



# Novel molecularly imprinted polymer using 1-( $\alpha$ -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

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## ABSTRACT

Novel water-compatible molecularly imprinted polymers were synthesized in methanol–water systems with Tratarzine as template and 1-( $\alpha$ -methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br) as functional monomer, which has  $\pi$ - $\pi$  hydrophobic, hydrogen-bonding and electrostatic interactions with template molecule. 1-MA-3MI-Br molecularly imprinted polymers (1-MA-3MI-Br-MIPs) were used as selective sorbents for the solid-phase extraction (SPE) of water-soluble acid dyes from wastewater and soft drink. The good linearity of the method was obtained in a range of 5.0–2000  $\mu\text{g/L}$  with the correlation coefficient of  $>0.999$ . The detection limits were in a range of 0.13–0.51  $\mu\text{g/L}$  for the water-soluble acid dyes in wastewater and 0.095–0.84  $\mu\text{g/L}$  for those in soft drink. The mean recoveries for the acid dyes are from 89.1% to 101.0% in spiked wastewater and 91.0–101.3% in spiked soft drink. Compared with strongly anion exchange solid phase extraction (SAX-SPE), mixture anion exchange solid phase extraction (MAX-SPE), and 1-MA-3MI-Br non-imprinted solid phase extraction (1-MA-3MI-Br-NISPE), almost all of the matrix interferences were removed by 1-MA-3MI-Br-MISPE, exhibiting higher selectivity, recovery and enrichment ability for the acid dyes and better baselines in the results of HPLC analysis.

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## 1. Introduction

Water-soluble acid dyes are extensively used as coloring agents in a variety of products such as textiles, paper, leather and foodstuff. Some of water-soluble acid dyes are permitted in foodstuff. Acceptable daily intake values for Amaranth, Sunset Yellow, and Tratarzine are 0–0.5 mg/kg, 0–2.5 mg/kg, and 0–7.5 mg/kg, respectively. However, acceptable daily intake values of water-soluble acid dyes are strictly controlled by laws and regulations in various countries [1]. Furthermore, owing to large-scale production and extensive application, water-soluble acid dyes have caused serious water environmental pollution. Since water-soluble acid dyes usually present in low concentrations or mingle with a large amount of interfering substances, it is urgently required to develop a high sensitive and selective analytical method for determination of water-soluble acid dyes in soft drink and wastewater.

Several methods have been developed for the analysis of water-soluble acid dyes, including capillary electrophoresis [2,3], high-performance liquid chromatography [4–6] and ion pair reversed-phase liquid chromatography [7,8]. A solid-phase extraction (SPE) process is generally needed in order to reduce the matrix interference and enrich the analytes by employing the methods mentioned above. SPE often used hydrophobic polymeric sorbents ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_{18}$ , and St-DVB), hydrophilic polymeric sorbents (Oasis HLB), ion-exchange sorbents (SAX), and mixed-mode ion-exchange sorbents (PAX, MAX). The acid dyes in samples are generally treated by ion-exchange sorbents and mixed-mode ion-exchange sorbents solid phase extraction. Although these ion-exchange sorbents solid phase extraction showed a good retention capacity for acid dyes, they showed poor selectivity for acid dyes in complex matrixes. Therefore, it is an urgent need to develop a newly selective SPE method for the enrichment of water-soluble acid dyes in soft drink and wastewater.

A relatively new development in the area of SPE is the use of molecularly imprinted polymers (MIPs) for the sample clean-up [9,10], which have selectivity adsorptions for a given analyte,

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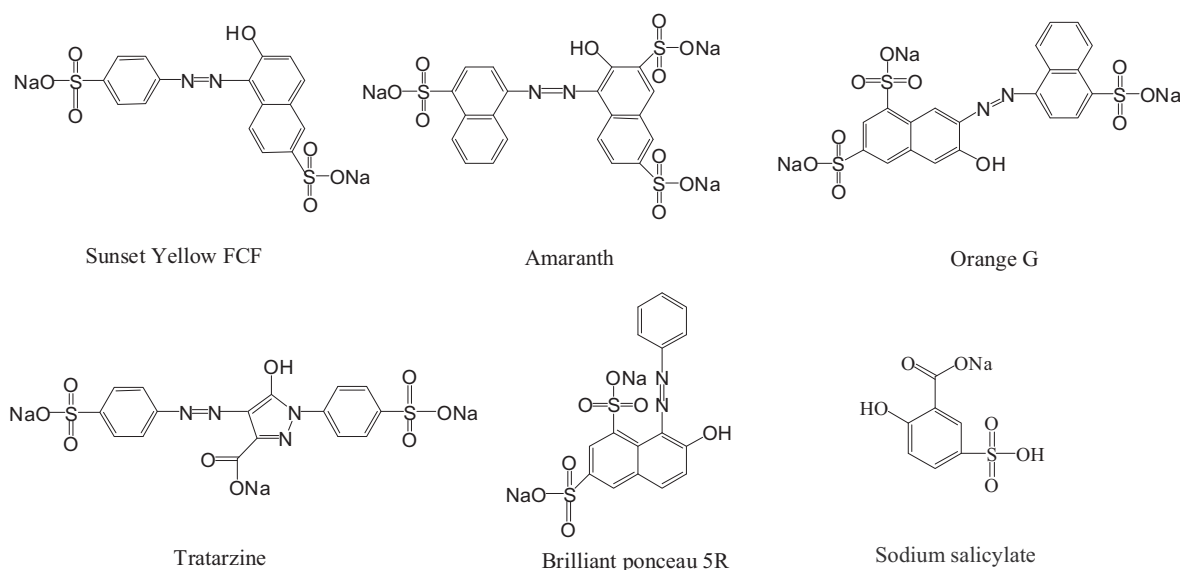


