technology and Applications. John Wiley & Sons Chichester (UK) 2012; p. 1-14.
http://dx.doi.org/10.1002/9781118359686.ch1

[96]  Vienken J. Membranes in Hemodialysis, in Membranes for the Life Sciences. Edited by Klaus-Viktor Peinemann and Suzana Pereira Nunes WILEY-VCH Verlag GmbH & Co. KGaA 2008.

[97]  Hou DY, Wang J, Qu D, Luan ZK, Zhao CW, Ren XJ. Desalination of brackish groundwater by direct contact membrane distillation. Water Sci Tech 2010; 61: 2010-13.

[98]  Algieri C, Drioli E, Donato L. Development of Mixed Matrix Membranes for Controlled Release of Ibuprofen. J Appl Polym Sci 2013; 128: 754-60.
http://dx.doi.org/10.1002/app.38102

[99]  Donato L, Algieri C, Rizzi A, Giorno L. Kinetic study of tyrosinase immobilized on polymeric membrane. J Memb Sci 2014; 454: 346-50.
http://dx.doi.org/10.1016/j.memsci.2013.12.029

[100]  Kim JH, Koros WJ, Paul DR. Effects of $CO_2$ exposure and physical aging on the gas permeability of thin 6FDA-based polyimide membranes: part 2 with crosslinking, J Membr Sci 2006; 282: 32-43.
http://dx.doi.org/10.1016/j.memsci.2006.05.003

[101]  Cassano A, Donato L, Drioli E. Ultrafiltration of kiwi fruit juice: Operating parameters, juice quality and membrane fouling, J Food Eng 2007; 79: 613-21.
http://dx.doi.org/10.1016/j.jfoodeng.2006.02.020

[102]  Drioli E, Romano M. Progress and new perspectives on integrated membrane operations for sustainable industrial growth. Ind Eng Chem Rev 2001; 40: 1277-300.
http://dx.doi.org/10.1021/ie0006209

[103]  Pala P, Sikdera J, Royb S, Giorno L. Process intensification in lactic acid production: A review of membrane based processes. Chem Eng Prog 2009; 48: 1549-59.
http://dx.doi.org/10.1016/j.cep.2009.09.003

[104]  Piletsky SA, Piletskaya EV, Panasyuk TL, Elskaya AV, Levi R, Karube I, Wulff G. Imprinted membranes for sensors technology: opposite behavior of covalently and noncovalently imprinted membranes. Macromolecules 1998, 31, 2137-40.
http://dx.doi.org/10.1021/ma970818d

[105]  Kobayashi T, Fukaya T, Abe M, Fujii N. Phase inversion molecular imprinting by using template copolymers for high substrate Langmuir 2002; 18: 2866-72.
http://dx.doi.org/10.1021/la0106586

[106]  Yang HH, Zhang SQ, Yang W, Chen XL, Zhuang ZX, Xu JG, Wang XR. Molecularly imprinted sol-gel nanotubes membrane for biochemical separations. J Am Chem Soc 2004; 126: 4054-5.
http://dx.doi.org/10.1021/ja0389570

[107]  Wang P, Hu W, Su W. Molecularly imprinted poly(methacrylamide-co-methacrylic acid) composite membranes for recognition of curcumin. Anal Chim Acta 2008; 615: 54-62.
http://dx.doi.org/10.1016/j.aca.2008.03.040

[108]  Shan PX, Yun L, Li QS, Al Qin L. Preparation and Recognition Properties of Levodropopizine Molecularly Imprinted Composite Membranes. Adv Mat Res 2011; 355: 399-401.

[109]  Tao Zhu, Dan Xu, Yiguang Wu, Jian Li, Meimei Zhou, Tian Tian, Yin Jiang, Fengting Li, Guangtao Li. Surface molecularly imprinted electrospun affinity membranes with multimodal pore structures for efficient separation of proteins, J Mater Chem B 2013; 1: 6449-6458.
http://dx.doi.org/10.1039/c3tb20973c

[110]  Piletsky SA, Dubei IY, Fedroyak DM, Kukhar VP. Substrate-selective polymeric membranes: selective transfer of nucleic acid components. Biopolym. Kletka 1990; 6: 55-58.
http://dx.doi.org/10.7124/bc.00028D

[111]  S Marx-Tibbon, I Willner. Photostimulated polymers: A light-regulated medium for transport of amino acids. J Chem Soc Chem Commun 1994; 10: 1261-62.
http://dx.doi.org/10.1039/c39940001261

[112]  Sergeyeva TA, Piletsky SA, Brovko AA *et al*. Conductometric sensor for atrazine detection based on molecularly imprinted polymer membrane. Analyst 1999; 124:331-34.
http://dx.doi.org/10.1039/a808484j

[113]  Kimaro A, Kelly LA, Murray GM. Molecularly imprinted ionically permeable membrane for uranyl ion. Chem Comm 2001; 14: 1282-83.
http://dx.doi.org/10.1039/b103077a

[114]  Ulbricht, M. Advanced functional polymer membranes. Polymer 2006: 47: 2217-262.

