Chapter

Wastewater Treatment Using Imprinted Polymeric Adsorbents

Burcu Okutucu

Abstract

In twenty-first century, numbers of synthetic dyes are used in many industries, for example paper, textile, cosmetic, leather for coloring, vs. The dyeing industries wastes is the most found contaminant to be recognized in wastewater. There are various treatment methods including oxidation processes, biological degradation, membrane filtration and coagulation/flocculation have been studied to treat dyeing wastewater. Unfortunately, these methods are high operational costs, complicated operations and possibility of producing more toxic products. Molecularly imprinted polymers (MIPs) are interesting and alternative polymeric adsorbents that can be applied in wastewater treatment for sample preparation and for the quantification of dyes present in wastewater. Molecular imprinting is a process in which functional and crosslinking monomers are co-polymerized in the presence of the target analyte, the imprint molecule. Initially, the functional monomer forms a complex and, after polymerization, their functional groups are held by the highly crosslinking polymeric structure. Upon leaching of the imprint molecule from the polymer matrix, a polymer with binding sites complementary in size and shape to the imprint molecule is created. MIPs can function under extreme conditions of pH, temperature and complex environment. Also, MIPs present wide recognition due to their stability, ease of production and low-cost potential.

Keywords: molecularly imprinted polymer, dye, solid phase extraction, magnetic molecularly imprinted polymers, adsorbent

1. Introduction

With the growth of human; society, science, technology the world is reaching to new high horizons but the cost which will pay in near future is going to be too high. The bad result of this rapid growth is big environmental pollution problem. One of the biggest risks is the water pollution. The major environmental concern worldwide is water pollution associated with release of many different pollutants [1]. Pollutants released into the environment in wastewater effluent, contaminate freshwater resources and are harmful to humans and the environment. These pollutants were released from many different chemical industries such as textile, dyestuffs, metal plating, paper, mining, fertilizer, battery manufacturing metallurgical, pesticides, fossil fuel, tannery, mining, various plastics. Micropollutants, which are mostly found in wastewater, can be pharmaceuticals, industrial chemicals, pesticides and so on. The textile industries micropollutants released in wastewater and sludge can be dyes, phosphorus, sulfamethazine and heavy metals [2]. The release of these contaminants has been increased because of recent rapid industrialization.

Many industries such as textile, dyestuffs, paper and plastics which are used dyes, use substantial volumes of water in process and also, they generate a considerable amount of colored wastewater [3]. Dye is found a lot amount of pollutant in wastewater. More than 10,000 commercially available dyes are existed and over 7×10^5 of dyes are produced annually throughout the world [4].

Wastewater which is rich by dyestuffs must be treated by many different techniques to eliminate dyes before they are discharged to the ecosystem because of large content of organic pollutants (polycyclic aromatic hydrocarbons, nonphenols, phatales, so on.). The results of many researches showed that about 2% of dyes produced form textile industries are directly discharged in wastewater. Many of these dyes are hazardous and a big threat to aquatic life due to their toxicity and carcinogenicity [3].

Dyes are typically classified in two ways: chemical composition and application class or end use. Based on the application method, dyes can be divided into acid, azoic, basic, direct, disperse, mordant, reactive, sulfur, and vat dyes. According to chemical compositions, dyes can be divided into azo, nitro, nitroso, diarylmethane, triarylmethane, xanthene, anthraquinoid, acridine, cyanine, quinone-imine, pthalocyanine, and thiazole dyes. The azo and anthraquinone dyes are two major classes of reactive dyes, which is released to wastewater as 90% of all organic pollutants. Due to their interaction with hydroxyl ions in the solution, these dyes are always wasted in the dyeing process, remained in the effluents and are hardly eliminated under aerobic conditions. Also, the azo dyes have stability against microbial attack. Reduction of azo bond frequently releases aromatic amines, which resist further degradation under anaerobic condition. The acute toxicity of azo dyes to humans are rather low according to the European Union criteria. The toxicity is generally not because of the dye itself, but because of its degradation products. Azo dyes can be caused contact dermatitis in the local lymph node assays. However azo dyes can be very toxic to several aquatic organisms including algae, fish. Because of presence of azo dyes in water; viability, reproduction rate, filtration feeding and O_2 consumption of the fishes reduced in the freshwater. Azo dyes also inhibit several biological processes, such as they can inhibit algal photosynthesis by reducing the penetration of light, they inhibit chemical oxygen demand (COD) reduction and respiratory activities of microbial populations. Which are ecologically very important. This may result in inhibition of microbial processes like wastewater treatment systems and natural biogeochemical cycles [2, 5, 6].

