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Synthesis and evaluation of a molecularly imprinted polymer for selective adsorption and quantification of Acid Green 16 textile dye in water samples

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ABSTRACT

An alternative for determining environmental pollutants, like textile dyes, is the use of molecularly imprinted polymers (MIPs) as solid phase extraction (SPE) or as sensor recognition systems. MIPs are tailor-made artificial receptor sites in a polymer, which present good affinity and selectivity. This work shows the synthesis of MIPs for the Acid Green 16 (AG16) textile dye and the results of rebinding, selectivity and application of this MIP in water samples. MIP synthesis was performed using AG16 dye (template), 1-vinylimidazole (functional monomer), ethylene-glycol-dimethacrylate (cross-link), 2,2′-azobis(2-methylpropionitrile) (initiator) and methanol (solvent) by bulk 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 water samples, presenting a recovery rate close to 100% and a better performance when compared to commercial SPE cartridges. Due to this excellent performance for AG16, the application of this MIP to determine dyes in different matrices of environmental importance is promising.

1. Introduction

The estimated production of synthetic dyes is 7×10^5–1×10^6 t per year worldwide and are used in textile dyeing, paper, pulp, plastics, color photographs, foods, cosmetics and other industrial products [1]. Despite the great interest and application of dyes, the disposal of wastewater containing dyes has become a serious environmental problem. In the textile industry, approximately 50% of the dye is lost during the dyeing process and about 10–15% is discarded in effluents [2], causing considerable environmental degradation, like the change of the natural coloring and formation of foam on water surface, when these textile effluents are released in rivers [3]. Moreover, dyes are within the most dangerous pollutants in wastewater, due to their permanence and high toxicity. Most of the synthetic dyes have carcinogenic, mutagenic and toxicological properties, which can threaten the health of a great variety of organisms [4,5].

Among the several dyes employed in the industrial sector, there is a wide range of types, which can be classified according to their application or chemical structure [6]. The triphenylmethane class is widely used for nylon, wool, cotton and silk pigmentation. This chromophore consists of three aryl radicals bound to a central carbon atom [7]. This dye class is one of the most common organic pollutants and causes environmental concerns due to its potential toxicity to animals and humans [8]. In effluents, these products absorb the sunlight and interfere with aquatic biological processes [9]. An example of triphenylmethane dye is Acid Green 16 (AG16; C.I. 44025), whose structure is shown in Fig. 1. This dye is largely used in the textile industry, especially for the dyeing of wool and silk; it presents a greenish blue solution when soluble in water, and green solution in ethanol [10]. Toxicological studies have shown evidence that the dye AG16 has genotoxic and mutagenic effects in mice [11].

Due to toxicological risks and environmental damage that the inadequate disposal of dyes can present, several studies have been developed to identify, quantify and degrade this kind of pollutant. There are many methodologies reported in the literature for determining dyes, mainly employing chromatography [12] and electrochemical [13,14] methods.

Although there is a variety of techniques for the determination of dyes, some of them have limitations and problems related to sample preparation, consuming a lot of time for analysis, high costs and the use of large amounts of solvents [15]. For this reason, an alternative that can be interesting, simple and promising for the detection and quantification of dyes is the use of molecularly imprinted polymers

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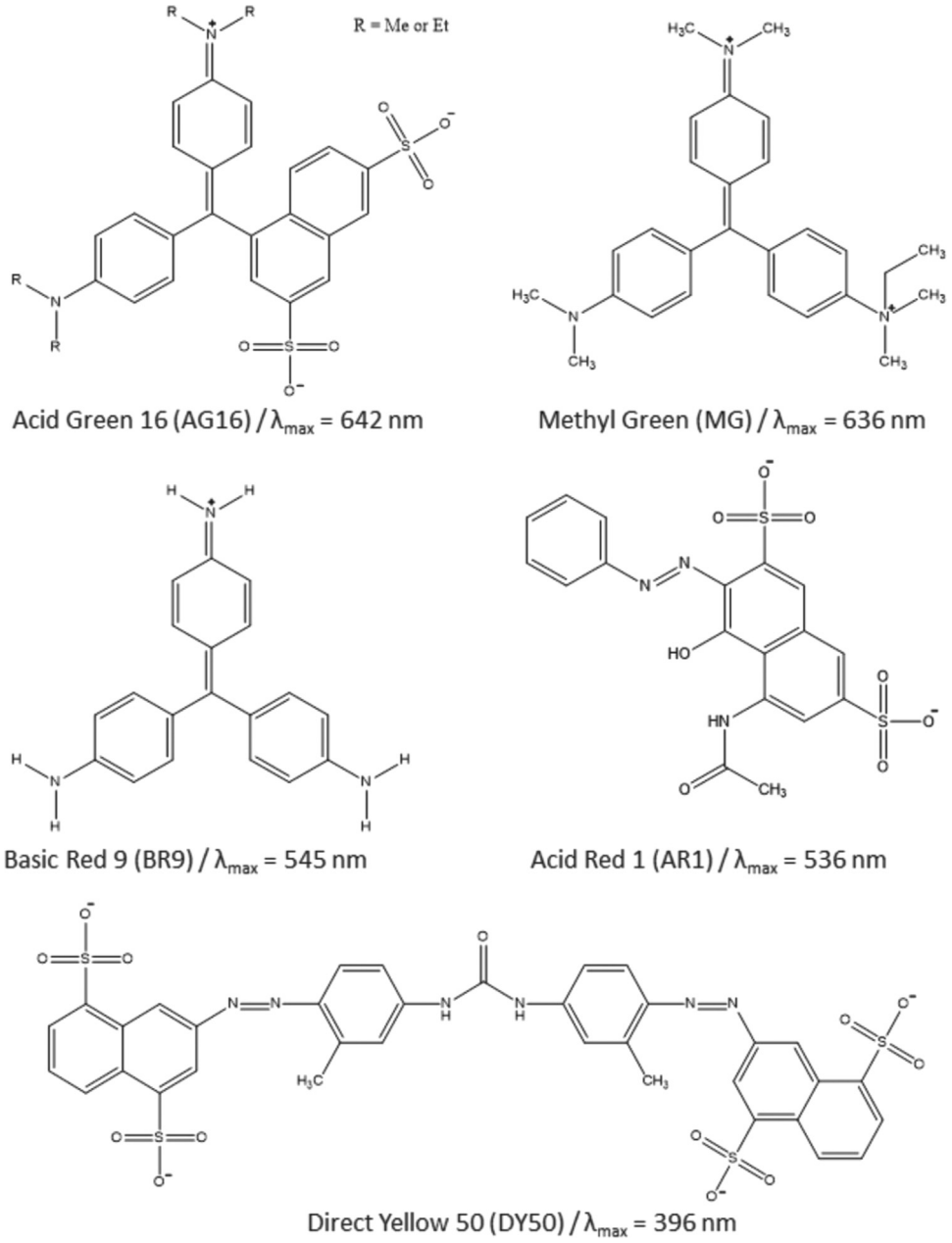