[115]  Joong KP, Jeong IS. Characteristics of Phenylalanine Imprinted Membrane Prepared by the Wet Phase Inversion Method. Korean J Chem Eng 2002; 19(6): 940-48.
http://dx.doi.org/10.1007/BF02707215

[116] Yoshikawa M, Izumi J, Kitao T, Sakamoto S. Molecularly imprinted polymeric membranes for optical resolution. J Membr Sci 1995; 108:171-75.
http://dx.doi.org/10.1016/0376-7388(95)00160-8

[117] Yoshikawa M, Izumi J, Kitao T. Alternative molecular imprinting, a facile way to introduce chiral recognition sites. React Funct Polym 1999; 42: 93-102.
http://dx.doi.org/10.1016/S1381-5148(98)00063-7

[118] Yoshikawa M, Ooi T, Izumi J. Alternative molecularly imprinted membranes from a derivative of a natural polymer, cellulose acetate. J Appl Polym Sci 1999; 72: 493-99.
http://dx.doi.org/10.1002/(SICI)1097-4628(19990425)72:4<493::AID-APP5>3.0.CO;2-U

[119] Yoshikawa M, Izumi J, Guiver MD, Robertson GP. Recognition and selective transport of nucleic acid components through molecularly imprinted polymeric membranes. Macromol Mater Eng 2001; 286: 52-59.
http://dx.doi.org/10.1002/1439-2054(20010101)286:1<52::AID-MAME52>3.0.CO;2-R

[120] Kobayashi T, Wang HY, Wang, Fujii N. Molecular Imprinting of Theophylline in Acrylonitrile-acrylic Acid Copolymer Membrane. Chem Lett 1995; 24: 927-28.
http://dx.doi.org/10.1246/cl.1995.927

[121] Trotta F, Baggiani C, Luda MP, Drioli E, Massari T. A molecular imprinted membrane for molecular discrimination of tetracycline hydrochloride. J Membr Sci 2005; 254: 13-19.
http://dx.doi.org/10.1016/j.memsci.2004.11.013

[122] Ramamoorthy M, Mathias U. Evaluation of molecularly imprinted polymer blend filtration membranes under solid phase extraction conditions. Sep Purif Technol 2004; 39: 211-19.
http://dx.doi.org/10.1016/j.seppur.2003.12.005

[123] Silvestri D, Barbani N, Coluccio ML, Pegoraro C, Giusti P, Cristallini C, Ciardelli G. Poly(ethylene-co-vinyl alcohol) Membranes with Specific Adsorption Properties for Potential Clinical Application. Sep Sci Technol 2007; 42: 2829-47.
http://dx.doi.org/10.1080/01496390701558292

[124] Donato L, Tasselli F, Drioli E. Molecularly imprinted membranes with affinity properties for folic acid. Separ Sci Technol 2010; 45: 2273-79.
http://dx.doi.org/10.1080/01496395.2010.510089

[125] Tasselli F, Donato L, Drioli E. Evaluation of molecularly imprinted membranes based on different acrylic copolymers. J Membr Sci 2008; 320: 167-72.
http://dx.doi.org/10.1016/j.memsci.2008.03.071

[126] Trotta F, Drioli E, Baggiani C, Lacopo D. Molecular imprinted polymeric membrane for naringin recognition. J Membr Sci 2002; 201: 77-84.
http://dx.doi.org/10.1016/S0376-7388(01)00705-0

[127] Pegoraro C, Silvestri D, Ciardelli G, Cristallini C, Barbani N. Molecularly imprinted poly(ethylene-co-vinyl alcohol) membranes for the specific recognition of phospholipids. Biosens Bioelectron 2008; 24: 748-55.
http://dx.doi.org/10.1016/j.bios.2008.06.050

[128] Faizal CK.M, Hoshina Y, Kobayashi T. Scaffold membranes for selective adsorption of α-tocopherol by phase inversion covalently imprinting technique. J Membr Sci 2008; 322: 503-11.
http://dx.doi.org/10.1016/j.memsci.2008.05.046

[129] Silvestri D, Barbani N, Cristallini C, Giusti P, Ciardelli G. Molecularly imprinted membranes for an improved recognition of biomolecules in aqueous medium. J Membr Sci 2006; 282: 284-95.
http://dx.doi.org/10.1016/j.memsci.2006.05.031

[130] Fan P, Wang B. Preparation of molecularly imprinted polymer membrane with blending trimethoprim-MIP and polysulfone and its transport properties. Kor J Chem Eng 2009; 26: 1813-20.
http://dx.doi.org/10.1007/s11814-009-0256-x

[131] Wang X, Zhang L, Ma C, Song R, Hou H, Li D. Enrichment and separation of silver from waste solutions by metal ion imprinted membrane. Hydrometallurgy 2009; 100: 82-6.
http://dx.doi.org/10.1016/j.hydromet.2009.10.006

[132] Ul-Haq N, Khan T, Park J.K. Enantioseparation with D-Phe- and L-Phe-imprinted PAN-based membranes by ultrafiltration. Chem Technol Biotechnol 2008; 83: 524-33.
http://dx.doi.org/10.1002/jctb.1827

[133] Wang HY, Xia SL, Sun H, Liu YK, Cao SK, Kobayashi, T. Molecularly imprinted copolymer membranes functionalized by phase inversion imprinting for uracil recognition and permselective binding. J Chromatogr B 2004; 804: 127-34.
http://dx.doi.org/10.1016/j.jchromb.2004.01.036

[134] Bryjak M, Duraj I. Molecularly imprinted membranes for removal of bisphenol A. Solvent Extr. Ion Exch. 201; 29: 432-39.