Over the last years, different physical, chemical and biological techniques have been developed to remove toxic dyes from wastewater and water reservoirs. All kinds of wastewater containing dyes cannot be treated with one technology. The methods for clean up wastewater are adsorption, electrolysis, ozonation, coagulation/flocculation, physical membrane separation, advanced oxidation processes and biological degradation process. Each technology has some merits and demerits. The demerits of many of these techniques are high cost and the formation of hazardous by products. The problems of some techniques can be listed; the quantification of different dyes related to complicated sample preparation procedures, long analysis times, and the use of large quantities of solvents [7]. Coagulation/flocculation usually generates large amounts of toxic sludge difficult to deal with. Physical membrane separation employing nanofiltration (NF) membrane is easy to bring pollution and lead to decreasing removal efficiency Advanced oxidation processes including chemical oxidation, catalytic degradation and electro chemical treatment consume high energy and are still quite costly for practical application [8]. Biological degradation with activated sludge cannot clean up wastewater due to the biodegradable difficulty of many synthetic dyes. The problem of anionic dyes is highly water soluble and difficult to remove by conventional methods. The nonionic

dyes (disperse dyes) do not ionize in an aqueous solution and their fused aromatic ring structure makes them highly resistant to degradation. However, a few cationic dyes like methyl blue can be easily removed by adsorption and advanced oxidation processes [4]. With the realization that a single technique cannot give universal solution, the recent trend in dye wastewater treatment is focused around integration of multiple techniques [7, 9].

Adsorption is a low-cost and effective method for expurgate of dye wastewater. The adsorption process is the best choice for the decolorization of dyes and gives the best results for removal of various types of dissolved coloring materials and also removes the entire dye molecule, leaving no fragments in the effluent. The adsorption has a high treatment efficiency and adsorbents can be regenerated for multiple reuses. The initial dye concentration, solution pH, temperature, contact time and adsorbent dosage are usually the main factors that govern the performance. Generally, removal of dyes from water and wastewater is carried out by adsorption using activated carbon. The disadvantage of activated carbon are expensive regeneration process and the decrease of adsorption capacity after regeneration. The other adsorption material can be nanoparticle adsorbents, low cost waste-based adsorbents and polymeric adsorbents. Polymeric adsorbents have the advantages of high flexibility in design, physical stability, porosity, uniform pore size distribution, high surface area, and chemical stability towards acids and bases, feasible regeneration and thermal durability but they are generally expensive materials [4]. The interesting and urgent research needs for a high-efficiency, low cost, attractive and reusable adsorbent for clean up wastewater [10].