Fig. 1. Chemical structures of AG16 and other textile dyes used in the selectivity study. AG16, AR1 and DY50 are sodium salts, while BR9 and MG are chlorides.

(MIP) to extract a specific or a class of dye in a more complex sample [16,17]. After the extraction, the dye's analysis employing the spectrophotometric technique becomes attractive due to the dye's chemical properties, which include: light absorption in the visible region, low cost and low technical requirements.

MIP performs specific recognition due to the formation of complementary cavities in specific size and shape of a particular analyte [18]. These polymers have attracted attention because they can be a promising tool for the development of biomimetic recognizers similar to specific biological systems, like substrate-enzymes and/or antigen-antibodies [19].

MIPs are produced by the growth of a structural polymer around a target molecule that is used as a template [20,21]. For MIP synthesis, a functional monomer is also added to the reactional system to interact with specific groups of the analyte, ensuring chemical selectivity to the MIP. Free radical polymerization is the most common for polymer synthesis and, in general, the reactions are initiated by heat or UV radiation [22,23]. Once the polymer has been formed, the template is removed from the polymeric structure by dissolution using a solvent whose analyte presents high solubility. Thus, the MIP cavities become available for rebinding to a specific molecule in complex samples, allowing their quantification [24].

Despite the fact that MIP have been reported since the 70 s [25], MIP for dyes are relatively new in literature and were initially published in 2005 [26]. Among published work, MIP for dyes are mainly used as sorbents for solid phase extraction (SPE, commonly called MISPE) due to their high selectivity in complex samples [27].

In order to obtain good performance from the imprinted polymer, a thorough study on the synthesis and behavior of imprinted polymers is essential. Therefore, joining the advantages of MIP with the chemical properties of dyes, this work presents MIP synthesis for the textile dye Acid Green 16 (AG16) and the results of rebinding performance, selectivity and application of this MIP in textile effluents.

2. Experimental

2.1. Reagents and apparatus

All chemicals, dyes and solvents were of analytical grade. MIP synthesis was performed using Acid Green 16 (AG16), 1-vinylimidazole (1VI), ethylene glycol dimethacrylate (EGDMA), 2,2′-Azobis(2-methylpropionitrile) (AIBN); and the selectivity analysis was carried out with Acid Red 1 (AR1), Direct Yellow 50 (DY50), Methyl Green (MG) and Basic Red 9 (BR9), all purchased from Sigma-Aldrich (USA). Methanol, purchased from J.T. Baker (USA), was employed for the removal of the template from the MIP structure and as porogenic solvent, with glacial acetic acid from Synth (Brazil). The monomers were employed as received. All solutions were prepared using water of Milli-Q quality (resistivity > 18 MΩ cm, Millipore, Inc., USA).

Degradation evaluation of AG16 dye was performed by high performance liquid chromatography of Agilent Technologies equipped with an Agilent 1200 Quaternary Pump, an Agilent 1200 High Performance Autosampler, an Agilent Column Oven and Agilent 1260 Diode Array Detector coupled to a Mass Spectrometer 3200 QTRAP (Linear Ion Trap Quadrupole LC/MS/MS Mass Spectrometer), AB Sciex Instruments operating in a positive mode and TurboIonSpray ionization. The parameters employed were: curtain gas: 20 psi, Ion Spray: 5.500 V, Gas 1: 50 psi, Gas 2: 50 psi, Temperature: 550 °C. The chromatographic conditions used were: water with 0.1% formic acid and methanol (20:80 v/v) as the mobile phase at a flow rate of 0.8 mL min^{-1}, detection wavelength of 642 nm, column temperature of 40 °C and injection volume of 40 µL. The chromatographic column Kinetex C18 (250×6.60 mm, 5 µm) were purchased from Phenomenex.