[135] Székely G, Valtcheva IB, Kim JF, Livingston A.G. Molecularly imprinted organic solvent nanofiltration membranes-Revealing molecular recognition and solute. React Funct Polym 2014, doi:10.1016/j.reactfunctpolym 2014; 03: 008.

[136] Takeda K, Kobayashi T. Hybrid molecularly imprinted membranes for targeted bisphenol derivatives. J Membr Sci 2006; 275: 61-9.
http://dx.doi.org/10.1016/j.memsci.2005.09.004

[137] Takeda K, Uemura K, Kobayashi T. Hybrid molecular imprinted membranes having selectivity and separation behavior to targeted indole derivatives. Anal Chim Acta 2007; 591: 40-8.
http://dx.doi.org/10.1016/j.aca.2007.02.017

[138] Silvestri D, Borrelli C, Giusti P, Cristallini C, Ciardelli G. Polymeric devices containing imprinted nanospheres: a novel approach to improve recognition in water for clinical uses, Anal. Chim Acta 2005; 542: 3-13.
http://dx.doi.org/10.1016/j.aca.2004.12.005

[139] Ku C, Faizal M, Kobayashi T. Tocopherol-Targeted Membrane Adsorbents Prepared by Hybrid Molecular Imprinting. Polym Eng Sci 2008; 48: 1085-93.
http://dx.doi.org/10.1002/pen.21053

[140] Borrelli C, Barsanti S, Silvestri D, Manesiotis P, Ciardelli G, Sellergren B. Selective depletion of riboflavine from beer using membranes incorporating imprinted polymer particles. J Food Process Pres 2011; 35: 112-28.
http://dx.doi.org/10.1111/j.1745-4549.2009.00464.x

[141] Rebelo TSCR, Almeida, SAA, Rafaela J, Guerreiro L, Conceição M, Montenegro BSM, Goreti M, Sales F. Trimethoprim-selective electrodes with molecularly imprinted polymers acting as ionophores and potentiometric transduction on graphite solid-contact. Microchem J 2011; 98: 21-8.
http://dx.doi.org/10.1016/j.microc.2010.10.006

[142] Kamel, AH, Moreira, FTC, Rebelo TSCR, Sales MGF. Molecularly-imprinted materials for potentiometric transduction: Application to the antibiotic enrofloxacin. Anal Lett 2011; 44: 2107-23.
http://dx.doi.org/10.1080/00032719.2010.546021

[143] Guerreiro JRL, Freitas V, Sales MGF. New sensing materials of molecularly-imprinted polymers for the selective recognition of chlortetracycline. Microchem J 2011; 97: 173-81.
http://dx.doi.org/10.1016/j.microc.2010.08.011

[144] Hong W, Yanyan Z, Mingcheng N, Zhongyi J. Molecularly imprinted organic-inorganic hybrid membranes for selective separation of phenylalanine isomers and its analogue. Sep Purif Technol 2009; 68: 97-104.
http://dx.doi.org/10.1016/j.seppur.2009.04.014

[145] Kalim R, Schomäcker R, Yüce S, Brüggemann O. Catalysis of β-elimination applying membranes with incorporated molecularly imprinted polymer particles. Polym Bull 2005; 55: 287-97.
http://dx.doi.org/10.1007/s00289-005-0438-6

[146] Yuqing Z, Xing Shan S, Xiaoquan G. Development of a molecularly imprinted membrane for selective separation of flavonoids. Sep Purif Technol 2011; 76: 337-44.
http://dx.doi.org/10.1016/j.seppur.2010.10.024

[147] Asman S, Yusof NA, Abdullah AA, Haron MDJ. Synthesis and characterization of hybrid molecularly imprinted polymer (MIP) membranes for removal of methylene blue (MB). Molecules 2012; 17: 1916-28.
http://dx.doi.org/10.3390/molecules17021916

[148] Wang HY, Kobayashi T, Fujii N. Surface molecular imprinting on photo-sensitive dithiocarbanoyl polyacrylonitrile membranes using photograft polymerization. J Chem Technol Biot 1997; 70: 355-62.
http://dx.doi.org/10.1002/(SICI)1097-4660(199712)70:4<355::AID-JCTB793>3.0.CO:2-#

[149] Ulbricht M, Kochkodan V, Weigel W. Molecularly imprinted composite membranes for selective binding of desmetryn from aqueous solutions Desalination 2002; 149: 323-28.
http://dx.doi.org/10.1016/S0011-9164(02)00802-0

[150] Gkementzoglou C, Kotrotsiou O, Kiparissides C. Synthesis of Novel Composite Membranes Based on Molecularly Imprinted Polymers for Removal of Triazine Herbicides from Water. Ind Eng Chem Res 2013; 52: 14001-010.
http://dx.doi.org/10.1021/ie400479c

[151] Sergeyeva TA, Matuschewski H, Piletsky SA, Bendig J, Schedler U, Ulbricht M. Molecularly imprinted polymer membranes for substance-selective solid-phase extraction from water by surface photo-grafting polymerization. J Chromatogr A 2001; 907: 89-99.
http://dx.doi.org/10.1016/S0021-9673(00)01053-0

[152] Kochkodan V, Hilal N, Melnik V, Kochkodan O, Vasilenko O. Selective recognition of organic pollutants in aqueous solutions with composite imprinted membranes. Adv Colloid Interfac 2010; 159: 180-88.
http://dx.doi.org/10.1016/j.cis.2010.06.006