Fig. 1. Molecular structures of the five water-soluble acid dyes.

or a group of structurally analogous compounds, so it has a very good effect to enrich target molecule. Furthermore, it has been successfully employed in the determination of many analytes such as antibiotics [11], mycotoxins [12], triazines [13], endocrine disruptors [14], uracils [15], imides [16], tetracycline antibiotics [17], nanoattapulgite [18], amphetamine drugs [19]. However, the MIPs polymerization process or sample preparation were always conducted in the aprotic and low polar organic solvents. If the presence of polar solvents, especially water, the hydrogen bonds formed between the templates and the functional monomers would be inevitably weakened. It results in non-specific adsorption of sorbents and the poor level of recognition of the strong hydrophilic target molecules. Several examples have been presented for the determination of antiepileptics [20], triazine [21,22],  $\beta$ -blockers [23], organophosphorous pesticides [24], chlorophenoxyacetic acids [25], and methylxanthines [26] in aqueous waters by MIPs. However, these water-compatible MIPs do not have enough hydrophilic groups and only provide the potential to form hydrogen bonding. To the best of our knowledge, a few MIPs for anion compound [27] were reported in the literature. Therefore, it is very important to develop a novel water-compatible MIPs for anion compound with hydrophilic functional monomers which has multiple potentials to form interactions with template molecule.

The aim of this work was the application of novel MIPs, which were synthesized in methanol-water systems using 1-MA-3MI-Br as functional monomer, to develop a sensitive and selective analytical method to determine five water-soluble acid dyes. The method can be applied for the preconcentration and extraction of target compounds from both soft drink and wastewater. The molecular structures of the five water-soluble acid dyes are shown in Fig. 1. To prove the better performance of 1-MA-3MI-Br-MISPE, a comparison with SAX-SPE, MAX-SPE, MAA-MISPE, and 4-VP-MISPE was also included in this work.

## 2. Experimental

### 2.1. Reagents

Trim ethylolpropane trimethacrylate (TRIM) were obtained from Chinese Qianjin Chemistry Reagent Factory (Tianjin, China). 4-Vinyl pyridine (4-VP), methacrylic acid (MAA), and 2,2-azobisisobutyronitrile (AIBN) were purchased from Beijing

Chemical Reagent Factory (Beijing, China). Amaranth, Brilliant Ponceau 5R, Orange G, Sunset Yellow FCF, and Tratarzine were supplied by Pure Crystal Shanghai Reagent Co. Ltd. (Shanghai, China). Methanol, acetic acid, ammonia solution (28%) and ammonium acetate were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). HPLC-grade methanol was purchased from Dima Technology (Richmond Hill, USA). Cleanert SAX-SPE (1 mL, 100 mg) was purchased from Agela Technologies (Tianjing, China). Oasis MAX (6 mL, 150 mg) was purchased from Waters (Milford, MA, USA). 1-( $\alpha$ -methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br) was synthesized in our laboratory which structure was confirmed by  $^1\text{H}$  NMR and IR analysis. Water was purified through a Milli-Q water system (Bedford, USA).

### 2.2. High-performance liquid chromatography analysis

Aliquots of 10  $\mu\text{L}$  were analyzed on an HPLC system (HP1100, Agilent, USA), which is consisted with a HPLC pump operating at a flow rate of 1.0 mL/min, and DAD monitoring with the effluent at 254 nm for all compounds. The analytical column was a 250 mm  $\times$  4.6 mm, 5  $\mu\text{m}$   $\text{C}_{18}$  column (Agilent, USA). The mobile phase was methanol: 20 mM ammonium acetate buffer solution (20:80, v/v).