The size and morphology of the polymers was characterized using field emission scanning electron microscopy using a JEOL JSM 6330 F. Brunauer-Emmett-Teller (BET) surface area was determined from nitrogen adsorption isotherms using a Micromeritics ASAP 2010 Surface Area Analyzer. Absorbance measurements were done on Hewlett Packard 8454 diode array spectrophotometer using a quartz cuvette with 1.0 cm of pathlength.

The Fourier transform infrared (FTIR) analysis was performed using a FTIR Vertex 70 spectrometer from Bruker with a HeNe laser source and a DLaTGS detector, using a wavenumber range of 4000–400 cm^{-1}.

For the thermal behavior evaluation of the polymers was employed a SDT 2960 thermoanalyzer from TA Instruments. The analyzes were performed in the range from 30 to 500 °C, heating rate of 10 °C min^{-1}, dry air atmosphere with flow rate of 100 mL min^{-1}.

2.2. MIP synthesis

The polymer synthesis was prepared by bulk polymerization and it was inspired by Foguel and co-workers [28]. Initially, 0.08 mmol of AG16 (template), 0.24 mmol of 1VI (functional monomer) and 6.0 mL of methanol (porogenic solvent) were added to a glass tube and stirred for 2 min using a Vortex stirrer. After letting the mixture rest for 2 h, 16 mmol of EGDMA (cross-link) and 0.024 mmol of AIBN (initiator) was added. The mixture was purged with nitrogen for 10 min, the glass tube was then sealed with Parafilm and polymerization was done overnight at 60 °C in a waterbath. The bulk polymers were ground manually with a mortar and pestle, sieved, and subjected to wash in a Soxhlet system with 3 rounds of methanol/acetic acid (7/3) and 3 rounds of methanol for complete extraction of the analyte. Non-imprinted polymers (NIP) were synthesized in the same way, but without the addition of the imprinting template.

2.3. Rebinding evaluation of AG16 to the polymers

MIP performance was evaluated by rebinding analysis of analyte to imprinted and non-imprinted polymers. A stock solution of 300 µmol L^{-1} of AG16 was prepared in water; and the polymer's particles, at a concentration of 20 mg mL^{-1}, were suspended by sonication in water. From this stock, different parameters were evaluated, such as polymer concentration, incubation time and isotherm adsorption.

The analysis of polymer amounts was performed in 2.0 mL polypropylene microcentrifuge tubes using different concentrations of polymer suspension, from 1 to 8 mg mL^{-1}. For this, a determinate volume of polymer stock suspension was added in the tube, followed by the addition of 100 µL of 300 µmol L^{-1} AG16 dye. Then, the final volume was adjusted to 1.0 mL. The tubes were incubated for 60 min at ambient temperature on a tube rotator. The interaction time was performed using the same methodology, employing 8 mg mL^{-1} of polymer and 30 µmol L^{-1} AG16 with different quantities of time for interaction (10–480 min). For the adsorption isotherm, 8 mg mL^{-1} polymer was incubated for 60 min with several AG16 concentrations (5–240 µmol L^{-1}).

In all analysis, after the incubation time, the tubes were centrifuged for 30 min at 15,000 rpm, following absorbance measurements of the supernatants using a fixed wavelength of 642 nm.

All optimization steps were performed in triplicate.

2.4. Selectivity studies

The selectivity of MIP-AG16 cavities was performed using four different dyes, commonly employed in the textile industry, and the rebinding percentage of each dye to the polymer was compared to the rebinding of AG16. The dyes used in this study were Methyl Green (MG), Basic Red 9 (BR9), Acid Red 1 (AR1), and Direct Yellow 50 (DY50), whose structures and maximum absorption wavelengths are shown in Fig. 1.

This study was performed in polypropylene microcentrifuge tubes, where 100 µL of 500 µmol L^{-1} of each dye was added to different tubes, followed by 400 µL of 20 mg mL^{-1} polymer (MIP/NIP) and 500 µL of water, thus the final concentration in each tube was 8 mg mL^{-1} and 50 µmol L^{-1} of polymer and dye, respectively. The tubes were incubated for 60 min at room temperature on a tube rotator, followed by centrifugation for 30 min at 15,000 rpm. Absorbance measurements at the wavelength (indicated in Fig. 1) of the dye analyzed were performed on the supernatants. The amount of dye bound to the polymers was calculated by subtracting the amount of unbound dye from the initial amount of dye added to the mixture. The selectivity studies were performed in triplicate.

2.5. Analysis in samples

The performance of the MIP was evaluated using it as SPE for determination of the concentration of AG16 present in a water samples. The experiment was performed with tap water and industrial effluent, both with no AG16 spiking. The treated water was collected directly from the tap and the effluent sample was collected from a textile industry in Araraquara, Brazil before any kind of treatment. The company reported that this effluent had no AG16, since this dye was not used during the dyeing process.