[153] Liu Z, Lv Y, Gao J, Li X, Zhai X, Zhao J, Xu X. Molecularly imprinted poly(MAA-co-AM) Composite membranes for selective recognition of nicosulfuron herbicide. J Appl Pol Sci 2012; 126: 1247-56.
http://dx.doi.org/10.1002/app.36938

[154] Donato L, Figoli, A, Drioli, E. Novel composite poly(4-vinylpiridine)/polypropylene membranes with recognition properties for (S)-naproxen. J Pharm Biomed Anal 2005; 37: 1003-08.
http://dx.doi.org/10.1016/j.jpba.2004.09.020

[155] Wang JY, Xua ZL, Wu P, Yin SJ. Binding constant and transport property of S-Naproxen molecularly imprinted composite membrane. J Membr Sci 2009; 331: 84-90.
http://dx.doi.org/10.1016/j.memsci.2009.01.016

[156] Wang JY, Liu F, Xu ZL, Li K. Theophylline molecular imprint composite membranes prepared from poly (vinylidene fluoride) (PVDF) substrate. Chem En Sci 2010; 65: 3322-30.
http://dx.doi.org/10.1016/j.ces.2010.02.024

[157] Ye YT, Ma X-H, Xu ZL, Zhang Y. Theophylline Molecular Imprinted Composite Membranes Prepared on a Ceramic Hollow Fiber Substrate. Ind Eng Chem Res 2014; 53; 346-54.
http://dx.doi.org/10.1021/ie4024534

[158] Tonglairoum P, Chaijaroenluk W, Rojanarata T, Ngawhirunpat T, Akkaramongkolporn P, Opanasopit P. Development and Characterization of Propranolol Selective Molecular Imprinted Polymer Composite Electrospun Nanofiber Membrane. AAPS Pharm Sci Tech 2013; 14: 838-46.
http://dx.doi.org/10.1208/s12249-013-9970-0

[159] Wang SJ, Xu ZL, Feng JL, Bing NC, Yang ZG. Molecular imprinted membranes for the recognition of lovastatin acid in aqueous medium by a template analogue strategy. J Membr Sci 2008; 313: 97-105.
http://dx.doi.org/10.1016/j.memsci.2007.12.067

[160] Zhu XY, Zheng ZJ, Xie J, Wang P. Selective separation of magnolol using molecularly imprinted membranes. J Sep Sci 2012; 35: 315-319.
http://dx.doi.org/10.1002/jssc.201100731

[161] Hilal N, Kochkodan V, Busca G, Kochkodan O, Atkin BP. Thin layer composite molecularly imprinted membranes for selective separation of cAMP. Sep Purif Technol 2003; 31: 281-89.
http://dx.doi.org/10.1016/S1383-5866(02)00205-8

[162] Ciardelli G, Borrelli C, Silvestri D, Cristallini C, Barbani N, Giusti P. Supported imprinted nanospheres for the selective recognition of cholesterol. Biosens Bioelectron 2006; 21: 2329-38.
http://dx.doi.org/10.1016/j.bios.2005.12.027

[163] Zhou Y, Yu B, Levon K. Potentiometric sernsor for dipicolinic acid. Biosens Bioelectron 2005; 20: 1851-55.
http://dx.doi.org/10.1016/j.bios.2004.05.005

[164] Ceolin G, Navarro-Villoslada F, Moreno-Bondi MC, Horvai G, Horvath V. Accelerated development procedure for molecularly imprinted polymers using membrane filterplates. J Comb Chem 2009; 11: 645-52.
http://dx.doi.org/10.1021/cc900022u

[165] Zhang M, Huang J, Yu P, Chen X. Preparation and characteristics of protein molecularly imprinted membranes on the surface of multiwalled carbon nanotubes. Talanta 2010; 81: 162-66.
http://dx.doi.org/10.1016/j.talanta.2009.11.052

[166] Kunitake T, Lee SW. Molecular imprinting in ultrathin titania gel films *via* surface gel process. Anal Chim Acta 2004; 504: 1-6.
http://dx.doi.org/10.1016/S0003-2670(03)00811-0

[167] Whitcombe MJ, Kirsch N, Nicholls IA. Molecular imprinting science and technology: A survey of the literature for the years 2004-2011. J Mol Recognit 2014; 27: 297-401.
http://dx.doi.org/10.1002/jmr.2347

[168] Crini G. Studies on adsorption of dyes on beta-cyclodextrin polymer. Bioresource Technol 2003; 90: 193-8.
http://dx.doi.org/10.1016/S0960-8524(03)00111-1

[169] Pearce CI, Lloyd JR, Guthrie JT. The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes Pigments 2003; 58: 179-86.
http://dx.doi.org/10.1016/S0143-7208(03)00064-0

[170] Vandevivere PC, Bianche R, Verstraete W. Treatment and reuse of wasdtewater from the textile wet-processing industry: review of emerging technologies. I Chem Technol Biotechnol 72: 289-302.

