



Synthesis, characterization, and application of nano-molecularly imprinted polymer for fast solid-phase extraction of tartrazine from water environment

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ABSTRACT

In this paper, a new water-compatible nano-molecularly imprinted polymer (MIP) of tartrazine with high-efficiency and a non-imprinted polymer (NIP) were synthesized by precipitation polymerization in aqueous medium as a green method and were characterized. Acrylamide and N,N'-methylene-bis-acrylamide were used as functional monomer and cross-linking agent, respectively. The synthesized MIP and NIP were characterized using thermal gravimetric analysis, differential scanning calorimetry, scanning electron microscopy, and fourier transform infrared spectroscopy. The MIP as a selective sorbent and the NIP as a blank were used to remove tartrazine, using solid-phase extraction from water environment. The effects of pH, time, MIP dosage, and tartrazine concentration on removing tartrazine were studied. The results show that the obtained MIP exhibits higher affinity for tartrazine. The imprinting-induced extraction was confirmed by determination of recovery values for NIP (8%) and MIP (91%). The binding capacity of MIP for this template was 147.6 mg g⁻¹.

Keywords: Nano-molecularly imprinted polymers; Tartrazine removal; Solid-phase extraction; Non-imprinted polymer; Water environment; Green synthesis

1. Introduction

Water-soluble dyes are commonly used as coloring agents in a variety of products, such as foodstuff, textile, and plastics. Some of these dyes used in the food industry have acceptable daily intake (ADI) values that are strictly controlled by laws and regulations in various countries [1]. The dyes present in water, even

at very low concentrations, are highly visible, undesirable, and some of them are difficult to degrade because of their complex structures.

Owing to large-scale production and increase of applications, these dyes have caused serious water environmental pollution. Nowadays, because of these problems, it is urgently required to develop highly selective and sensitive methods to determine or remove water-soluble dyes in water and waste water [2].

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Tartrazine (FD and C Yellow No. 5, C.I. No.19140/1980 and Food Yellow No. 4) is chemically the trisodium 5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-*H*-pyrazol-3-carboxylate. It is a water-soluble powder which is widely used in food products, drugs, cosmetics, and pharmaceuticals [3,4]. The ADI per person is 0–7.5 mg kg⁻¹ body weight [1,5].

Tartrazine is found as a food additive in the following foodstuffs: soft drinks, instant puddings, flavored chips, custard powder, soups, sauces, ice cream, candy, chewing gum, marzipan, jam, jelly marmalade, mustard, yogurt, and many convenient foods, including glycerin, lemon, and honey products. Soaps, hair products, moisturizers, crayons, stamp dyes, vitamins, antacids, and medicinal capsules also can contain tartrazine. It appears to cause the most allergic and/or intolerance reactions of all the azo dyes, particularly amongst those with an aspirin intolerance and asthmatics. Tartrazine sensitivity is mainly manifested by urticaria. Other reactions can include migraine, blurred vision, and itching [6–10].

In order to remove tartrazine from water, several adsorbents were used, such as polystyrene anion-exchange resins [6], hen feathers [11], and magnetic molecularly imprinted polymer (MIP) [12]. Molecularly imprinting is a convenient and powerful technique for preparing polymeric materials with artificial receptors. The technique of MIP is based on the molecular memory of the substrate to be recognized (template) and memorized in polymeric materials during their preparation. Subsequently, the extraction of the template from the polymer gives specific recognition sites. The polymer which contains sites with high affinity for the template has different applications [13–16]. There is a dearth of MIP synthesized for the removal and extraction of dyes from water environment reported in the literature [1,12,17]. Coupling MIP and solid-phase extraction (SPE) would make it possible to combine the advantages of both molecular recognition and traditional separation methods. The SPE method has several advantages including, faster, more reproducible, and cleaner extraction [13]. Molecularly imprinted polymer solid-phase extraction (MISPE) is a well-recognized technique for the selective extraction and the pre-concentration of the analytes present at low levels in chemically complex samples [18]. MISPE not only lets the analytes to be pre-concentrated, but also lets the other compounds present in the sample matrix to be removed [19,20]. It is important to control the particle size of sorbent for different applications, such as selection and separation. The disadvantage of bulk-method polymerization for synthesis of MIP is that the obtained polymer has to be crushed. Then, the irregular particles generally exhibit low-separation

efficiency for target molecules, but precipitation polymerization causes the uniformly sized polymers [21].

In this paper, a new nano-MIP of tartrazine and a non-imprinted polymer (NIP) were synthesized by precipitation polymerization in aqueous medium as a green method and characterized. MIP was synthesized with a mole ratio of template to monomer (1:2). Acryl amide and *N,N'*-methylene-bis-acrylamide were used as functional monomer and cross-linking agent, respectively. The synthesized MIP and NIP were characterized using thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and fourier transform infrared spectroscopy (FT-IR). The MIP and NIP were used to remove tartrazine using solid-phase extraction. The effects of pH, time, MIP dosage, and tartrazine concentration on tartrazine removal were investigated.