### 2.3. Preparation of 1-MA-3MI-Br-MIPs, MAA-MIPs, and 4-VP-MIPs

Three imprinted polymers were prepared by non-covalent approach with different monomers of 1-MA-3MI-Br, MAA and 4-VP. The molar ratios of functional monomer/Tratarzine (template) in the starting solution were 2.0/0.5 mmol, and the mixture was dissolved in 20 mL porogenic solvents (methanol:water, 8:2, v/v). After the 12 h pre-polymerization process at room temperature, AIBN (60.0 mg, 0.36 mmol) as initiator and TRIM as cross-linker (5.0800 g, 15.0 mmol) were added to the mixture solution. Then, the solution was deoxygenated with nitrogen for 10 min because free radical polymerization could be inhibited by oxygen. After that, the reactor was sealed with parafilm and then polymerized at 65  $^\circ\text{C}$  for 24 h. The resulting particles were washed by methanol-ammonia solution (9:1, v/v) in a Soxhlet extraction system until no template molecule could be detected by HPLC. Subsequently, the products were washed with methanol to remove residual ammonia solution

and dried at 50 °C. Non-imprinted polymers (NIPs) were prepared with the same procedures as above described and only difference was that no Tratarzine was added into the reaction mixture.

The surface morphology of the MIPs was characterized by a Quanta 200 field emission scanning electron microscope (FESEM, Tokyo, Japan).

#### 2.4. Selectivity experiments

In order to investigate the selectivity of the adsorbent, static adsorption experiment results were used for evaluation. The competitive absorption experiments were conducted by preparing mixture of sodium salicylate and Tratarzine, and each substance initial concentration was 200 µg/L.

#### 2.5. MISPE, SAX-SPE and MAX-SPE conditions

The column was packed by wet filling. The dry MIPs (100 mg) were added to methanol/water (8:2, v/v), stirred to be uniform, and then the suspension of mixed solution was filled into the cartridges at a flow rate of 1 mL/min. The SPE-cartridges filled with MIPs (1-MA-3MI-Br-MIPs or 4-VP-MIPs) were conditioned with 3 mL of methanol and 3 mL acid water (adjusted to pH 2 with HCl) prior to use. Unless mentioned otherwise, the extraction was processed as follows. 35 mL soft drink or wastewater samples were loaded in 1-MA-3MI-Br-MISPE columns at a flow rate of 1 mL/min, and 26 mL soft drink or wastewater samples were loaded in 4-VP-MISPE columns at the same flow rate. After that, the cartridges were washed by 10 mL methanol and dried under vacuum. Finally, the SPE cartridges were eluted with 2 mL methanol/ammonia solution (9:1, v/v).

The SPE-cartridges filled with MAA-MIPs were conditioned with 3 mL methanol and 3 mL water. 12.0 mL soft drink samples or wastewater were loaded in SPE columns at the flow rate of 1 mL/min and then the cartridges were washed by 10 mL methanol/water (8:2, v/v). The SPE cartridges were eluted with 2 mL methanol/ammonia solution (9:1, v/v) at the flow rate of 1 mL/min.

The SAX-SPE columns were conditioned with 3 mL methanol and 3 mL acid water. 34 mL soft drink or wastewater samples (pH 2) were loaded in SPE columns at the flow rate of 1 mL/min and then the cartridges were washed by 10 mL methanol. Finally, the SPE cartridges were eluted with 2 mL methanol/hydrochloric acid solution (8:2, v/v) at the flow rate of 1 mL/min.

The MAX-SPE columns were conditioned with 3 mL of methanol and 3 mL water. 50 mL soft drink or wastewater samples were loaded in SPE columns at the flow rate of 1 mL/min. Then the cartridges were washed by 5% ammonia solution and 10 mL methanol, respectively. Finally, the SPE cartridges were eluted with 2 mL methanol/hydrochloric acid solution (8:2, v/v) at the flow rate of 1 mL/min. These effluents were condensed by drying under a gentle flow of nitrogen at room temperature. The residues were dissolved in 0.3 mL water for HPLC analysis.

#### 2.6. Sample preparation

The wastewater was collected from factory in Nanchang, China. The soft drink was purchased from local supermarket in Nanchang. pH values of wastewater and soft drink samples were adjusted to 2 with HCl. The samples were filtered through a 0.45 µm membrane (Whatman, UK) prior to SPE procedure.

#### 2.7. The work solution preparation for the calibration curve

Calibration curves for the acid dyes in the wastewater and soft drink samples were obtained by fortifying the standard substances

of Tratarzine, Amaranth, Orange G, Brilliant Ponceau 5R and Sunset Yellow FCF into the blank specimens. The concentrations of the standard substances are in a range of 5.0–1000 µg/L.