The samples were contaminated with the AG16 dye in three different concentrations: 4, 20 and 80 µmol L^{-1}. After the addition of the analyte, the solutions were vigorously stirred and allowed to sit for 24 h.

For the recovery analysis, 100 mg of MIP/NIP particles were filled in an empty 3 mL SPE tube. The top and bottom of filter filler had polyethylene frits. Subsequently, 10 mL of ultrapure water was used to condition the cartridges at a flow rate of 2 mL min^{-1}. Then, 25 mL of AG16 standard solution in water or the spiked sample solutions, with different concentrations, were passed through the cartridges at the flow rate of 0.5 mL min^{-1}. Then, 10 mL of methanol was used for dye elution at a flow rate of 2 mL min^{-1}. The methanol was chosen in this step due to high solubility of the dye in this solvent. The collected

extracts were analyzed using a UV–vis spectrophotometer. The same procedure was carried out using commercial SPE cartridges filled with C18, MIP for fluoroquinolone and MIP for nitroimidazole, however only the industrial effluent contaminated with 4 μmol L^{-1} was analyzed. All experiments were performed in triplicate.

3. Results and discussion

3.1. Degradation evaluation of AG16

The stability of the AG16 was qualitatively evaluated from the preparation of a dye solution at a concentration of 10 mg mL^{-1} in deionized water. This solution was exposed to natural sunlight for 7 (Fig. S2) and 20 days (Fig. S3) and analyzed by HPLC-MS/MS. The chromatographic signal and the ion fragmentation of these dye solutions were compared to a standard solution of AG16 freshly prepared at the concentration of 500 μg mL^{-1} (Fig. S1).

Despite the fact that the chromatographic peaks had shown a slight difference in retention time for each analysis, the spectra of the fragmented ion presented *m/z* of 595, which referred to the AG16. This difference found between the retention time of peaks is probably due to some changes in the charge of the molecule. Thus, we can affirm that AG16 is present in the sample, even after 20 days of sunlight exposure. An important point to note, in the results obtained for this dye, is that the intensity of the peak in the chromatograms after 7 and 20 days of exposure to sunlight showed no significant decrease in the amount of dye between these two analyses, revealing that there is almost no degradation of this compound. This result also highlights the importance of developing a method for determining this dye in environmental matrices, since it is a persistent and toxic pollutant.

3.2. Characterization of polymers

The morphology of the NIP and MIP was examined via FE-SEM. The main goal was to evaluate the physical appearance of the polymers' particles. As it can be observed in Fig. 2, both polymers were agglomerated in the shape of spherical particles. MIP particles had more uniform sizes and shapes than NIP. The average size of MIP's particles was 2.5 ± 0.3 μm in diameter, while the NIP had particles between 31 ± 5 nm and 3.1 ± 0.7 μm.

The porosity of polymers was calculated by BET surface areas. NIP presented a superficial area of 27.0 $m^2 g^{-1}$ and pore volume of 0.0074 $m^3 g^{-1}$. On the other hand, MIP had 194.3 $m^2 g^{-1}$ and 0.0625 $m^3 g^{-1}$ of superficial area and pore volume, respectively. Observing these results, it is evident that the cavity for the AG16 dye was formed in the MIP. Since the imprinted polymer showed a surface area and pore volume of 7.2 and 8.4 times, respectively, bigger than the NIP. According to the pore size of the MIP (4.0 nm), it can be classified as a mesoporous polymer material [29].

The infrared spectrum of MIP was compared with the spectra of the reagents used to the synthesis: AG16, 1VI and EGDMA (Fig. 3). The FTIR spectrum for the dye AG16 (Fig. 3A) presents the characteristic bands of the sulfonate groups between 1376 and 769 cm^{-1}, in addition to the bands referring to the aromatic rings between 1605 and 1440 cm^{-1}. As the MIP was analyzed after removal of the dye from the polymeric structure, no signal regarding the AG16 dye was observed. The functional monomer (1VI) presents intense signals in the region of lower frequency (between 1640 and 870 cm^{-1}) referring to the bonds between carbon and nitrogen atoms, besides the characteristic peaks of the vinyl group. As shown in Fig. 3B, the MIP does not present 1VI characteristic bands, probably due to low amount of this reagent in the polymer structure if compared to the structural monomer amount, thus the 1VI amount is below the detection limit of the equipment. By EGDMA spectrum (Fig. 3C) is verified that the MIP structure is basically composed by the structural monomer. Since MIP presents the characteristic bands of the ester group in 1716 and 1294 cm^{-1}, related to carbonyl (C=O) stretching and C-O bond, respectively. In addition, a significant decrease in the signal intensity of the double bond between the carbons (C=C) in 1637 cm^{-1} was also observed, showing that polymerization occurred by the breaks of the double bonds between the carbons by the radical initiator.