2. Experimental

2.1. Materials

Tartrazine sodium chloride with purity of 98% was used as a yellow powder, freely soluble in water, and was purchased from the ministry of health and medical education (Tehran, Iran). Acryl amide (AA), *N,N'*-methylene-bis-acrylamid, potassium persulfate (KPS), and other chemicals were of analytical reagent grade and obtained from Merck (Germany).

2.2. Synthesis of MIP and NIP

The schematic representation of tartrazine imprinting/removal from the imprinted polymer is shown in Fig. 1. The MIP of tartrazine was prepared by non-covalent approach. The mole ratio of template/functional monomer was 1:2. In a typical preparation, Tartrazine (1 mmol, 0.265 mg) as the template and AA (2 mmol, 0.07 mg) as the functional monomer were dissolved, in 40 ml of distilled water and the solution was stirred for 2 h to preorganize. *N,N'*-methylene-bis-acrylamide (10 mmol, 0.77 mg), as a cross-linking agent, was added to the mixture and was then dispersed uniformly by sonication. After sonication, the mixture was purged with N₂ for 10 min and the glass tube was sealed under this atmosphere. The reaction initiator KPS (0.185 mmol, 0.025 mg) was added to the reaction mixture. Afterwards, the glass tube was stirred in a water bath maintained at 70°C for 22 h. The produced polymer was filtered using a centrifuge. The obtained particles were washed with hot distilled water/ammonia solution (8:2, *v/v*), and followed by extraction in soxhlet apparatus using hot water for 2 d. The complete removal of tartrazine was investigated by a UV-vis spectrophotometer (PERKIN-ELMER) at

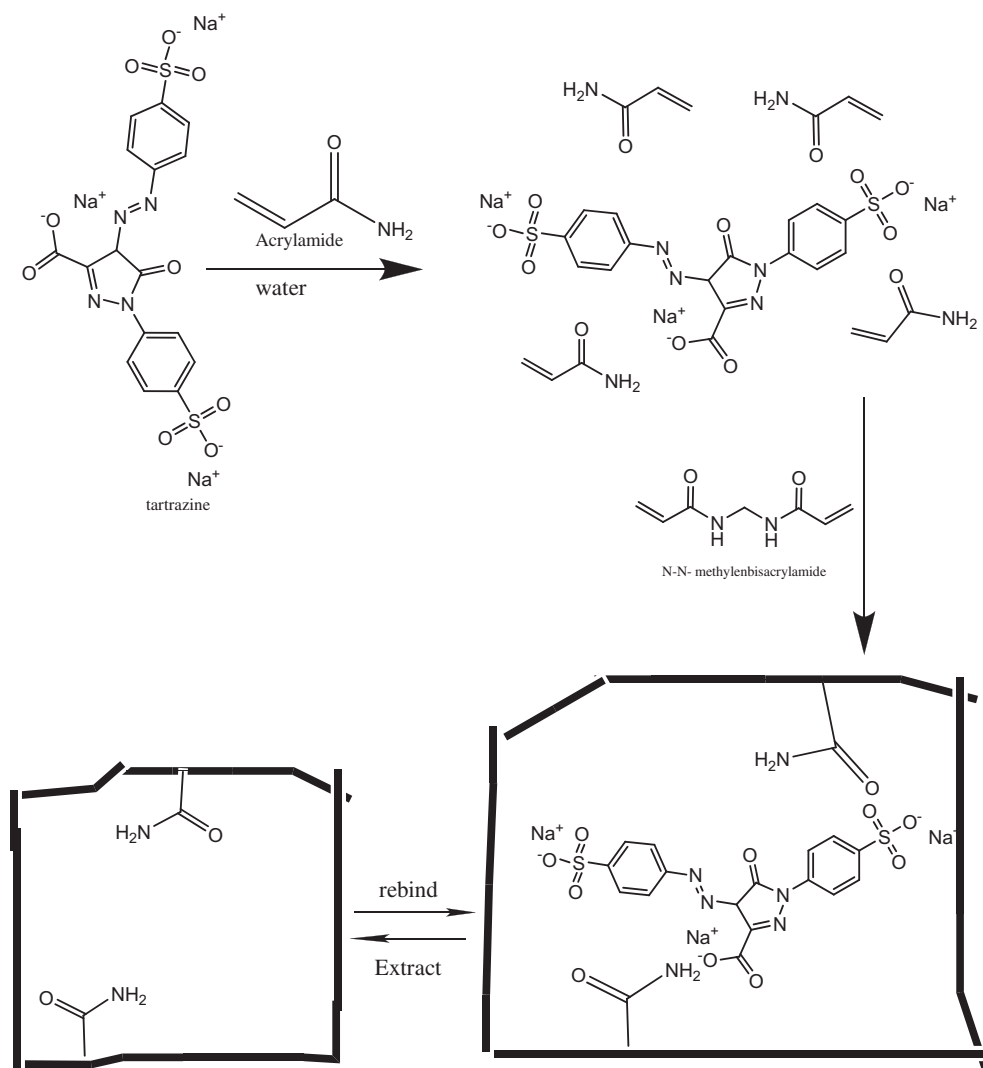


Fig. 1. Schematic synthesis of MIP.