2. Molecularly imprinted polymers (MIPs)

Molecularly imprinted polymers (MIPs) are interesting materials that can be applied in environmental research for sample preparation, to clean up and for the quantification of contaminants present in wastewater. The advantages of MIPs are related to their small size, high surface area, and specific selectivity towards target molecules. Molecular imprinting can be prepared with nanoscale surface recognition sites for target molecules, providing high binding capacities and fast mass transfer rates. MIPs have resistance under extreme conditions of pH, temperature, and complex environment. The preparation route of molecular imprinting is in which functional and crosslinking monomers are co-polymerized in the presence of the target analyte (the imprint molecule). Initially, the functional monomer forms a complex (monomer-target analyte) via covalent or noncovalent interactions and, after polymerization, their functional groups are held by the highly crosslinking polymeric structure. Upon leaching of the imprint molecule from the polymer matrix, a polymer with binding sites complementary in size and shape to the imprint molecule is created. This polymer is now capable of selectively rebinding the imprint molecule [6, 9–11]. In covalent approach; the imprinted molecule is covalently coupled to a polymerizable molecule. The binding of template with monomers are relies on reversible covalent bonds. After copolymerization with crosslinker, the imprint molecule is chemically cleaved from the highly crosslinked polymer with harsh conditions. In non-covalent approach which is usually used for preparing MIP is composed of self-assembly between the template and monomer, followed by a crosslinked co-polymerization. The template molecules interact with monomers (during imprinting procedure and the rebinding) via non-covalent interactions, e.g. ionic, hydrophobic and hydrogen bonding [12].

MIPs have been successfully used as an alternative adsorbent in several analytical fields such as separation of enantiomers in liquid chromatography (LC) or capillary

electrochromatography (CEC), binding assays, sensors and solid-phase extraction (SPE). SPE is the most advanced application area of the MIP. In recent years, the number of papers which the MIP is used for SPE sorbents (MISPE) increased MISPE is used in the areas of environmental, food and pharmaceutical analysis as selective sorbents for the extraction or for the clean-up of different classes of compounds from various complex matrices [13]. Concerning more specifically the determination of dyes in wastewater, there were too many examples that mentioned above with MISPE. The application of MIP particles in chromatography, can be packed in a column between two frits and be used off-line or they can also pack in a small column to be coupled on-line with LC. The principle of the extraction on a MIP is the same classical SPE sorbents. The desorption of the analytes is achieved by percolating a solvent in order to disrupt the interactions between the analytes and the MIP. Nevertheless, there are more and more applications of MIPs directly to real wastewater samples without a preliminary treatment [14]. The importance of the washing step and the difficulty to optimize this step was the most important problem of MIP usage.

The successful preparation of MIPs depends on the choice of monomers, the crosslinkers, and the appropriate polymerization conditions. The structure and the functionalities of the template molecule-monomer interaction define the subsequent properties of the binding sites. The criteria to consider when selecting a candidate template molecule are its cost, its availability and its chemical functionalities defining which is the ability to strongly interact with monomers. In non-covalent imprinting, the interactions involved are weak; and the excess amount of template should be used. The main factor which is important for MIP process is choosing the best monomer. The role of the monomer is to provide functional groups which can form a complex with the template by covalent or non-covalent interactions. The strength of the interactions between template and monomer affects the affinity of MIPs and determines the accuracy and selectivity of recognition sites [13]. Many techniques are used to select best suitable monomer. The rational design (computer simulation) and analytical techniques includes nuclear magnetic resonance, UV-vis, Fourier-transform infrared spectroscopy and isothermal titration calorimetry have been studied [15].

The common monomers, which are used for molecular imprinting, are methacrylic acid (MAA), acrylic acid (AA), 2- or 4-vinylpyridine (2- or 4-VP), acrylamide, trifluoromethacrylic acid, 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate, acrylic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, 4-vinylbenzene boronic acid, 1-vinyl imidazole, allylamine, itaconic acid, urocanic ethyl ester, methacrylamide, acrylonitrile and styrene. MAA named as a "universal" functional monomer due to its unique characteristics, being capable to act as a hydrogen-bond donor and acceptor and showing good suitability for ionic interactions. The monomer is chosen according to functional groups of template molecule. The attempts for finding new functional monomers for synthesis of MIPs continued. Because of their special structures, β-cyclodextrins (β-CDs) can be interesting monomers. The β-CDs are composed of cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic cavity. The molar ratio between template and monomer are important because this ratio affect the affinity and imprinting efficiency of MIPs. The lower molar ratios mean less binding sites in polymers. The over-high ratios mean higher non-specific binding capacity and decrease the binding selectivity. For best imprinting efficiency, the molar ratio of templates to monomers have to be optimized [14, 15].