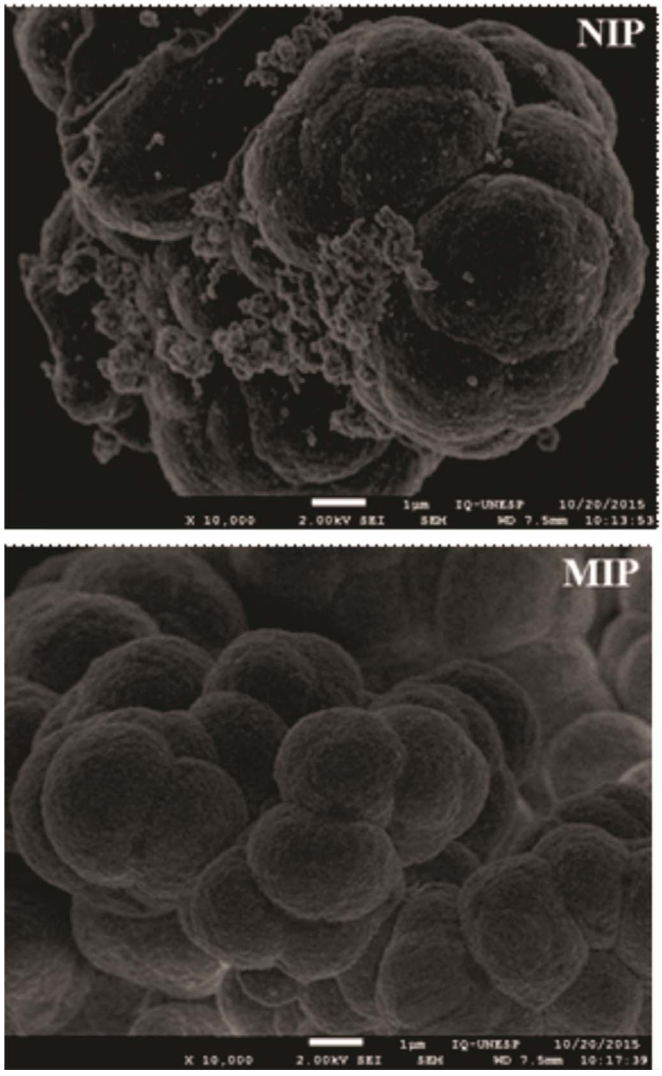

Fig. 2. Scanning electron microscopy images showing the size and morphology of bulk NIP and MIP with magnification 10,000.

The thermal stability of the polymers was verified by thermogravimetric (TG) and differential thermal analysis (DTA), as showed in Fig. 4. From the TG analyzes, both the NIP and the MIP showed similar thermal behavior. There is loss of adsorbed water in the polymer structure up to 100 °C. The material remains stable in the range from 100 to 255 °C, from this temperature there is the polymer decomposition, this transition corresponds to exothermic peaks according to the DTA analysis. Therefore, the polymers are considered stable at relatively high temperatures.

3.3. Binding analysis of AG16 to the polymers

The polymers' performance was initially analyzed by rebinding AG16 to the MIP's cavities varying the amount of polymers. For this, 30 μmol L^{-1} of AG16 was incubated with different concentrations of polymers for 60 min and the percentage of bound dye to the NIP and MIP was evaluated (Fig. 5A). Increasing the polymer concentration favored the rebinding of the analyte to the polymers. The percentage of rebound dye to the MIP was stable from 4 mg mL^{-1} on. The rebinding of the dye to the MIP reached 83% when using 10 mg mL^{-1} of polymer