[171] Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganathan K. Removal of dyes from aqueous solutions by cellulosic waste orange peel. Bioresour Technol 1996; 57: 37-43.
http://dx.doi.org/10.1016/0960-8524(96)00044-2

[172] Kyzas GZ, Bikiaris DN, Lazaridi NK. Selective separation of basic and reactive dyes by molecularly imprintedpolymers (MIPs), Chem Eng J 2009; 149: 263-72.
http://dx.doi.org/10.1016/j.cej.2008.11.002

[173] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog Polymer Sci 2005; 30: 38-70.
http://dx.doi.org/10.1016/j.progpolymsci.2004.11.002

[174] Kiernan JA. Classification and naming of dyes, stains and fluorochromes. Biotech Histochem 2001; 76: 261-78.
http://dx.doi.org/10.1080/bih.76.5-6.261.278

[175] Forgacs E, Cserhàti, Oros G. Removal of synthetic dyes from wastewaters: a review, Environ Int 2004; 30: 953-71.
http://dx.doi.org/10.1016/j.envint.2004.02.001

[176] Chiou MS, Ho PY, Li HY. Adsoprtion of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes Pigments 2004; 60: 69-84.
http://dx.doi.org/10.1016/S0143-7208(03)00140-2

[177] Kyzas GZ, Lazaridis NK. Reactive and basic dyes removal by sorption onto chitosan derivatives. Colloid Interf Sci 2009; 331: 32-9.
http://dx.doi.org/10.1016/j.jcis.2008.11.003

[178] Juang RS, Tseng RL, Wu FC. Role of microporosity of activated carbons on their adsorption abilities for phenols and dyes. Adsorption 2001; 7: 65-72.
http://dx.doi.org/10.1023/A:1011225001324

[179] Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from acqueous solution by adsorption: A review, Adv Colloid Interfac 2014; 209: 172-84.
http://dx.doi.org/10.1016/j.cis.2014.04.002

[180] Sun D, Zhang Z, Wang M, Wu Y. Adsorption of reactive dyes on activated cabon developed from Enteromorpha prolifera, Am J Anal Chem 2013; 4: 17-26.
http://dx.doi.org/10.4236/ajac.2013.47A003

[181] Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 2003; 97: 219-43.
http://dx.doi.org/10.1016/S0304-3894(02)00263-7

[182] Dragan ES, Dinu IA. Removal of azp dyes from aqueous solution by coagulation/flocculation with strong polycations, Res J Chem Environ 2008; 12: 5-11.

[183] Meyers RA. Encyclopedia of environmental analysis and remediation. Wiley. New York 1998; 1422-65.

[184] Singh K, Arora S. Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Envir Sci Tech 2011; 41: 807-78.
http://dx.doi.org/10.1080/10643380903218376

[185] Gao BY, Wang Y, Yue QY, Wei JC, Li Q. Color removal from simulated dye water and actul wastewater using a composite coagulant prepared by polyferric chloride and polydimethyldiallylammonium chloride. Sep Purif Technol 2007; 54: 157-63.
http://dx.doi.org/10.1016/j.seppur.2006.08.026

[186] Sudha M, Saranya A, Selvakumar G, Sivakumar N. Microbial degradation of Azo Dyes: A review. Int J Microbial App Sci 2014; 3: 670-90.

[187] Mugdha A, Usha M. Enzymatic treatment of wastewater containing dyestuff using different delivery systems. Sci Rews Chem Com 2012; 2: 31-40.

[188] Adam W, Lzarus M, Saha-Mollera C, Weichold O, Hoch U, Haring D, Schreirer P. Biotransformation with peroxidase. Adv Biochem Eng Biotechnol 1999; 63: 73-107.
http://dx.doi.org/10.1007/3-540-69791-8_4

[189] Chacko JT, Subramaniam K. Enzymatic degradation of azo-dyes-A review. Int J Environ Sci 2011; 1: 1250-60.

[190] Blanquez P, Casa N, Font X, Gabarrel, X, Sarra M, Caminal, G, Vincent T. Mechanism of textile metal dye biotransformation by Trametes versicolour. J Water Res 2004; 38: 2166-72.
http://dx.doi.org/10.1016/j.watres.2004.01.019

[191] Novotny C, Svobodova K, Kasinath A, Erbanova P. Biodegradation of synthetic dyes by Irpex lacteus under various growth conditions. Dech Monog 2004; 54: 215-23.

[192] Chivukula M, Renganathan V. Phenolic azo dyes oxidation by laccase from Pyricularia oryzae. Appl Environ Microbial 1995; 61: 4347-77.

[193] Wong Y, Yu J. Laccase-catalysed decolorization of synthetic dyes. Water Res 1999; 33: 3512-20.
http://dx.doi.org/10.1016/S0043-1354(99)00066-4

[194] Duran N, Esposito E. Potential applications of oxidative enzymes and phenoloxidase-like compounds in wastewater and soil treatment: a review. Appl Catal B-Environ 2000; 28: 83-99.
http://dx.doi.org/10.1016/S0926-3373(00)00168-5

[195] Bhunia A, Durani S, Wangikar PP. Horseradish peroxidase catalyzed degradation of industrially important dyes. Biotechnol Bioeng 2001; 72: 562-67.
http://dx.doi.org/10.1002/1097-0290(20010305)72:5<562::AID-BIT1020>3.0.CO:2-S

[196] Zucca P, Rescigno A, Pintus M, Rinaldi AC, Sanjust E. Degradation of textile dyes using immobilized lignin peroxidase-like metalloporhirines under mild experimental conditions. Chem Cent J 2012; 6: 161-67.
http://dx.doi.org/10.1186/1752-153X-6-161

[197] Kuo WG. Decolorazing dye wastewater with Fenton's reagent. Water Res 1992; 26: 881-86.
http://dx.doi.org/10.1016/0043-1354(92)90192-7

[198] Matafonova G, Batoev V. Recent progress on application of UV excilasmps for degradation of organic pollutants and microbial inactivation. Chemosfere 2012; 89: 637-47.
http://dx.doi.org/10.1016/j.chemosphere.2012.06.012

[199] Thomas S, Sreekanth R, Sijiumon VA, Aravind UK, Aravindakumar CT. Oxidative degradation of Acid Red 1 in aqueous medium. Chem Eng J 2014; 244: 473-82.
http://dx.doi.org/10.1016/j.cej.2014.01.037

[200] Khan H, Ahmad N, Yasar A, Shahid R. Advanced oxidative decolorization of red C1-5B: effects of dye concentration, process optimization and reaction kinetics. Polish J Environ Stud. 2010; 19: 83-92.