428 nm until the tartrazine spectra disappeared. The template extraction from the polymer created selective cavities. The NIP was also exactly synthesized with the same procedure. Excluding the tartrazine template from the formation synthesis of NIP, is to verify that the retention of template was due to the molecular recognition sites and not non-specific binding.

2.3. Characterization

FT-IR spectra of ground polymers were recorded to study functional groups (Bruker model EQUINOX 55). The thermal analysis of the polymer was carried out on model PL-STA-1500 TGA and DSC instruments from Polymer Laboratories' Company (Church Stretton, Shropshire, UK). SEM was used to study the morphology of polymer particles (SEM; Philips XLC) and

dynamic light scattering (DLS) were used to show the particle size and size distribution (Malvern Zetasizer ZS, Malvern UK).

2.4. Batch binding assay (adsorption and desorption)

In order to measure the template binding, adsorption of tartrazine from aqueous solution was investigated in batch experiments. The general procedure for the extraction of tartrazine was as follows: In adsorption step, 100 mg of imprinted polymer particles was added into a 10 ml aqueous solution of tartrazine, with a concentration of 3×10^{-5} M. The pH was adjusted at 2. The mixture was stirred continuously at 25°C for 1 h, and then centrifuged. Then the concentration of free tartrazine was determined by UV-vis spectrophotometer.

The instrument response was periodically checked with the known tartrazine standard solution. Percentage of tartrazine extraction was calculated from the following equation [13]:

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the concentrations of tartrazine before and after extraction procedure, respectively. The tartrazine was desorbed from the MIP by treatment of 10 ml of hot water and ammonia solution (8:2, v/v) with continuously stirring at 70°C for 1 h. The final desorbed tartrazine concentration in the aqueous phase was determined. The same procedure was also carried out for NIP particles.

3. Results and discussion

3.1. Characterization of MIP and NIP

The FT-IR spectra of non-washed and washed MIP and washed NIP were studied at 4,000–400 cm^{-1} . Similar characteristic peaks indicate the similarity between the backbone structures of the different polymers. A strong peak at $\sim 1,675\text{--}1,678 \text{ cm}^{-1}$ attributed to the

vibration mode of C=O was observed in the FT-IR spectra of the washed blank (NIP), non-washed and washed MIP. As a result of the hydrogen bonding with the $-\text{NH}_2$ group of AA, the binding vibration at 3,436 and 1,372 cm^{-1} in non-washed MIP were shifted to 3,441 and 1,386 cm^{-1} in the washed MIP. A sharp peak in 1,034 cm^{-1} shown in non-washed MIP is related to $-\text{SO}_3\text{H}$ of tartrazine, which disappears in washed MIP spectra.

The TGA plot of non-washed and washed MIP and washed NIP was shown in Fig. 2(a). The TGA revealed two decomposition states in non-washed MIP particles: one mass loss starting at near 85°C which is ascribed to the decomposition of free monomer and the other one starting at 250°C is related to the tartrazine decomposition at the melting point. All the materials were completely decomposed before reaching the temperature of near 400°C.

Fig. 2(b) shows the DSC plot of non-washed and washed MIP and NIP. It shows two melting point steps which have occurred in MIP and NIP. The first one is near 85°C, which is related to monomer and the second one is observed near 400°C, which is associated to the decomposition of polymer. One more melting point step has occurred in non-washed MIP near 250°C, which is related to tartrazine.