The role of the cross-linker in imprinted polymer is to organize the functional groups of functional monomers around imprinted molecules, and to form highly rigid polymer The common cross-linkers which is used ethylene glycol

dimethacrylate (EGDMA), trimethylolpropane trimethacrylate (TRIM), N,N-methylene bisacrylamide (MBAA) and divinylbenzene (DVB), pentaerythritol triacrylate, 1,4-diacryloyl piperazine [15]. Types and amounts of cross-linkers effects the selectivity and binding capacity of MIPs. If the amount of cross-linkers is too low, MIPs cannot maintain stable cavity configuration. The over-high amounts of cross-linkers will reduce the number of recognition sites.

The solvent is one of the other most important factors determining effective molecular recognition. Because the accuracy of the assembly between the template and the monomer is related to the physical and chemical characteristics of the solvent. The solvent, which is used while preparing MIPs, named as porogen. The porogen acts as not only a solvent but also cavity maker. Aprotic/low polar organic solvents (toluene, acetonitrile, chloroform) are often used in non-covalent polymerization processes in order to obtain good imprinting efficiency. Nevertheless, the MIPs prepared in organic solvent cannot be compatible with aqueous media usage. A few studies reported the use of polar/protic media (methanol, ethanol, water) for the synthesis of MIPs. The development of water-compatible MIPs is an interesting area are going to study [16].

Actually, MIPs are synthesized by free radical polymerization, generated by the thermal or photo homolysis of a chemical bond on an initiator. The most widely used initiators for MIPs synthesis are benzoyl peroxide (BPO), 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 2-azobis(2-methylpropionitrile) (AIBN) and 2,20-azo-bis(2,4-dimethyl) valeronitrile (ABDV) [17].

3. Synthesis methods of MIPs

The synthesis method of MIPs can be a different type. Bulk, suspension, emulsion, precipitation, multi-step swelling, and surface imprinting were the methods which were summarized. Bulk polymerization is the common method to prepare MIPs. The bulk polymerization is rapid, simple preparation, needs no sophisticated or expensive instrumentation. But after polymerization of the bulk polymer, it has to be crushed, ground and sieved to an appropriate size. After grinding, the polymer was in irregular particles in shape and size, and also some high affinity binding sites are destroyed. Bulk polymers have a heterogeneous binding site distribution which is limited the use of MIPs in chromatography. The other techniques of preparing imprinting polymers are suspension polymerization, emulsion polymerization, seed polymerization, precipitation polymerization and surface imprinting. The more homogeneous binding site distribution can be taken by these techniques. The MIPs which is prepared by conventional suspension polymerization, where water is used as a continuous phase to form a droplet of pre-polymerization mixtures in the presence of a stabilizer or surfactant. However, the MIPs prepared by suspension polymerization is polydisperse in size (a few to a few hundred micrometers) and displayed poor recognition. The liquid perfluorocarbon or mineral oil (liquid paraffin) can be used while preparing MIPs by suspension polymerization technique to prevent poor recognition. But, liquid perfluorocarbons immiscible with almost all organic solvents (chloroform, dichloromethane, toluene), monomers and cross-linkers. The emulsion polymerization is as an effective method to produce monodispersed polymeric particles. The disadvantage of emulsion polymerization was the presence of remnants of surfactant in polymerization media. Precipitation polymerization have some advantages in synthesizing spherical particles such as free of surfactant, in one single preparative step and with excellent control over the particle size. The seed polymerization, a typical multi-step swelling and polymerization, produced monodispersed