[201] Wang Y. Solar photocatalytic degradation of eight commercial dyes in $TiO_2$ suspension. Water Res 2000; 34: 990-994.
http://dx.doi.org/10.1016/S0043-1354(99)00210-9

[202] Zhang Z, Wang W, Shang M, Yin W. Low-temperature combustion synthesis of $Bi_2WO_6$ nanoparticles as a visible-light-driven photocatalyst. J Hazard Mater 2010; 177: 1013-18.
http://dx.doi.org/10.1016/j.jhazmat.2010.01.020

[203] Khataee A, Fathinia M, Aber S, Zarei M. Optimization of photocatalytic treatment of dye solution on supported $TiO_2$ nanoparticles by central composite design: Intermediates identification. J Hazard Mater 2010; 181: 886-97.
http://dx.doi.org/10.1016/j.jhazmat.2010.05.096

[204] Augugliro V, Baiocchi C, Prevot AB, García-López E, Loddo V, Malato S, Marcì G, Palmisano L, Pazzi M, Premauro E. Azo-dyes photocatalytic degradation in aqueous suspension of $TiO_2$ under solar irradiation. Chemosphere 2002; 49: 1223-30.
http://dx.doi.org/10.1016/S0045-6535(02)00489-7

[205] Riga A, Soutsas K, Ntampegliotis K, Karayannis V, Papapolymerou G. Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-dyes. Comparison of $H_2O_2$/UV, Fenton, UV/Fenton, $TiO_2$/UV and $TiO_2$/UV/$H_2O_2$ processes. Desalination 2007; 211: 72-86.
http://dx.doi.org/10.1016/j.desal.2006.04.082

[206] Pelizzetti E. Concluding remarks on heterogeneous solar photocatalysis. Sol Energy mater sol Cells 1995; 38: 453-457.
http://dx.doi.org/10.1016/0927-0248(94)00237-1

[207] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972; 37: 238-250.

[208] Gupta VK, Jain R, Mittal A, Saleh TA, Nayak A, Agarwal S, Sikarwar S. Photo-catalytic degradation of toxic dye amaranth on $TiO_2$/UV in aqueous suspensions. Mater Sci Eng 2012; C32: 12-17.
http://dx.doi.org/10.1016/j.msec.2011.08.018

[209] Balachandran K, Venkatesh R, Sivaraj R, Rajiv P. $TiO_2$ nanoparticles versus $TiO_2$-$SiO_2$ nanocomposites: A comparative study of photo catalysis on acid red 88. Spetreochim Acta A Mol Biomol Spectrosc 2014; 128: 468-74.
http://dx.doi.org/10.1016/j.saa.2014.02.127

[210] Srisukphun T, Chiemchaisri C, Urase T, Yamamoto K. Experimentation and modeling of foulant interaction and reverse osmosis membrane fouling during textile wastewater reclamation Sep Purif Technol 2009; 68: 37-49.

[211] Akbari A, Remigy JC, Aptel P. 2002. Treatment of textile dye effluent using a polyamide-based nanofiltration membrane. Chem Eng Process 2002; 41: 601-09.
http://dx.doi.org/10.1016/S0255-2701(01)00181-7

[212] Lau WJ, Ismail AF. Polymeric nanofiltration membranes for textile dye wastewater treatment: Preparation, performance evaluation, transport modelling, and fouling control-a review. Desalination 2009; 245: 321-48.
http://dx.doi.org/10.1016/j.desal.2007.12.058

[213] Petrinic I, Andersen NPR, Šostar-Turk S, Le Marechal AM. The removal of reactive dye printing compounds using nanofiltration. Dyes Pigments 2007; 74: 512-18.
http://dx.doi.org/10.1016/j.dyepig.2006.11.003

[214] Vishnu G, Joseph K. Nanofiltration and ozonation for decolorisation and salt recovery from reactive dye bath. Color Technol 2007; 1223: 260-66.
http://dx.doi.org/10.1111/j.1478-4408.2007.00093.x

[215] Liasng CZ, Sun SP, Li FY, Ong YK, Chung TS. Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofilitration. J Membr Sci 2014; 469: 306-15.
http://dx.doi.org/10.1016/j.memsci.2014.06.057

[216] Mustafa N, Al Nakib H. Reverse osmisi polyamide membrane for the removal of blue and yellow dye from waste water. Iraqi J Chem Petrol Eng 2013; 14: 49-55.

[217] Fradj AB, Hamouda SB, Ouni H, Lafi R, Gzara L, Hafiane A. Removal of methylene blue from aqueous solutions by poly(acrylic acid) and (polyammonium acrylate) assisted ultr.