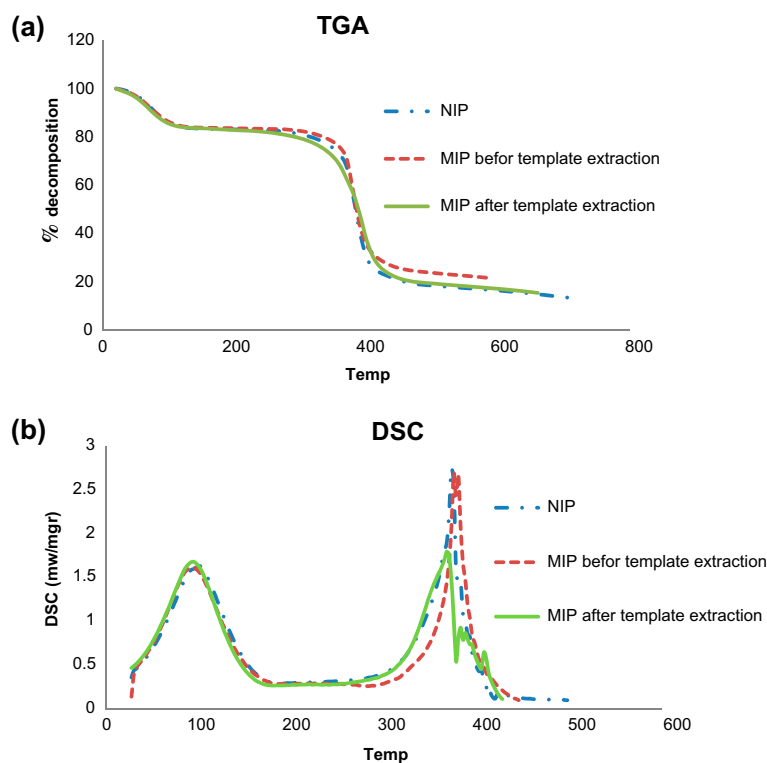


Fig. 2. (a) TGA plot and (b) DSC plot of polymers.

SEM was employed to establish the shape and surface morphology of the produced polymer particles. The polymer particles were sputter coated with gold.

As can be seen in Fig. 3(a) the porous surface could be clearly observed for the MIP. Microphotograph of MIP particles in 30,000 \times magnification shows that the sizes of particles are in nano-scale which is illustrated in Fig. 3(b).

Particle size measurements were performed by DLS analysis. Narrow particle size distributions were observed for MIP in Fig. 3(c). The poly dispersity index and Z-average for MIP were 0.176 and 73, respectively. These results show that the particle sizes are in nano-scale.

3.2. Optimization of MIP composition

Several variable experimental parameters influence the characteristic of the MIP in terms of capacity, affinity, and selectivity towards the analyte. These parameters include, mole ratio of monomer to template, nature of cross-linker and solvent, polymerization method, and temperature effect [22].

The first step was to obtain the best mole ratio of functional monomer to template. In most cases, finding an appropriate mole ratio of components is one of the most important primitives to enhance the affinity between polymers and template, which results in the increase of the number of MIP recognition sites. The prepolymerized complex concentration can be