### 3. Results and discussion

#### 3.1. Fabrication mechanism of 1-MA-3MI-Br-MIPs

Since the 1-MA-3MI-Br is with  $\pi$ - $\pi$  stacking and hydrogen-bonding, high electrostatic interactions with the hydrophobic template molecule can be formed, showing a promising potential in extracting the water-soluble acid dyes. As can be seen from Fig. 2, there are two  $\text{SO}_3^-$ ,  $\text{COO}^-$ ,  $-\text{OH}$  and pyrazole ring group in the Tratarzine molecule. Electrostatic interactions due to  $\text{SO}_3^-$ ,  $\text{COO}^-$ , hydrogen-bonding interactions from  $-\text{OH}$  and the  $\pi$ - $\pi$  stacking from pyrazole ring group with 1-MA-3MI-Br result in the tight combination between them. Although 4-VP is with the hydrogen-bonding and electrostatic interactions, the combination on the template is still poor due to the lack of  $\pi$ - $\pi$  stacking, much less the MAA monomer which only can provide the hydrogen-bonding interaction. Furthermore, the absorbability of 1-MA-3MI-Br-MIPs is stable because the  $\pi$ - $\pi$  stacking and electrostatic interactions with template molecule are difficult to be disturbed in aqueous solutions. Consequently, it is definite that 1-MA-3MI-Br-MIPs will show higher specific recognition ability than MAA-MIPs and 4-VP-MIPs.

SEM images in Fig. 3 exhibit the topomorphology the MAA-MIPs (A), 4-VP-MIPs, and 1-MA-3MI-Br-MIPs (C). Particles of the MAA-MIPs (Fig. 3A) and 4-VP-MIPs (Fig. 3B) exhibit a more porous, rough structure and the wide distribution range of the particle size (0.5–3 µm). Compared with the particles in Fig. 3A and B, Fig. 3C shows that the 1-MA-3MI-Br-MIPs particles is with much smaller size (0.3 µm) and more narrow distribution scope, indicating the larger surface area. Sodium sulfosalicylate, which structure is similar with that of Tratarzine, was chosen as control substance to evaluate the selectivity of the 1-MA-3MI-Br-MIPs. Our investigation results show that the adsorption amount of Tratarzine is 27.47 µmol/g onto the 1-MA-3MI-Br-MIPs while the value for sodium sulfosalicylate is only 9.01 µmol/g, suggesting the high selectivity of the 1-MA-3MI-Br-MIPs. The selectivity factor of 1-MA-3MI-Br-MIP defined as the ratio of the absorption capacity of Tratarzine to that of sodium sulfosalicylate is calculated to be 3.05.

#### 3.2. Evaluation of the molecularly imprinted polymers

##### 3.2.1. Optimization of loading conditions

Firstly, pH value of the sample was investigated to optimize the interactions between the water-soluble acid dyes and 1-MA-3MI-Br-MIPs in the loading process. Accordingly, the pH values of the blank wastewater samples spiked with 2 µg/mL acid dyes were adjusted to 2. 35 mL spiked solutions were percolated through the 1-MA-3MI-Br-MIPs-SPE. The recovery of each acid dye in this loading process was determined by HPLC analysis. The compounds were strongly retained on the 1-MA-3MI-Br-MIPs when the samples were prepared in acidified wastewater (pH 2). However, when the samples were prepared in wastewater of pH 7, only 45% analyte was retained. These observations illustrate that high electrostatic interactions between the acid dyes and the imidazolium in 1-MA-3MI-Br-MIPs in the solution of low pH value can generate higher affinity than that in alkaline and neutral solutions. In addition, wastewater spiked with 2 µg/mL water-soluble acid dyes with different volumes of 10, 20, 30, 35, 40, 45 mL were loaded into 1-MA-3MI-Br-MISPE column to investigate maximal loading volume. The eluent was collected and analyzed by HPLC. The results show that maximal loading volume is 35 mL. The sample could not be adsorbed completely when the loading volume was more than