[218] Gong SL, Yu ZJ, Meng LZ, Hu L, He YB. Dye-Molecular-Imprinted Polysiloxanes. II. Preparation, Characterization, and Recognition Behavior. Journal of Appl Poly Sci 2004; 93: 637-643.
http://dx.doi.org/10.1002/app.20486

[219] Yan S, Gao Z, Fang Y, Cheng Y, Zhou H, Wang H. Characterization and quality assessment of binding properties of malachite green molecularly imprinted polymers prepared by precipitation polymerization in acetonitrile. Dyes and Pigments 2007; 74: 572-577.
http://dx.doi.org/10.1016/j.dyepig.2006.03.021

[220] Culp SJ, Beland FA. Malachite green: a toxicological review. J Am Coll Toxicol 1996; 15: 219-38.
http://dx.doi.org/10.3109/10915819609008715

[221] Fernandes C, Lalitha VS, Rao KVK. Enhancing effect of malachite green on the development of hepatic pre-neoplastic lesions induced by N-nitrosodiethylamine in rats. Carcinogenesis 1991; 12: 839-45.
http://dx.doi.org/10.1093/carcin/12.5.839

[222] Ramamoorthy M, Ulbricht M. Molecular imprinting of cellulose acetate-sulfonated polysulfone blend membranes for Rhodamine B by phase inversion technique. J Membr Sci 2003; 217: 207-14.
http://dx.doi.org/10.1016/S0376-7388(03)00133-9

[223] Ma Y, Jin X, Zhou M, Zhang Z, Teng X, Chen H. Chemiluminescence behavior based on oxidation reac-tion of Rhodamine B with cerium(IV) in sulfuric acid medium. Anal Chim Acta 2003; 489: 173-81.
http://dx.doi.org/10.1016/S0003-2670(03)00756-6

[224] Yua JX, Li BH, Sun XM, Yuan J, Chia R. Polymer modified biomass of bakers yeast for enhancement adsorption of methylene blue, Rhodamine B and basic magenta. J Hazard Mater 2009; 168: 1147-54.
http://dx.doi.org/10.1016/j.jhazmat.2009.02.144

[225] Li L, Liu H, Lei X, Zhai Y. Electrospun nanofiber membranes containing molecularly imprinted polymer (MIP) for Rhodamine B (RhB). Adv Chem Eng Sci 2012; 2: 266-74.
http://dx.doi.org/10.4236/aces.2012.22031

[226] Greiner A, Wendorff JH. Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angew Chem Int Edit 2006; 46: 5670-703.
http://dx.doi.org/10.1002/anie.200604646

[227] Liu X, Yu D, Yu Y, Ji S. Preparation of a magnetic molecularly imprinted polymer for selective recognition of Rhodamine B. Appl Surf Sci 2014; 320: 138-145.
http://dx.doi.org/10.1016/j.apsusc.2014.08.122

[228] Su X, Li X, Li J, Liu M, Lei F, Tan X, Li P, Luo W. Synthesis and characterization of core–shell magnetic molecularly imprinted polymers for solid-phase extraction and determination of Rhodamine B in food. Food Chem 2015; 171: 292-97.
http://dx.doi.org/10.1016/j.foodchem.2014.09.024

[229] Okutucu B, Akkaya A, Pazarlioglu NK. Molecularly imprinted polymers for some reactive dyes. Preparative Biochemistry and Biotechnology, 2010; 40: 366-376.
http://dx.doi.org/10.1080/10826068.2010.525428

[230] Al-Degs YS, Abu-Surrah AS, Ibrahim KA. Preparation of highly selective solid-phase extractants for Cibacron reactive dyes using molecularly imprinted polymers. Anal and Bioanal Chem 2009; 393: 1055-62.
http://dx.doi.org/10.1007/s00216-008-2502-1

[231] Kyzas GZ, Bikiaris DN, Lazaridis NK. Selective separation of basic and reactive dyes by molecularly imprinted polymers (MIPs). Chem Eng J 2009; 149: 263-72.
http://dx.doi.org/10.1016/j.cej.2008.11.002

[232] Kyzas GZ, Lazaridis NK, Bikiaris DN. Optimization of chitosan and cyclodextrin molecularly imprinted polymer synthesis for dye adsorption. Carbohyd Polym 2013; 91: 198-208.
http://dx.doi.org/10.1016/j.carbpol.2012.08.016

[233] Asman S, Yusof NA, Abdullah AH, Haron MJ. Synthesis and characterization of hybrid molecularly imprinted polymer (MIP) membranes for removal of methylene blue (MB). Molecules 2012; 17: 1916-28.
http://dx.doi.org/10.3390/molecules17021916

[234] Zhao K, Feng L, Lin H, Fu Y, Lin B, Cui W, Li S, Wei J. Adsorption and photocatalytic degradation of methyl orange imprinted composite membranes using $TiO_2$/calcium alginate hydrogel as matrix. Catal Today 2014; 236: 127-34.
http://dx.doi.org/10.1016/j.cattod.2014.03.041

[235] Luo X, Zhan Y, Tu X, Huang Y, Luo S, Yan L. Novel molecularly imprinted polymer using 1-(α-methyl acrylate)-3-methyl imidazolium bromide as functional monomer for simultaneous extraction and determination of water-soluble acid dyes in wastewater and soft drink by solid phase extraction and high performance liquid chromatography. J Chromatogr A 2011; 1218: 1115-21.
http://dx.doi.org/10.1016/j.chroma.2010.12.081