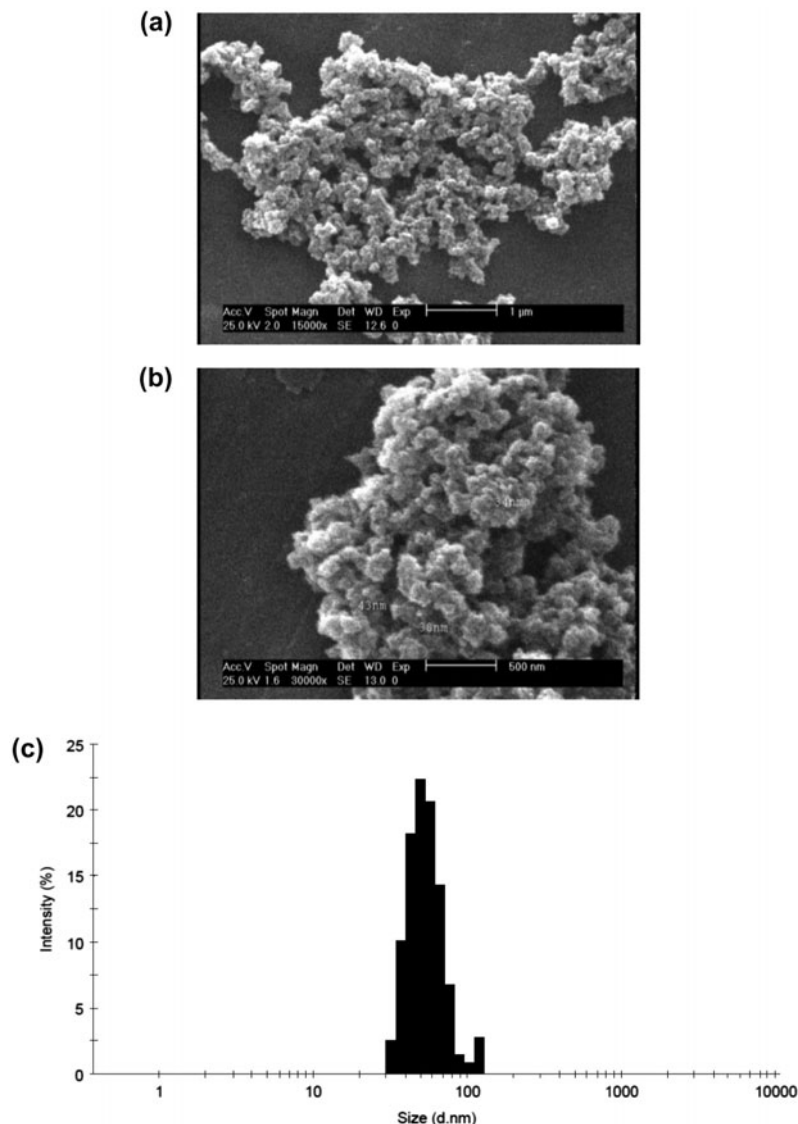


Fig. 3. Scanning electron micrographs of (a) porous surface in 15,000 \times magnifications, (b) particle size of washed MIP in 30,000 \times magnification and particle size distribution of MIP, and (c) measured by DLS.

increased by incrementing the concentration of template, and this increase does not influence the polymer structure. The template is incorporated into the final polymer by non-covalent interactions and removed after the completion of the imprinting process. However, high ratios of functional monomer to template should result in an increase in non-specific affinity [23]. Because of the mentioned reason and the number of functional groups in a monomer and template we select the mole ratio of 1:2 (template/monomer) in our work to prevent non-selective interaction between monomers.

Solvent plays an important role in the formation of porous structure of the MIP. The morphological properties of porosity and surface areas are determined by the type of solvent. Porosity arises from phase separation, from the solvent, and from the growing polymer during polymerization. The solvent with higher solubility phase, which separates later in the polymerization, provides materials with smaller pore size distributions and greater surface area [23–25]. In MIP synthesis typically, aprotic polar solvents are used but polar solvents can also be used. These solvents solvate the polar functional groups of the monomer, leaving them exposed at the pore walls after solvent removal [26]. We use water as solvent in our work, since it is the greenest and cheapest solvent and also that the template, monomer, and cross-linking agent have a good solubility in water.

The preparation of hydrophilic tartrazine MIP was guided by the sulfonate groups of dye and $-\text{NH}_2$ in monomer. Acrylamide generates the hydrophilic surface, and the cross-linker is also hydrophilic to improve wetting by water [27].

3.3. Effect of time on MIP extraction

The extraction is increased by the increment of extraction time up to 120 min which had achieved 100% extraction, but 60 min is chosen to be the optimum time of extraction, in which maximum selective extraction occurs (Fig. 4(a)). The obtained MIP was washed by 10 ml of washing eluent mix of water/ammonia (8:2, *v/v*) and the results of the desorption chart are as shown in Fig. 4(b).

3.4. Effect of pH, MIP dosage, and solution concentration on MIP extraction

Synthesis of MIP often has been applied for small and neutral template molecules rather than polar molecules with ionizable group [17]. In this study, we used a high molar mass and polare template, tartra-

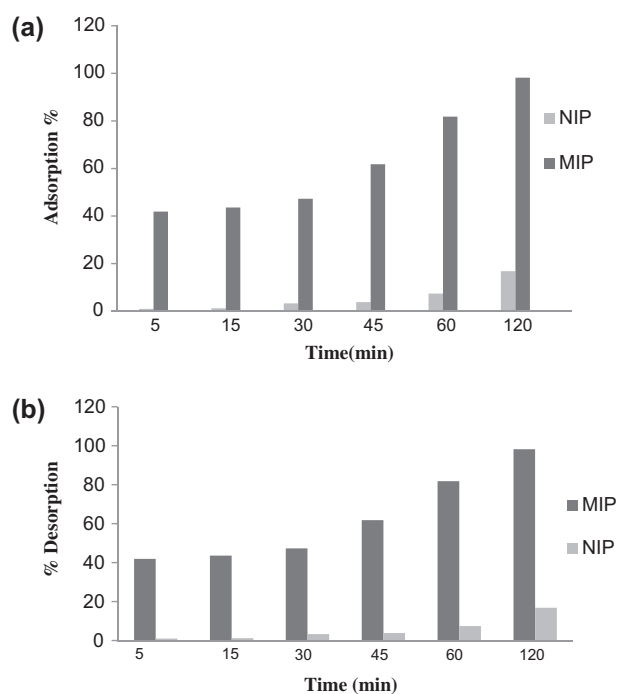


Fig. 4. Effect of time on (a) adsorption and (b) desorption.

zine, with ionizable sulfonate groups. After polymerization, it is necessary to optimize the critical factor for maximum removal.

The pH value has a large influence on the extent of adsorption of dye from the solution, because it could influence the properties of the sorbent. Determining the optimum pH in which the most adsorption occurs is important to reach the maximum capacity of polymer. Adsorption of tartrazine was investigated at pH values of 2, 4, 6, 8, and 10. The effect of pH adsorption on the recovery percentage of tartrazine is illustrated in Fig. 5(a). The percentage value of tartrazine extraction had increased, when the pH was decreased to 2. The adsorption could be ascribed to the interaction between functional groups of polymer and analyte that are favored by the pH alterations. The interaction between tartrazine and MIP is caused by hydrogen bonding and electrostatic interaction between undissociated amide group on polymer surface and sulfonated groups of the dye [17]. The plot shows negligible influence on the NIP process.