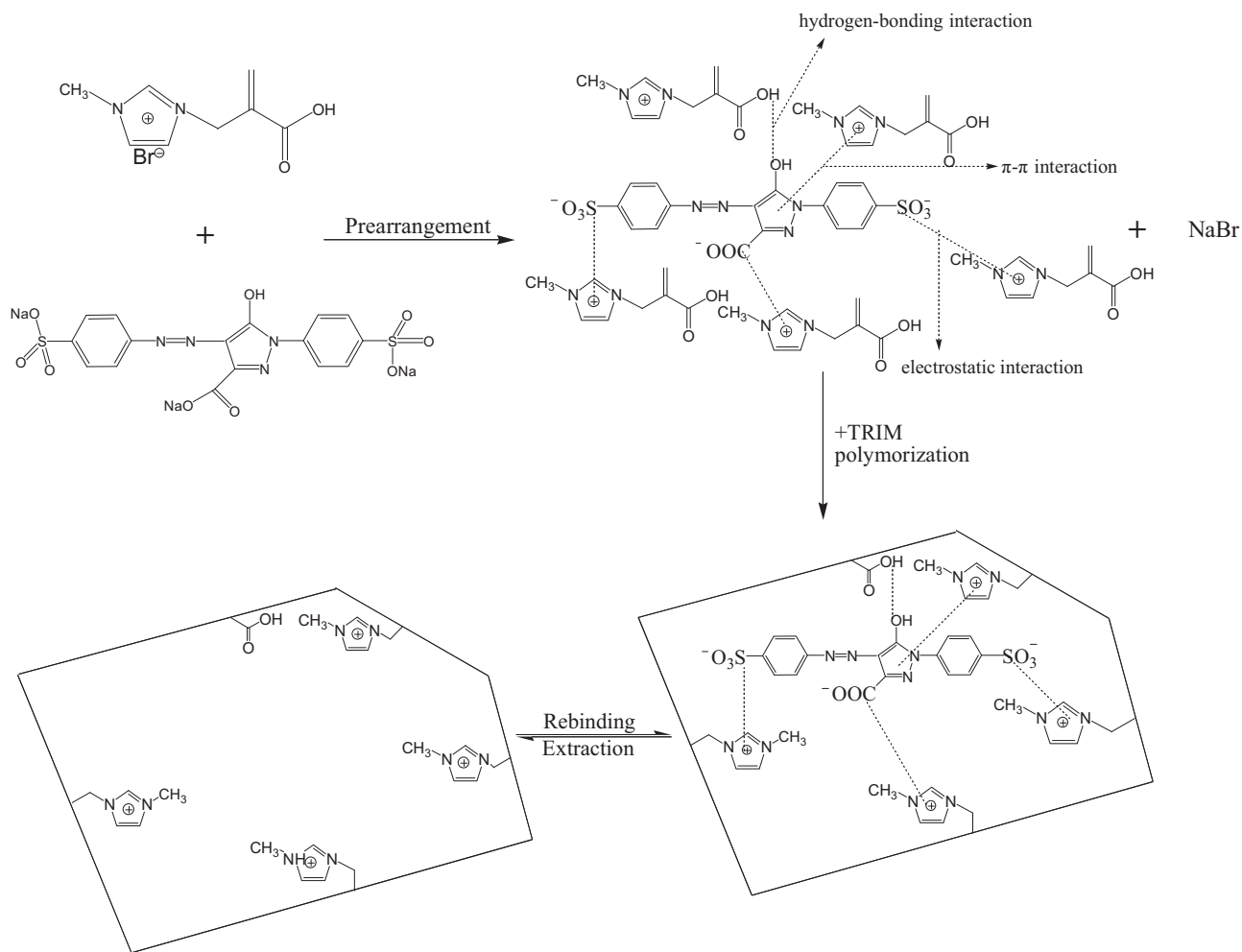


Fig. 2. Schematic illustration of the fabrication mechanism of the 1-MA-3MI-Br-MIPs.

35 mL. Taking the above reason into account, the loading condition for 1-MA-3MI-Br-MISPE columns is 35 mL in wastewater at pH 2.

### 3.2.2. Optimizing the volume of washing solution

As is known to us, the washing solvent is one of the crucial factors to increase the specific interactions between the analytes and binding sites, and simultaneously decrease the non-specific inter-

actions in the polymer [19]. In this study, 35 mL spiked wastewater with water-soluble acid dyes (pH 2) was loaded into the cartridge as described above. Wash the cartridge using methanol with variable volume of 2, 5, 10, 15, and 20 mL. The experimental results showed that less methanol cannot remove all of the polar impurities from the 1-MA-3MI-Br-MISPE columns while excess methanol can result in the loss of the water-soluble acid dyes. Based on the recoveries obtained and the ability to remove matrix of polar com-