[236] Fana L, Y Z, Li X, Luo C, Lu F, Qiu H. Removal of Alizarin red from water environment using magnetic chitosan with Alizarin Red as imprinted molecules, Colloid Surface B 2012; 91: 250-57.
http://dx.doi.org/10.1016/j.colsurfb.2011.11.014

[237] Krupadam RJ1, Khan MS, Wate SR. Removal of probable human carcinogenic polycyclic aromatic hydrocarbons from contaminated water using molecularly imprinted polymer. Water Res 2010; 44: 681-8.
http://dx.doi.org/10.1016/j.watres.2009.09.044

[238] Puoci F, Garrafa C, Iemma F, Muzzalupo R, Spizzirri U, Picci N. Molecularly imprinted solid phase extraction for detection of Sudan I in food matrices. Food Chem 2005; 93: 349-53.
http://dx.doi.org/10.1016/j.foodchem.2004.11.014

[239] Baggiani C, Anfossi L, Baravalle Pa, Giovannoli C, Giraudi G, Barolo C, Viscardi G. Determination of banned Sudan dyes in food samples molecularly imprinted solid phase extraction-high performance liquid chromatography. J Sep Sci 2009; 32: 3292-300.
http://dx.doi.org/10.1002/jssc.200900126

[240]  Xu XY, Tian XG, Cai LG, Xu ZL, Lei HT, Wang H, Sun YM. Molecularly imprinted polymer based surface plasmon resonance sensors for detection of Sudan dyes, Anal. Methods 2014; 6: 3751-57.
http://dx.doi.org/10.1039/c3ay42230e

[241]  Hu X, Fan Y, Zhang Y, Dai G, Cai Q, Cao Y, Guo C. Molecularly imprinted polymer coated solid-phase micr-oextraction fiber prepared by surface reversible addition-fragmentation chain transfer polymerization for monitoring of Sudan dyes in chilly tomato sauce and chilly pepper samples. Anal Chim Acta 2012; 731: 40-48.
http://dx.doi.org/10.1016/j.aca.2012.04.013

[242]  Qiao FX, Chen P. Molecularly imprinted-solid phase extraction for multi-residues analysis of Sudan dyes in sausage. Asian J Chem 2012: 24. 1107-10.

[243]  Yan H, Qiao J, Pei Y, Long T, Ding W, Xie K. Molecularly imprinted solid-phase extraction coupled to liquid chromatography for determination of Sudan dyes in preserved beancurds. Food Chem 2012; 132: 649-54.
http://dx.doi.org/10.1016/j.foodchem.2011.10.105

[244]  Qiao F, Geng Y, He C, Wu Y, Pan P. Molecularly imprinted microspheres as SPE sorbent for selective extraction of four Sudan dyes in catsup products. J Chromatogr B 2011; 879: 2891-96.
http://dx.doi.org/10.1016/j.jchromb.2011.08.019

[245]  Hu Xi, Cai Q, Fan Y, Ye T, Cao Y, Guo C. Molecularly imprinted polymer coated solid-phase microextraction fibers for determination of Sudan I-IV dyes in hot chili powder and poultry feed samples. J Chromatogr A 2012; 1219: 39-46.
http://dx.doi.org/10.1016/j.chroma.2011.10.089

[246]  Yan H, Wang H, Qiao J, Yang G. Molecularly imprinted matrix solid-phase dispersion combined with dispersive liquid-liquid microextraction for the determination of four Sudan dyes in egg yolk. J Chromatogr A 2011; 1218: 2182-88.
http://dx.doi.org/10.1016/j.chroma.2011.02.042

[247]  Chen S, Du D, Huang J, Zhang A, Tu H, Zhang A. Rational design and application of molecularly imprinted sol–gel polymer for the electrochemically selective and sensitive determination of Sudan I. Talanta 2011; 84: 451-56.
http://dx.doi.org/10.1016/j.talanta.2011.01.047

[248]  Zhan J, Fang G, Yan Z, Pan M, Liu C, Wang S. Preparation of a semicovalent, molecularly surface imprinted polymer for the rapid determination of trace acid orange II in food and environmental samples. Anal Bioanal Chem 2013; 405: 6353-63.
http://dx.doi.org/10.1007/s00216-013-7036-5

[249]  Li Xi, Li M, Li J, Lei F, Su X, Liu M, Lia P, Tan X. Synthesis and characterization of molecularly imprinted polymers with modified rosin as a crosslinker and selective SPE-HPLC detection of basic orange II in foods. Anal Methods 2014; 6:6397-406.
http://dx.doi.org/10.1039/C4AY00810C

[250]  Long Z, Lu Y, Zhang M, Qiu H. Selective recognition and discrimination of water-soluble azo dyes by a seven-channel molecularly imprinted polymer sensor array. J Sep Sci 2014; 37: 2764-70.
http://dx.doi.org/10.1002/jssc.201400684

[251]  Wang P, Hu W, Su W. Molecularly imprinted poly (methacryl amide-co-methacrylic acid) composite membranes for recognition of curcumin. Anal Chim Acta 2008; 615: 54-62.
http://dx.doi.org/10.1016/j.aca.2008.03.040

[252]  Han Q, Wang Xi, Yang Z, Zhu W, Zhou X, Jiang H. $Fe_3O_4$@rGO doped molecularly imprinted polymer membrane based on magnetic field directed self-assembly for the determination of amaranth. Talanta 2014; 123: 101-08.
http://dx.doi.org/10.1016/j.talanta.2014.01.060