One of the dependency parameters of the extraction efficiency could be the certain extent of the polymer dosage used in the experiment. To study this possible dependence, the extraction of tartrazine from the solution was investigated at different MIP dosages (0.01, 0.05, 0.1, and 0.15 g). Maximum efficiency is achieved at 0.1 g of MIP (Fig. 5(b)).

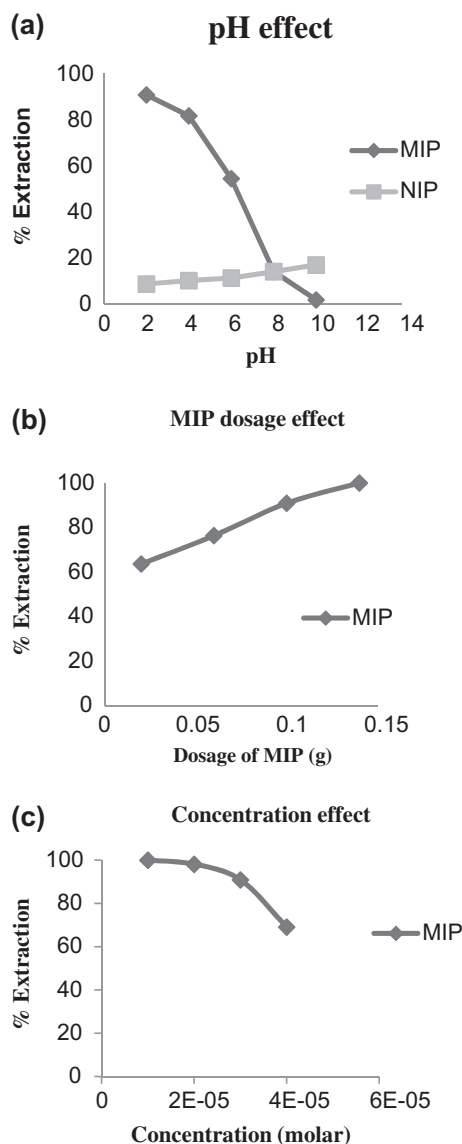


Fig. 5. Effect of (a) pH solution, (b) MIP dosage, and (c) concentration of solution on the efficiency of tartrazine extraction.

Under the optimized condition to achieve better concentration, calibration curve was obtained by the protocol measured at increasing concentration, in a range from 10^{-5} M to 7×10^{-5} M of tartrazine (Fig. 5(c)). The result showed good linearity (0.999) in the range and 3×10^{-5} M of tartrazine selected was as a standard solution.

3.5. Capacity of MIP

The complete characterization of an MIP requires the measuring of its capacity. The capacity of the sorbent is an important factor. The capacity of an MIP

corresponds to the maximum amount of a compound that can be retained on the MIP in a given condition. Therefore, the determination of the capacity was carried out by measuring the extraction recoveries on the MIP for aqueous solution spiked with various amount of tartrazine [28,29]. To investigate the adsorption template, 10 ml of tartrazine solution in different concentrations was contacted with 100 mg of sorbent in the batch mode. The concentration of the remaining tartrazine in the solution was determined by UV in 428 nm. According to the results, the maximum amount of tartrazine that can be absorbed by MIP was found to be 147.6 mg g^{-1} at pH 2. Fig. 6 represents the obtained capacity curve. The results of batch binding assay were confirmed by determination of recovery values and obtained to be 8 and 91% for NIP and MIP, respectively. These results show that the synthesized MIP is a more porous material than NIP.

3.6. Selectivity coefficient of sorbent

Selectivity coefficient is an important parameter to evaluate the properties of an MIP. MIPs are usually evaluated to verify their recognition properties for a target analyte. For batch rebinding experiments, a known mass of template in solution is added to a vial containing a fixed mass of polymer. When the system has reached the equilibrium, the concentration of free template in solution is measured and the mass of template absorbed to the MIP is calculated [30]. Sunset Yellow FCF (also known as Orange Yellow S, FD and C Yellow 6 or C.I. 15985) is a synthetic yellow azo dye (Fig. 7). It is a food color and offers orange–yellow color [31]. In our research, to study the selectivity of MIP; 100 mg of MIP was added to 10 ml of sunset yellow solution with a concentration of 3×10^{-5} M. We used sunset yellow for selectivity study because of its similarity in structure and color to Tartrazine. Both of them are Azo dyes with yellow color. The adsorption capacity of sunset yellow FCF was obtained 31% for

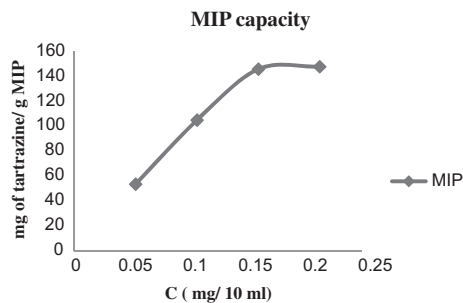


Fig. 6. Effect of Tartrazine concentration on the adsorption capacity for MIP.