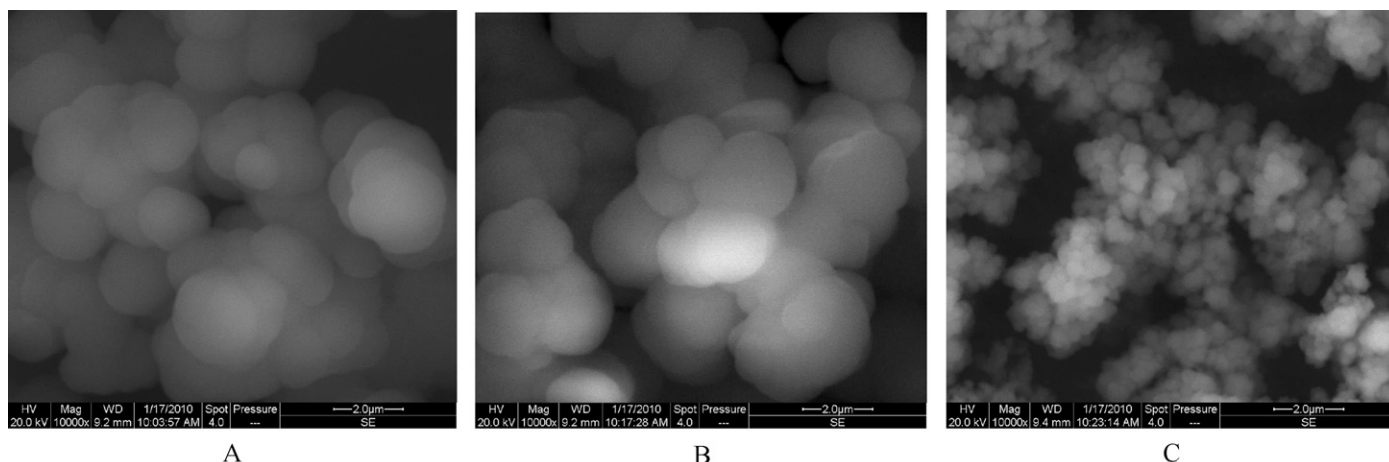


Fig. 3. SEM images of MIPs particles with (A) MAA (B) 4-VP (C) 1-MA-3MI-Br as functional monomer.



**Table 1**  
Recovery of five kinds of water-soluble acid dyes using optical MISPE protocol on MIP and NIP column ( $n=3$ ).

	Recovery (%)					
	MIP			NIP		
	Washing	Elute	Total	Washing	Elute	Total
Tratarzine	n.d. <sup>a</sup>	97.7	97.7	30.8	72.0	102.8
Amaranth	1.1	92.3	93.4	30.1	50.1	80.2
Orange G	3.5	95.4	98.9	36.6	53.2	89.8
Brilliant Ponceau 5R	2.1	96.3	98.3	52.7	48.2	100.9
Sunset Yellow FCF	n.d. <sup>a</sup>	97.6	97.6	50.1	53.4	103.5

<sup>a</sup> Not detected triplicate experiments were performed for each polymer.

pounds, 10 mL is the optimized volume of the methanol washing solution.

### 3.2.3. Optimization of eluent condition

The mixture methanol: ammonia solution (9:1, v/v) was used to elute water-soluble acid dyes from the 1-MA-3MI-Br-MISPE cartridges. Different volumes of the eluent in a range of 1.00–5.00 mL were applied. When eluent volumes were 2.00 mL, the recoveries of the five water-soluble acid dyes were the highest, the recoveries of Tratarzine, Amaranth, Orange G, Brilliant Ponceau 5R, and Sunset Yellow FCF were 97.7%, 92.3%, 95.4%, 96.3%, and 97.6%, respectively. Based on these results, 2.00 mL was employed as the optimized eluent volume.

### 3.2.4. Determination of the repeatability of the 1-MA-3MI-Br-MIPs cartridge

The rebinding/elution process was repeated 20 times using a same 1-MA-3MI-Br-MIPs cartridge. Under the optimized conditions mentioned above, the RSD values of extraction efficiencies of Tratarzine, Amaranth, Orange G, Brilliant Ponceau 5R, and Sunset Yellow FCF were 1.6%, 3.9%, 3.7%, 3.0%, and 1.7%, respectively, indicating the good repeatability and reusability of 1-MA-3MI-Br-MIPs packed cartridges.

### 3.3. Specificity of 1-MA-3MI-Br-MISPE

Five water-soluble acid dyes samples spiked in blank soft drink were extracted by 1-MA-3MI-Br-MISPE and 1-MA-3MI-Br-NISPE using the optimal 1-MA-3MI-Br-MISPE protocol (Table 1). The recoveries of five kinds of water-soluble acid dyes by 1-MA-3MI-Br-MISPE cartridges ranged from 92.3% to 97.7% which were much higher than those (from 48.2% to 72.0%) by using 1-MA-3MI-Br-NISPE. The observations indicate that the imprinted polymers can selectively separate and enrich the water-soluble acid dyes from the soft drink.

### 3.4. Comparison of extraction performances and enrichment ability for water-soluble acid dyes of three different MISPE, SAX, and MAX

The maximal loading volume onto 1-MA-3MI-Br-MIPs, 4-VP-MIPs, MAA-MIPs, SAX, and MAX were investigated to evaluate their

enrichment abilities. In wastewater, the corresponding volume for 1-MA-3MI-Br-MIPs, 4-VP-MIPs, MAA-MIPs, SAX, and MAX are 35, 26, 12, 34, and 50 mL, respectively. The final extracted solutions were evaporated to get dried products which were dissolved in 0.3 mL water for HPLC analysis, their final concentration factors are 116.7, 86.7, 40.0, 113.3, and 166.7, respectively. The concentration factor of MA-MI-MIPs-SPE (100 mg) is just slightly larger than that of SAX-SPE (100 mg), but smaller than MAX (150 mg). However, the amounts of sorbent in MAX are more than MA-MI-MIPs, so MA-MI-MIPs still obtain a better enrich ability. Moreover, compared with MAA-MIPs and 4-VP-MIPs, the 1-MA-3MI-Br-MIPs show better enrichment ability for water-soluble acid dyes, resulting from the three interactions (hydrogen bonding, electrostatic interaction and  $\pi$ - $\pi$  stacking with template molecule). Moreover, the capacity for enriching water-soluble acid dyes of 4-VP-MIPs is also higher than MAA-MIPs. That is because 4-VP-MIPs are with both hydrogen bonding and electrostatic interaction while there is only hydrogen bonding in MAA-MIPs. In summary, multiple interactions can enhance recognition ability of MIPs for target compounds in water environment.