MIPs. In this technique, the use of water was weakened recognition. In addition, the multistep procedure is very time-consuming. Surface imprinting is another technique nowadays using MIPs mostly synthesized. The biggest problem of MIP was bleaching of template molecule due to the high cross-linking nature of MIPs, which will result in incomplete template removal, and slow mass transfer. Fortunately, this problem can be resolved by surface imprinting, in which the imprinted templates are situated at the surface of the material's surface. Compared to traditional MIPs, surface imprinted polymers possess not only higher binding capacity but also faster mass transfer and binding kinetics. Many particles have been used for the surface imprinting process, such as activated silica, Fe_3O_4 (magnetic) nanoparticles, chitosan, activated polystyrene beads, quantum dots (QDs) and alumina membranes. The magnetic separation is an effective technique for separation of complicated samples. The magnetic nanoparticles have an advantage of its fast recovery, high efficiency, low cost, and direct purification from a mixture without any pretreatment. In recent years, magnetic MIPs have become a hotspot based on the significant advantages of magnetic separation over conventional methods. Generally, preparation of MIPs-coated magnetic nanoparticles (MNPs) involves three steps: (1) preparation of Fe_3O_4 MNPs; (2) surface modification of Fe_3O_4 MNP with TEOS, oleic acid, ethylene glycol or poly (vinyl alcohol) and (3) synthesis of surface imprinted MNPs using a sol–gel process or free radical polymerization [16–18].

4. Examples of MIPs applied for wastewater treatment

Till 1980s, according to MIP database number of MIP paper was published. Eighty percent of these papers were the usage of MIPs as SPE adsorbent. By the usage of nanoparticles for MIPs, the new papers were about the surface imprinting and also to use them in SPE. The some examples were summarized above. The most attractive and useful examples were chosen.

First example was the paper of Deng et al. [8]. Deng et al. was studied Ti(IV) functionalized chitosan molecularly imprinted polymer (Ti-CSMIP). While preparing chitosan imprinted polymer he used Ti^{4+} as Lewis acidic for producing metal hydroxyl group and protonated surface of MIP. He used Ti(IV) functionalized chitosan molecularly imprinted polymer to recognize reactive brilliant red (X-3B) in aqueous solution. The dye behaved as a Lewis base. The MIP was characterized by FTIR, SEM, XRD, BET, elemental and zeta potential analysis. Batch adsorption experiments (sorption isotherm, kinetics) and reusability were performed to evaluate adsorption condition. Regeneration experiments indicated that Ti-CSMIP was an effective sorbent for the selective removal of azo anionic dye in aqueous solutions. The difference of the study was; the Ti-CSMIP used as adsorption and also recognition. By using Ti^{4+} as a Lewis acid, the recognition problem of dye, which is limited due to its macromolecular structure, was overcoming. The Ti(IV) functionalized chitosan MIP was recognized dye macromolecules as template, because X-3B was behaved as a Lewis base. In this study, the first step is preparing Tİ-CSMIP. First of all, chitosan was dissolved and mixed with $Ti(SO_4)_2$ Then $Ti(SO_4)_2$/CS mixture was cross-linked with KH-560. After gelation, the product was treated by microwave for 20 min and the obtained product was washed with distilled water and dried. The product was added into X-3B solution after stirring the product was ready. The X-3B was removed using NaOH and HCl, respectively. Non-imprinted polymer (Ti-CSNIP) was prepared with the same procedure in the absence of the template molecule. Experiment of pH effect indicated X-3B sorption on Ti-CSMIP

was dependent on solution. The Temkin and Sips models was used as equilibrium model recycling experiments demonstrated that Ti-CSMIP had a greater potential even after several cycles of regeneration.