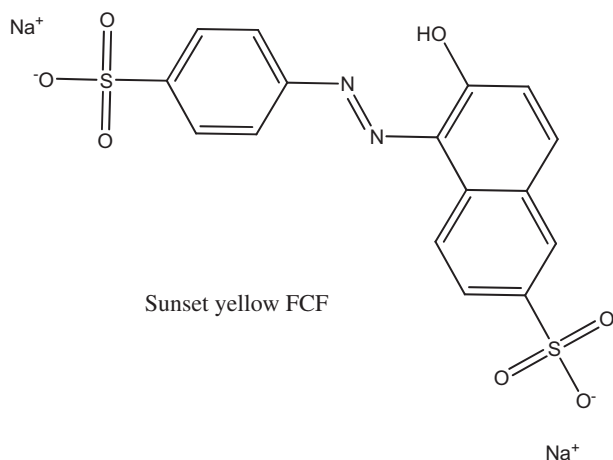


Fig. 7. Sunset yellow FCF structure.

Table 1
Distribution ratio (K_D) and selectivity factor (K_{sel}) of MIP and NIP for tartrazin and sunset yellow

Color	K_D (MIP) (Ml g^{-1})	K_D (NIP) (Ml g^{-1})	K_{sel} (MIP)	K_{sel} (NIP)
Tartrazin	1011.11	8.69	–	–
Sunset yellow CFC	44.93	11.69	22.50	0.73

MIP and 11% for NIP. Distribution ratio (K_D) and selectivity factor (K_{sel}) were calculated (Table 1) for MIP and NIP of Tartrazin and sunset yellow FCF [13,27]. The results suggest that the MIP of Tartrazin exhibited excellent selectivity for Tartrazine when compared to sunset yellow.

4. Conclusion

In this research, high selectivity nano-MIP was synthesized for tartrazine. The MIP showed high affinity to template since it eliminated the color of the solution completely and as it is known for removing dyes from the water environment which is so important. The synthesis of polymer was carried out in water, which is the greenest solvent. The effects of pH, time, tartrazine concentration, and MIP dosage were optimized to remove tartrazine. The results show that nano-scale MIP was a selective adsorbent to remove tartrazine from water environment.

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References

- [1] X. Luo, Y. Zhan, X. Tu, Y. Huang, Sh. Luo, L. Yan, Novel molecularly imprinted polymer using 1-(α -methyl acrylate)-3-methylimidazolium 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* 1218 (2011) 1115–1121.
- [2] A.R. Khataee, M.B. Kasiri, Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: Influence of the chemical structure of dyes, *J. Mol. Cat. A* 328 (2010) 8–26.
- [3] Scientific Committee for Food, Reports of the Scientific Committee for Food 14th series, (1984).
- [4] Joint FAO/WHO Expert Committee on Food Additives, 8th Report of the joint FAO/WHO expert committee on food additives, Specifications for identity and purity and toxicological evaluation of food colours, WHO Food Add. Ser. 25 (1966) 88–92.
- [5] T. Tanaka, O. Takahashi, Sh. Oishi, A. Ogata, Effects of tartrazine on exploratory behavior in a three-generation toxicity study in mice, *Reproduct. Toxic* 26 (2008) 156–163.
- [6] M. Wawrzkiwicz, Z. Hubicki, Removal of tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins, *J. Hazard Mat.* 164 (2009) 502–509.
- [7] C. Collins-Williams, Clinical spectrum of adverse reactions to tartrazine, *J. Asthma* 22 (1985) 139–143.
- [8] J.R. Dipalma, Tartrazine sensitivity, *Am. Family Physic.* 42 (1990) 1347–1350.
- [9] R.E. Desmind, J.J. Trautlein, Tartrazine (FD and C Yellow 5) anaphylaxis: A case Report, *Ann. Allergy* 46 (1981) 81–82.
- [10] J. Baumgardner, Persistent urticaria caused by a common coloring agent, *Postgr. Med.* 85 (1989) 265–266.
- [11] A. Mittal, L. Kurup, J. Mittal, Freundlich and Langmuir adsorption isotherms and kinetics for the removal of tartrazine from aqueous solutions using hen feathers, *J. Hazard Mat.* 146 (2007) 243–248.
- [12] X. Luo, Y. Zhan, Y. Huang, L. Yang, X. Tu, Sh. Luo, Removal of water-soluble acid dyes from water environment using a novel magnetic molecularly imprinted polymer, *J. Hazard Mat.* 187 (2011) 274–282.
- [13] N. Arabzadeh, M. Abdouss, Synthesis and characterization of molecularly imprinted polymers for selective solid-phase extraction of pseudoephedrine, *Colloid J.* 72 (2010) 446–455.
- [14] F. Trotta, C. Baggiani, M.P. Luda, E. Drioli, T. Massari, A molecular imprinted membrane for molecular discrimination of tetracycline hydrochloride, *J. Memb. Sci.* 254 (2005) 13–19.
- [15] G. Wulff, Molecular recognition in polymers prepared by imprinting with templates, *J. Reac. Poly.* 15 (1991) 233–237.
- [16] L. Donato, A. Figoli, E. Drioli, Novel composite poly(4-vinylpyridine)/polypropylene membranes with recognition properties for (S)-naproxen, *J. Pharm. Biomed. Anal.* 37 (2005) 1003–1008.