The recoveries of the acid dyes by employing 1-MA-3MI-Br-MIPs, 4-VP-MIPs, MAA-MIPs, SAX, and MAX were also investigated under the optimum conditions with the results listed in Table 2. The 1-MA-3MI-Br-MIPs exhibited higher recoveries than MAA-MIPs, 4-VP-MIPs, SAX, and MAX, suggesting the highly anti-interference property of the 1-MA-3MI-Br-MIPs.

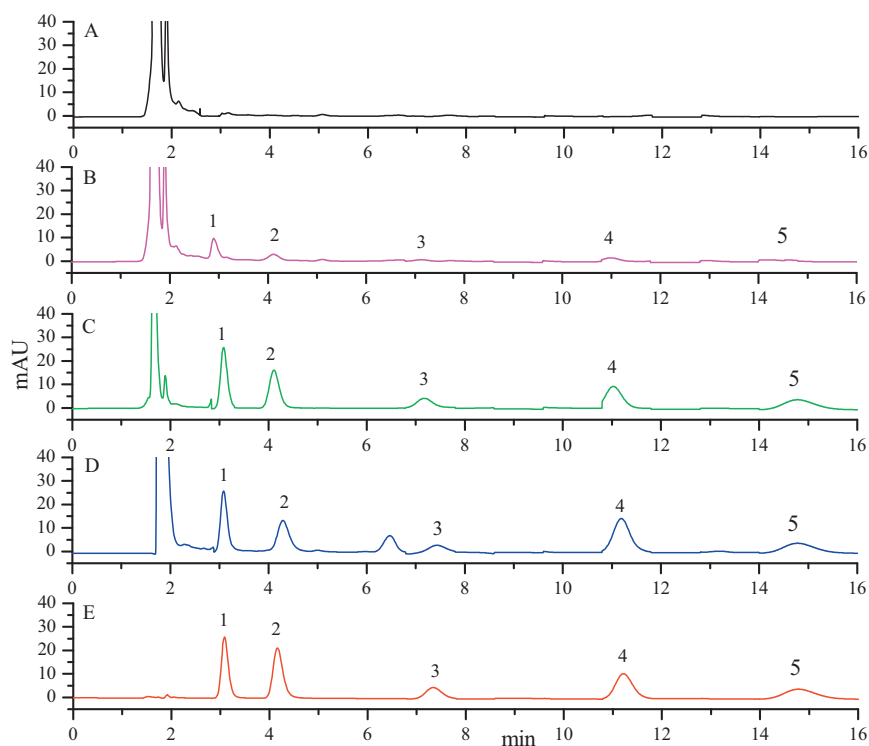
A soft drink sample described in the experimental section was treated by 1-MA-3MI-Br-MISPE, SAX-SPE, and MAX-SPE to compare the selectivity during the procedure of cleaning the complex matrices. Fig. 4 presents the chromatograms which correspond to the blank soft drink sample (A), 2  $\mu$ g/mL of acid dyes spiked soft drink sample (B), spiked soft drink sample after a clean-up on SAX-SPE (C), spiked soft drink sample after a clean-up on MAX-SPE (D), and spiked soft drink sample after a clean-up on 1-MA-3MI-Br-MISPE (E). The chromatogram obtained using SAX-SPE (Fig. 4C) and MAX-SPE (Fig. 4D) showed there was a large amount of co-extracted interfering substances at the beginning of the chromatogram. In return, the chromatogram obtained by 1-MA-3MI-Br-MISPE (Fig. 4E) confirmed most interfering substances were removed, facilitating the subsequent detection and quantification of five kinds of water-soluble acid dyes in this complex matrix. In a word, the chromatogram using 1-MA-3MI-Br-MISPE depicts better baselines and selectivity than that obtained after SAX-SPE and MAX-SPE.