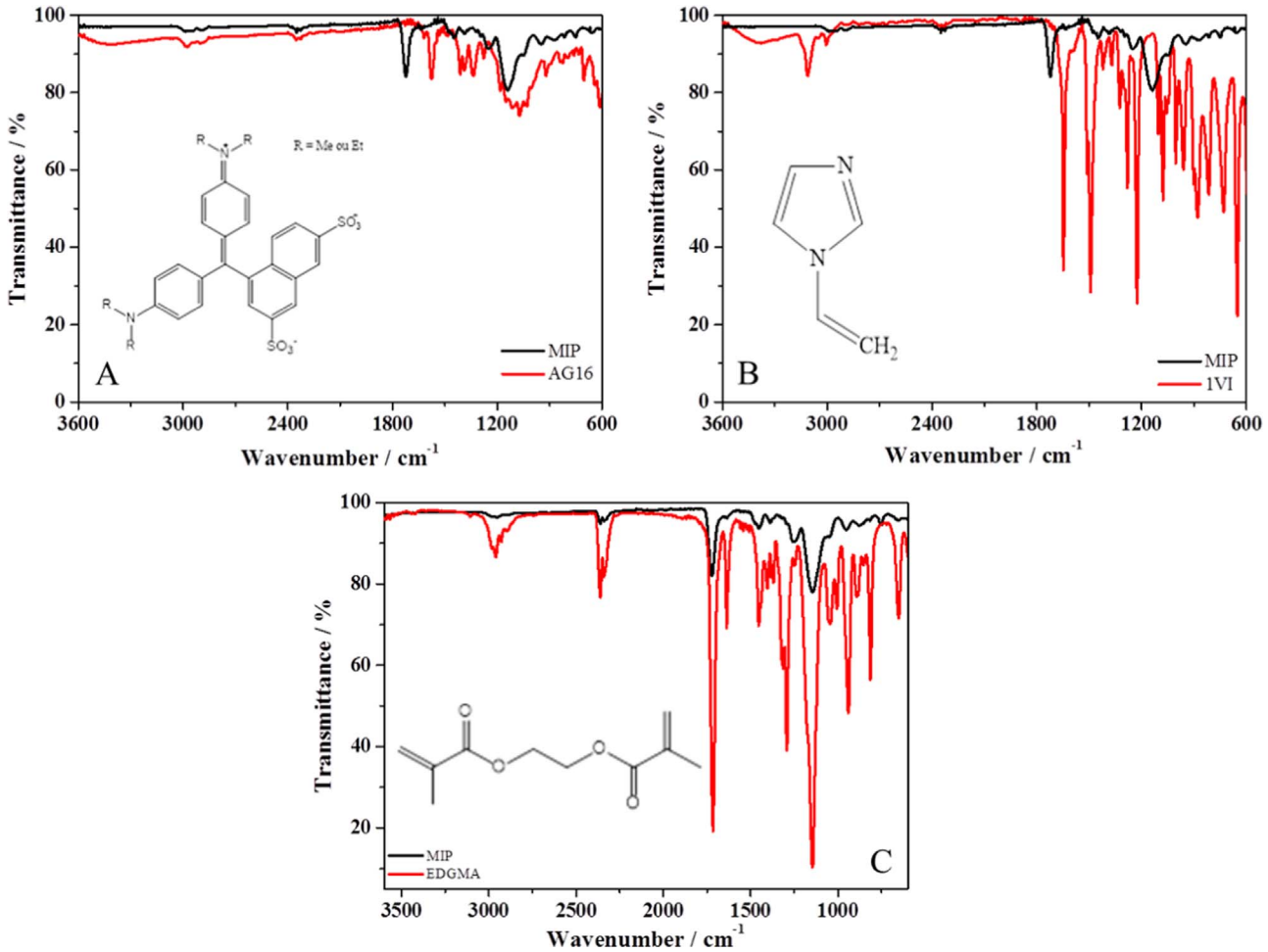

Fig. 3. Spectra in infrared region of MIP and the reagents of synthesis: (A) Acid Green 16, (B) 1-vinylimidazole and (C) ethylene glycol dimethacrylate.

against 32% to the NIP. However, in subsequent studies, 8 mg mL^{-1} of polymer was employed, because this concentration presented the greatest difference between imprinted and non-imprinted polymers (55%) and, additionally, had the lowest variation among the measurements.

To optimize the rebinding of the dye to the MIP's cavities, the incubation time was evaluated in a range from 15 to 480 min (Fig. 5B). Independently of the time analyzed for the interaction between the analyte and the polymers, the rebinding percentage of AG16 to MIP was higher than the NIP. In MIP, the rebinding percentage increased until 60 min, which presented the highest rebinding percentage (95%). After this time, the amount of bound dye remains constant. While the rebinding percentage of the dye to the NIP rises until 120 min and, then, there is no significant variation. For the subsequent steps, the interaction time of 60 min was used, due to the higher rebinding percentage to the MIP and largest difference compared to the NIP (approximately 70%).

3.4. Isotherm adsorption of AG16 to the polymers

The evaluation of MIP performance was also carried out by isotherm adsorption, as reported by Valero-Navarro [30]. The isotherm adsorption is the amount of a solute adsorbed to an adsorbent (Q) as a function of equilibrium concentration of the solute. For this, a solution containing the analyte in different concentrations is placed in contact with the adsorbent at a constant temperature until equilibrium. Thus, it is possible to determine the amount of adsorbed material. The value of Q was calculated by Eq. (1) [31].

$$Q = \frac{(C - C_f)xV}{m_{pol}} \quad (1)$$

The isotherm curve was performed in a range from 5 to 240 μmol L^{-1} of AG16, the polymeric concentration was 8 mg mL^{-1} and the incubation time was 60 min (Fig. 6). The result was very satisfactory, since the amount of dye bound to the NIP was close to 0 mg g^{-1}, while the retention of the dye to the MIP presented a very significant Q value. Therefore, it is clear that selective cavities for AG16 were formed successfully on the MIP structure. Moreover, the percentage of nonspecific binding in the polymeric structure is low. This can be stated because of the low retention of the dye to the NIP.

From these results, the imprinted factor of the MIP was calculated (Table inset in Fig. 6). A great way of evaluating the performance of the imprinted polymer is by calculating the imprinted factor (I) of a MIP relative to a NIP [32]. This parameter is measured by the partition coefficient (K_P), which is the ratio of the average number of molecules bound to the polymer cavities (Q) and the concentration of the free molecule in solution (C) as shown in Eq. (2). Therefore, the value of I is obtained by ratio of the partition coefficient of a MIP ($K_{P,MIP}$) and the partition coefficient of a NIP ($K_{P,NIP}$) as represented by Eq. (3).

$$K_P = \frac{Q}{C_l} \quad (2)$$

$$I = \frac{K_{P,MIP}}{K_{P,NIP}} \quad (3)$$

The imprinted factor is considered satisfactory when it has a value that exceeds 1.0. The MIP for AG16 presented in this work has an