The second example was magnetic MIPs which was studied by Luo et al. [19]. He was studied magnetic and hydrophilic molecularly imprinted polymers (mag-MIPs) which were prepared by an inverse emulsion–suspension polymerization technique to remove water-soluble acid dyes from contaminated water. The attractive point of study was using 1-(1-methyl acrylate)-3-methylimidazolium bromide (1-MA-3-MI-Br) as a new functional monomer. The thermal stability, chemical structure and magnetic property of the 1-MA-3-MI-Br-mag-MIPs were characterized by the thermal-gravimetric analyzer (TGA), Fourier transform infrared spectrometer (FT-IR) and vibrating sample magnetometer (VSM), respectively. The first step was preparing novel magnetic nanoparticles and modifying surface by PEG. The final brown suspension was placed for 24 h quiescence, and the supernatant was discarded. The second step was preparing inverse emulsion. According to the method; 2 mL toluene with 0.1 g AIBN was mixed in 50 mL beaker. When AIBN was dissolved, 10 mL TRIM and a drop of Span 80 were added in the mixture and stirred to be uniform. Then 10 mL Fe_3O_4 magnetic fluid was added in the mixture. The mixture was stirred for 5 min, and then the mixture was submerged in the ultrasonic bath for 5-min. Finally, the inverse emulsion can be obtained. The third step was preparing mag-MIPs and magnetic non-imprinted polymers (mag-NIPs) were prepared via inverse emulsion–suspension polymerization. The procedure was summarized, 1 mmol tartrazine and 4 mmol 1-MA-3MI-Br were dissolved and prepolymerized for 30 min and mixed with inverse emulsion. Thirdly, the reaction mixture was heated and purged by N_2 to remove the oxygen. The reaction temperature was at 70°C for 12 h. After the reaction completed, the resulting mag-MIPs with uneluted molecule were filtered by 120 mesh sieve and washed by methanol and 60°C water. Finally, the products were washed by methanol:ammonia solution (9:1, v/v) for 24 h. The mag-NIPs were prepared by the same manner in the absence of template molecules. The several advantages of the water-compatible 1-MA-3-MI-Br-mag-MIPs to remove and recycle the water-soluble acid dyes in water media could be existed. Firstly, the removal efficiency towards water-soluble acid dyes is very high with all above 95% in wastewater. Secondly, the 1-MA-3-MI-Br-mag-MIPs can be reused at least five times without obvious decrease in the removal efficiency. Thirdly, due to the encapsulated Fe_3O_4, the 1-MA-3-MI-Br-mag-MIPs can be easily separated by external magnetic field.

The third example was the combination of MIP with biosensor [20]. Khan et al. was studied a biomimetic sensor which was prepared on carbon paste with magnetic molecularly imprinted polymer (mag-MIP) for sensitive and selective detection of methyl green dye. The mag-MIP was synthesized using a functional monomer that was selected before by computational simulation. The findings showed that imprinted biosensor can be suitable for real samples. The mag-MIP was synthesized by the process of polymerization in the existence of methyl green and the functional monomer acrylamide were dissolved in ethanol The reaction mixture was agitated in a water bath at 25°C for 12 h, followed by addition of $Fe_3O_4@$ SiO_2━C═C and shaking for a further 3 h. In the next step, EGDMA and AIBN were put to the system to the mixture that was further sonicated in a water bath for 5 min. The reaction mixture was thermal polymerized at 60°C for 24 h. The analyte molecule was then removed by Soxhlet extraction apparatus via methanol:acetic acid (9:1, v/v) washing solution. The product obtained (mag-MIP) was dried out at 60°C in vacuum. The magnetic non-molecularly imprinted polymer (mag-MIP) was prepared under the same conditions, but without the presence of the analyte.

This polymer showed higher binding capacity for methyl green, compared to the corresponding non-imprinted polymer. Electrochemical sensors using the mag-MIP produced by this method have some advantages that it was offering mechanical stability in solution and providing satisfactory performance of sensor in terms of sensitivity and selectivity.