### 3.5. Analysis of water-soluble acid dyes in wastewater and soft drink

Various parameters such as linearity, accuracy, repeatability, stability and LOD were investigated for evaluating the proposed method. The calibration curves were obtained by determining spiked soft drink and spiked wastewater. The linear ranges are 5.0–2000  $\mu$ g/L for five kinds of water-soluble acid dyes in blank soft drink and blank wastewater with all the correlation coefficients above 0.999. The work solutions of the five kinds of water-soluble

**Table 2**  
Recovery of five kinds of water-soluble acid dyes using MIPSPE and SAX ( $n=3$ ).

Sorbent	Tratarzine		Amaranth		Orange G		Brilliant Ponceau 5R		Sunset Yellow FCF	
	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)
1-MA-3MI-Br-MIP	97.7	1.6	92.3	3.9	95.4	3.7	96.3	3.0	97.6	1.7
4-VP-MIP	83.5	1.5	82.0	2.3	80.0	1.2	87.0	3.1	80.3	3.9
MAA-MIP	80.9	3.0	87.3	4.5	73.0	1.6	82.9	2.2	86.1	4.3
SAX	84.8	1.2	72.5	2.0	82.1	1.8	83.5	1.4	85.6	2.3
MAX	84.5	1.8	77.0	3.1	80.5	1.5	84.1	1.6	80.5	2.1



**Fig. 4.** Chromatograms of five water-soluble acid dyes in soft drink samples. Blank soft drink sample (A), 2 µg/mL of acid dyes spiked soft drink sample (B), spiked soft drink sample after a clean-up on SAX-SPE (C), spiked soft drink sample after a clean-up on MAX-SPE (D), and spiked soft drink sample after a clean-up on 1-MA-3MI-Br-MISPE (E). Loading volume: 5 mL, concentrated solution volume: 1 mL; Peak 1: Tartrazine; Peak 2: Amaranth; Peak 3: Orange G; Peak 4: Brilliant ponceau 5R; Peak 5: Sunset Yellow FCF.

**Table 3**

Recoveries and repeatability of five water-soluble acid dyes determined in spiked waste water and soft drink at three concentration levels ( $n = 3$ ).

Samples	Spiked (µg/L)	Tartrazine		Amaranth		Orange G		Brilliant Ponceau 5R		Sunset Yellow FCF	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Wastewater	10.0	96.3	3.0	97.9	3.7	92.2	2.6	89.1	2.7	92.7	2.8
	100.0	99.2	2.7	99.7	2.1	99.8	3.7	97.8	2.4	97.1	3.6
	1000.0	101.0	1.8	102.1	2.6	99.7	2.7	98.3	1.8	98.5	3.3
Soft drink 1	10.0	96.4	3.6	92.4	1.8	91.0	3.2	92.4	3.6	95.3	1.5
	100.0	97.7	1.6	92.3	3.9	95.4	3.7	96.3	3.0	97.6	1.7
	1000.0	99.1	2.2	95.8	2.3	97.0	1.8	99.1	1.8	98.9	2.1
Soft drink 2	10.0	94.1	1.9	96.7	1.9	93.1	1.9	91.2	3.7	94.9	1.9
	100.0	97.8	1.7	97.6	1.3	98.6	3.1	95.6	3.8	97.9	1.5
	1000.0	101.3	2.4	99.1	2.4	98.6	3.4	96.7	1.4	99.0	1.7

acid dyes were stable at 4 °C with only less than 3% of the dyes were degraded after being stored for 1 month. The LOD for five kinds of water-soluble acid dyes were in the range of 0.13–0.50 µg/L and 0.095–0.84 µg/L in wastewater and soft drink, respectively.

The repeatability and accuracy were assessed by analyzing spiked wastewater and two different soft drink samples with 10 µg/L, 100 µg/L, and 1000 µg/L water-soluble acid dyes. The results were summarized in Table 3. The average recoveries of wastewater and soft drink were higher than 89.1% and 91.0%, respectively. The relative standard deviations (RSD) of wastewater and soft drink were less than 3.7% and 3.9%, respectively. Above results demonstrate that the method has satisfactory recoveries and good reproducibility to analyze the water-soluble acid dyes.

#### 4. Conclusions

In this work, novel water-compatible MIPs using 1-( $\alpha$ -methyl acrylate)-3-methylimidazolium bromide as new functional monomer were synthesized and utilized as sorbents in SPE to

extract five kinds of water-soluble acid dyes from wastewater and soft drink. Moreover, compared with MAA-MIPs and 4-VP-MIPs, the extraction performance of 1-MA-3MI-Br-MIPs toward water-soluble acid dyes show a higher enrichment capacity. The  $\pi$ - $\pi$  stacking and electrostatic interactions mainly contribute to the specific recognition ability for water-soluble acid dyes. In addition, in composition with the SAX-SPE, MAX-SPE and 1-MA-3MI-Br-NISPE, almost all of the matrix interferences are removed after 1-MA-3MI-Br-MISPE. Better baselines, higher selectivity and recovery of acid dyes can be achieved. Consequently, the proposed 1-MA-3MI-Br-MISPE-HPLC method can be applied for the selective extraction and determination of water-soluble acid dyes in complex wastewater and soft drink.

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