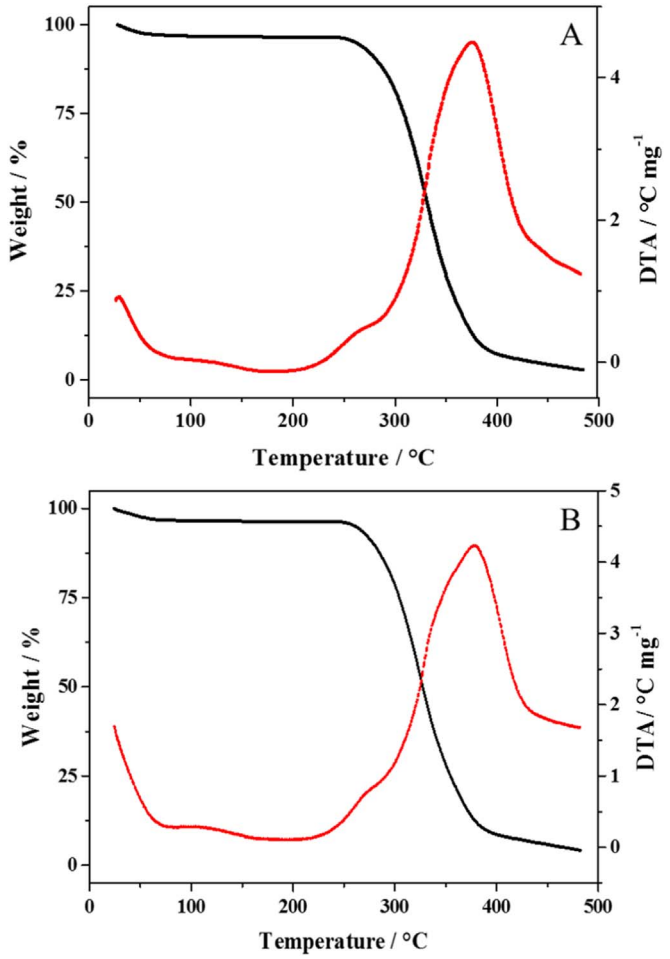

Fig. 4. Thermogravimetric analysis (black line) and differential thermal analysis (red line) for NIP (A) and MIP (B). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

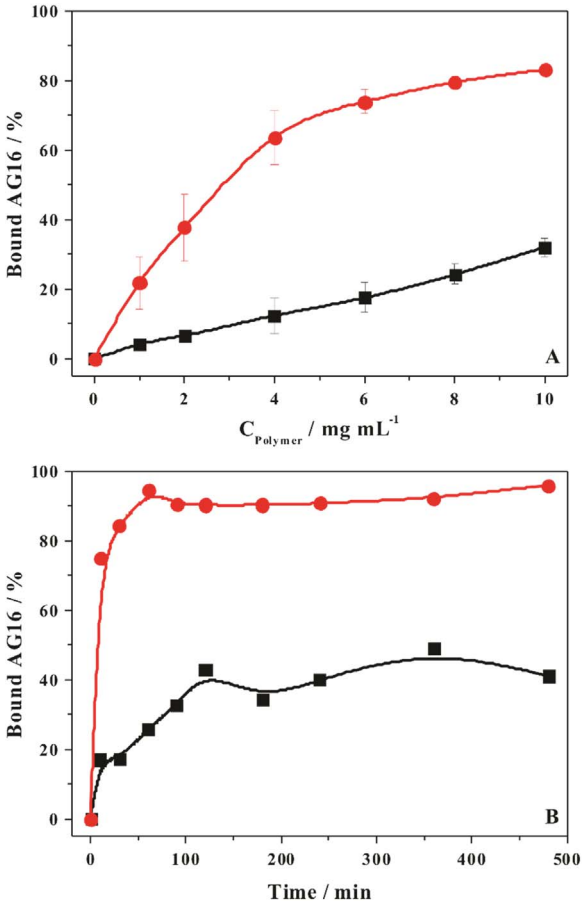

Fig. 5. (A) Equilibrium binding isotherms of 30 μmol L^{-1} AG16 with MIP (red circles) and NIP (black squares) in water with 1 h of interaction between analyte and polymers. (B) Interaction time analysis of AG16 (30 μmol L^{-1}) to the polymers (8 mg mL^{-1}) in water. Data are means from three independent experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

excellent imprinted factor, with a value of 6.91. This result shows that the AG16 dye has a high capacity to bind to the selective cavities of the MIP.

3.5. Selectivity analysis of MIP for AG16

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); whose structures are showed in Fig. 1. The analysis was carried out interacting 8 mg mL^{-1} of polymers and 50 μmol L^{-1} of each dye during 60 min and then the binding percentage was compared (Fig. 7).

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%. It is important to note that the cavity of the MIP was selective for the AG16 even when using compounds with similar structures and same chromophore group (MG and BR9) and dyes with available sulfonate groups (AR1 and DY50), which are responsible for ion-dipole interactions with functional monomers.

3.6. Recovery analysis of AG16 dye in sample of textile effluent

The polymer's efficiency to extract the AG16 dye from industrial textile effluent and tap water samples was evaluated using the MIP and NIP packaged in cartridges of SPE and the relative recovery is showed in Table 1.