The fourth example was different example from the others [7]. In this study, Yu et al. is studied selective, sensitive and reliable magnetic molecularly imprinted material to enrich and separate aromatic amines from azo dyes. The 4,4′-methylenebis(2-chloroaniline) (MOCA) was used as template molecule. The synthesis of magnetic molecularly imprinted polymer was performed on the surfaces of the magnetic silica gel spheres via thermal polymerization as mentioned paper, detailly. The steps can be summarized, $Fe_3O_4@SiO_2$ was prepared and washed sequentially with both ethanol and toluene. The second step was the surface of $Fe_3O_4@SiO_2$ was grafted with vinyl by using VETS and triethylamine. The final product of $Fe_3O_4@SiO_2@-CH=CH_2$ was separated and then dispersed in toluene. The synthesis of magnetic molecularly imprinted nanoparticles was done with EGDMA and 2-VP were used as the cross-linker and functional monomer, respectively. A template molecule of MOCA and 2-VP were dispersed in of toluene. Then, particles $Fe_3O_4@SiO_2@-CH=CH_2$, EDGMA and AIBN mixed with the MOCA+2-VP solution and purged with nitrogen. The thermal polymerization was performed with changing temperature. The non-imprinted particles were synthesized with the same procedures in the absence of MOCA. A solution of methanol and acetic acid (9:1, v/v) was used in a Soxhlet to remove the template molecule. The physical properties of mag-MIPs and NIPs were characterized, and the adsorption isotherms were studied. The adsorption process was described by a pseudo-second order model and the equilibrium data fitted well to a Freundlich equation. The other advantages of these magnetic molecularly imprinted polymers were dye removing from wastewaters effectively, and also discriminating carcinogenic aromatic amines which were the main structure of textile dyes.

The fifth example was one of real sample application [21]. Foguel et al. is studied MIPs for the Acid Green 16 (AG16) textile dye and the used this MIP for rebinding, selectivity and application of in wastewater samples. MIP synthesis was performed using AG16 dye (template), 1-vinylimidazole (functional monomer), ethylene-glycol-dimethacrylate (cross-linker), 2,2′-azobis(2-methylpropionitrile) (initiator) and methanol (solvent) by bulk polymer synthesis. The imprinted polymer presented excellent rebinding of 83%, an imprinted factor of 6.91 and great selectivity in comparison with other textile dyes. Additionally, the MIP showed high efficiency in the extraction of this dye in wastewater and have a better performance when compared to commercial SPE cartridges. In this study the selectivity of the MIP for AG16 was evaluated using four dyes, commonly used in the textile industry, with different structures and chromophore groups: Direct Yellow 50 (DY50), Acid Red 1 (AR1), Basic Red 9 (BR9) and Methyl Green (MG). MIP for AG16 is quite selective compared to the dyes DY50, AR1, MG and BR9, since approximately 86% of AG16 was bound to the MIP, while the binding percentage for these other four dyes was between 4% and 11%. The MIP proposed in this work showed great efficiency in the determination of the AG16 dye, since the synthesized MIP presented good rebinding of the analyte to the selective cavities of the MIP, high selectivity compared to other textile dyes and efficiency in the extraction of the compound of interest, when applied in a sample of textile wastewater.

The sixth example was about removal and also adsorption of dye on MIPs [22]. Okutucu et al. is studied a molecularly imprinted polymer (MIP) which textile dye (Direct Red 23) was used as template for decolorization of textile wastewater and also used for leaching of this dye from the wastewater by adsorption of onto

polymer. Acrylamide was used as a monomer and dimethyl sulfoxide was used as a porogen. The ethylene-glycol-dimethacrylate (cross-link), 2,2′-azobis(2-methylpropionitrile) (initiator) was used while preparing bulk polymer by thermal synthesis. The template was removed by methanol:conc. HCl washings. The selective recognition ability of the MIP was studied by an equilibrium-adsorption batch method. The effective adsorption properties of the polymer were tested in synthetic dye wastewater. The high adsorption rate and the amount of imprinted dye that was removed from the polymer was nearly 65%. Eighty percent of the dye was adsorbed by imprinted polymer in synthetic wastewater. The goal of this study is to prepare dye-imprinted polymer to research the molecular recognition characteristics, so that to get valuable results for contamination of dyes in wastewater. It is also important and valuable to recognize dye molecules and their removal from wastewater for the protection of the environment. The dye-imprinted polymer can also be used as a solid-phase adsorbent for Direct Red 23 dye to detect whether it was present in wastewater. Adsorption of dye molecules onto a sorbent can be an effective, low-cost method of decolorization of textile wastewater. Most of the techniques used for this aim were the high cost of production and the regeneration also makes them uneconomical. Molecular imprinting polymers are a new kind of materials which can be economical and effective adsorbents. The removing effect of MIP was seen at **Figure 1**.