- [17] Y.S. Al-Degs, A.S. Abu-Surrah, K.A. Ibrahim, Preparation of highly selective solid-phase extractants for cibacron reactive dyes using molecularly imprinted polymers, *Anal. Bio. Chem.* 393 (2009) 1055–1062.
- [18] A. Zurutuza, S. Bayouhd, P.A. Cormack, L. Dambies, J. Deere, R. Bischoff, D.C. Sherrington, Molecularly imprinted solid-phase extraction of cocaine metabolites from aqueous samples, *J. Anal. Chim. Acta* 542 (2005) 14–19.
- [19] X. Jiang, C. Zhao, N. Jiang, H. Zhang, M. Liu, Selective solid-phase extraction using molecular imprinted polymer for the analysis of diethylstilbestrol, *Food Chem.* 108 (2008) 1061–1067.
- [20] R. Marce, F. Borrull, P.A.G. Cormack, D.C. Sherrington, Application of molecularly imprinted polymers to solid-phase extraction of compounds from environmental and biological samples, *J. Anal. Chem.* 25 (2006) 143–154.
- [21] F.G. Tamayo, J.L. Casillas, A. Martin-Esteban, Evaluation of new selective molecularly imprinted polymers prepared by precipitation polymerisation for the extraction of phenylurea herbicides, *J. Chromatogr. A* 1069 (2005) 173–181.
- [22] D.A. Spivak, Optimization, evaluation, and characterization of molecularly imprinted polymers, *J. Adv. Drug. Del. Rev.* 57 (2005) 1779–1794.
- [23] A. Rachkov, N. Minoura, Recognition of oxytocin and oxytocin-related peptides in aqueous media using a molecularly imprinted polymer synthesized by the epitope approach, *J. Chromatogr. A* 889 (2000) 111–118.
- [24] A. Guyot, D.C. Sherrington, P. Hodge, *Synthesis and Separations using Functional Polymers*, New York, NY: Wiley 35 (1989) 1–36.
- [25] L. Lloyd, Rigid macroporous copolymers as stationary phases in high-performance liquid chromatography, *J. Chromatogr. A* 544 (1991) 201–217.
- [26] B. Dirion, Z. Cobb, E. Schillinger, L.I. Andersson, B. Sellergren, Water-compatible molecularly imprinted polymers obtained via high-throughput synthesis and experimental design, *J. Am. Chem. Soc.* 125 (2003) 15101–15109.
- [27] G.Z. Kyzas, N.D. Bikiaris, N.K. Lazaridis, Selective separation of basic and reactive dyes by molecularly imprinted polymers (MIPs), *J. Chem. Eng.* 149 (2009) 263–272.
- [28] R. Panahi, E. Vasheghani-Farahani, S.A. Shojaosadati, Separation of L-lysine from dilute aqueous solution using molecular imprinting technique, *Biochem. Eng.* 35 (2007) 352–356.
- [29] F. Chapuis, J.U. Mullot, V. Pichon, G. Tuffal, M.C. Hennion, Molecularly imprinted polymers for the clean-up of a basic drug from environmental and biological samples, *J. Chromatogr. A* 1135 (2006) 127–134.
- [30] W.M. Mullett, M. Wallis, K. Levsen, J. Borlak, J. Pawliszyn, Multidimensional on-line sample preparation of verapamil and its metabolites by a molecularly imprinted polymer coupled to liquid chromatography–mass spectrometry, *J. Chromatogr. B* 801 (2004) 297–306.
- [31] E. Diacu, C.P. Ene, Simultaneous determination of tartrazine and sunset yellow in soft drinks by liquid chromatography, *J. Rev. Chim.* 60 (2009) 745–749.