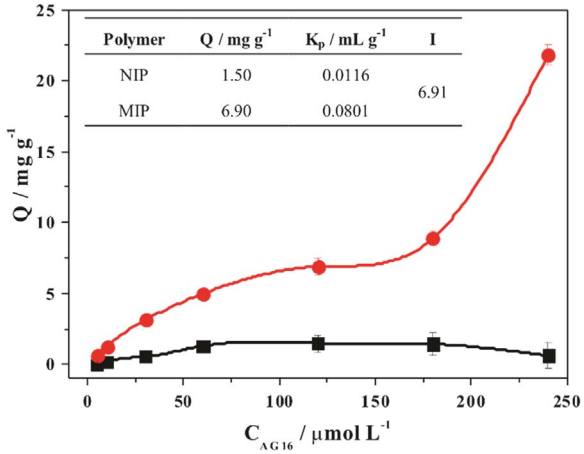

Fig. 6. Isotherm adsorption of AG16 to the 8 mg mL^{-1} of MIP (red circles) and NIP (black squares) in water with 1 h of interaction. Inset: rebinding parameters of AG16 (120 μmol L^{-1}) to the polymers from the determination of rebinding capacity (Q), the partition coefficient (Kp) and imprinted factor (I). Data are means from three independent experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The extraction of the AG16 dye proved to be excellent for both samples when a low concentration of analyte (4 μmol L^{-1}) was presented in the sample, since the MIP had a relative recovery around 96%, while the NIP's recoveries were between 26–36%. However, when

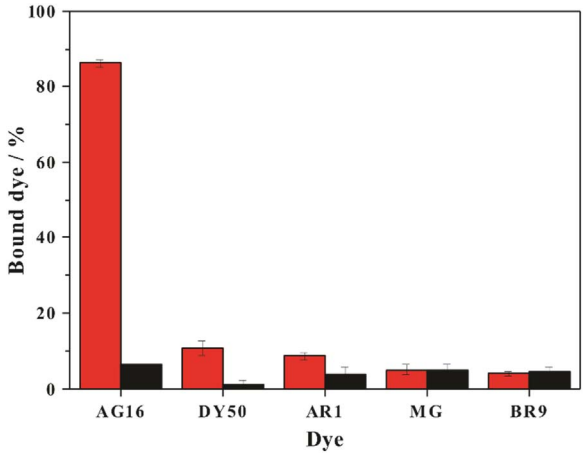

Fig. 7. Binding of different textile dyes (50 μmol L^{-1}) to 8 mg mL^{-1} NIP (black bar) and MIP (red bar) for AG16-templated in water. Absorbance was measured at the wavelength of the dye analyzed. Data are means from three independent experiments. The error bars represent standard deviations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1
Relative recovery values of the AG16 dye in textile effluent and tap water samples (n =3).

Solution	Concentration (μmol L^{-1})	Solid phase	Relative recovery (%)
Standard solution of AG16 dye	4.0	NIP	32.4 ± 2.1
		MIP	97.5 ± 1.7
Industrial effluent	4.0	NIP	26.9 ± 0.8
		MIP	95.2 ± 1.1
		C18	12.9 ± 3.6
		$MIP_{fluoroquinolone}$	33.6 ± 2.9
		$MIP_{nitroimidazole}$	42.2 ± 4.3
	20.0	NIP	45.3 ± 6.4
		MIP	51.6 ± 4.7
	80.0	NIP	11.8 ± 9.1
		MIP	12.5 ± 9.3
Tap water	4.0	NIP	36.3 ± 1.3
		MIP	96.8 ± 1.1
	20.0	NIP	49.7 ± 4.3
		MIP	55.2 ± 4.1
	80.0	NIP	14.9 ± 7.8
		MIP	15.3 ± 5.4

the AG16 is in higher concentrations in the samples, as 20 and 80 μmol L^{-1}, the recovery percentages decreased and the difference between the value of adsorption of NIP and MIP was smaller.

For the industrial effluent at 20 μmol L^{-1}, the recovery was 45.3% and 51.6% for NIP and MIP, respectively. While, at 80 μmol L^{-1} was 11.8 for NIP and 12.5% for MIP. The tap water recoveries presented similar value. Therefore, the MIP for AG16 showed better performance for samples with low concentration of the dye. This result was already expected because, as the amount of analyte is increased, the MIP cavities are filled, until all of them are filled. From this saturation, occurs an effect inverse than those expected, that is a decrease in the adsorption capacity of the polymers.

It is important highlighted the relative recovery percentage obtained by the MIP was far superior to that obtained by the commercial cartridges, showing that the use of this MIP for extraction of the dye in industrial effluents is entirely feasible.

The inter-day stability of the MIP into the SPE cartridges was also evaluated. For this study, five cartridges filled with MIP were prepared and keep at room temperature. One of the cartridges was analyzed immediately after the preparation and the others were used after 1, 4, 7 and 10 days. For this analysis, tap water contaminated with 4 μmol L^{-1} was employed. The MIP-cartridges presented an excellent performance, since the deviation between measures was only 1.2%.

Moreover, MIP-cartridge reuse was analyzed employing the cartridges of the previous study. For all the cartridges, it was evaluated three reuses. In the first measurement, the recovery was 97.4 ± 1.8%, in the second 89.2 ± 3.1% and in the last 75.3 ± 5.6%. According this results, the MIP lost 8% and 23% of efficiency in the second and third use.

4. Conclusions

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 effluent. Therefore, due to the excellent performance of this MIP, its use as a SPE or element recognizer of optical sensors can be a promising alternative for the determination of this pollutant in environmentally important samples.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://doi:10.1016/j.talanta.2017.04.013.

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