The seventh example was the example of using β-cyclodextrin as a monomer for MIP synthesizing [23]. In this study, Hu et al. were synthesized a magnetic β-cyclodextrin polymer (MNP-CM-CDP) which could be used in aqueous media. Kinetic isotherms and a dye adsorption method provided Langmuir. By using MNP-CM-CDP model pollutants (BPA, MB, BO_2, RhB, Cr(III), Pb(II), Zn(II), and Cu(II)) were rapidly and efficiently removed from the aqueous solution. Because of magnetic character, the polymer could be easily separated from the solution under an external magnetic field. The synthesis of the magnetic β-cyclodextrin polymer was done at three steps, with TFTPN used as rigid crosslinker, EPI used as flexible crosslinker, chloroacetic used as carboxymethyl agent, Fe_3O_4 used as magnetic matrix and deionized water used as solvent. First step was, β-TFTPN was dissolved in EPI and then added dropwise to cyclodextrin in NaOH solution. After magnetic stirring for 3 h at 100°C, the solution was filtered. The precipitate was washed with water and THF, and then dried. The second step was synthesis of the CME-CDP. The T-E-CDP was dispersed into NaOH and chloroacetic acid was added. After magnetic stirring, the solution was cooled and neutralized with hydrochloric acid. The CME-CDP was obtained. Third step was synthesis of the MNP-CM-CDP. The magnetic β-cyclodextrin polymer (MNP-CM-CDP) was synthesized by one-step coprecipitation. Fe solutions and the CME-CDP were mixed,
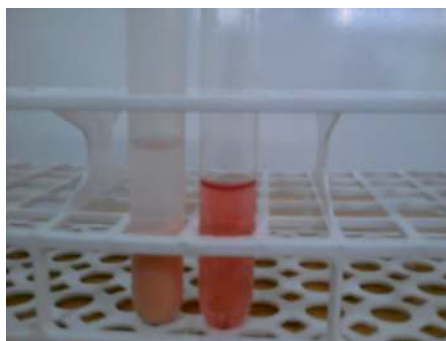

Figure 1.
The removal of Direct Red 23 with MIP [12].

then $NH_3 \cdot H_2O$ (25%, 5 mL) was added dropwise under nitrogen. The precipitate was washed with deionized water five times and then dried. The adsorption of dyes and metal ions is mainly dependent on the pH and this condition was also studied and optimized. The polymerization was performed by green synthesis route, due to use β-cyclodextrin good adsorption performance, easy regeneration, and simple operation. The results indicated that the MNP-CM-CDP is a promising adsorbent in commerce for purifying dyeing wastewater and can be produced on a large scale in industry.

5. Conclusion

Saving water to save the planet and to make the future of human was the most important aim. There are many materials existed that can be used. These are activated carbon, clay minerals, zeolites and biomaterials. The main purpose of all these materials was adsorption of wastes in water. Such as zeolites are crystalline substances with pores which was permitted only the passage of certain size. Zeolites can occur naturally or synthesized in laboratory. They are mainly constituted by Al, O and some metals. They are mostly negatively charged, and their surface can be modified. So, the surface can be treated with multiple classes of contaminants. There are many studies about dye adsorption with different zeolites in wastewater [24, 25]. The zeolites only can remove dyes by adsorption on their surface, but MIPs can ability of recognition, quantification and adsorption. All of these excellent characteristics make MIPs good alternative adsorbents for wastewater treatment. The ease of preparation, resistance to hard conditions (pH, temperature, storage stability, vs.), easily to study with real complex examples (directly wastewater) make MIPs more suitable for different samples. In this chapter, the characteristic components of MIP, synthesizing methods and some examples of treatment of wastewater by MIPs were summarized.

Author details

Burcu Okutucu
Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, Turkey

*Address all correspondence to: burcu.okutucu@ege.edu.tr

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