Preparation of highly selective solid-phase extractants for Cibacron reactive dyes using molecularly imprinted polymers

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Abstract Selective polymeric extractants were prepared for preconcentration of Cibacron reactive red dye, a dye that is often applied with Cibacron reactive blue and Cibacron reactive yellow for dyeing of fabrics. The best extractant was fabricated (in chloroform) using methacrylic acid (as monomer), ethylene glycol dimethacrylate (as crosslinker), AIBN (as initiator for polymerization), and red dye as template molecule, with a molar stoichiometric ratio of 8.0:40.0:2.5:0.63, respectively. The structure of the molecularly imprinted polymer (MIP) was robust, and resisted dissolution up to 260 °C. Compared with the un-imprinted polymer, the imprinted product has a large specific surface area which improved its adsorption capacity. The effect of imprinting was obvious from the adsorption capacity measured at pH 4 for red dye (the imprinted molecule), which was increased from 24.0 to 79.3 mg g\(^{-1}\) after imprinting. Equilibrium adsorption studies revealed that the dye-imprinted-polymer enables efficient extraction of red dye even in the presence of blue and yellow dyes which have similar chemical natures to the red dye. The selectivity coefficients \(S_{\text{red dye/dye}}\) were 13.9 and 17.1 relative to the yellow and blue dyes, respectively. The MIP was found to be effective for red dye preconcentration, with a preconcentration factor of 100, from tap water and treated textile wastewater. The factors affecting extraction of red dye by the MIP were studied and optimized. Under the optimized extraction conditions, red dye was selectively quantified in the presence of other competing dyes at a concentration of 20 µg L\(^{-1}\) from different water systems with satisfactory recoveries (91–95%) and RSD values (∼5.0%).

Keywords Reactive dyes · Separation · Molecularly imprinted polymers · Solid-phase extraction

Introduction

Adsorbents with high adsorption capacity and selectivity toward particular solutes are necessary in many fields including chromatographic separation, purification processes, and wastewater treatment. For a long time, selectivity of an adsorbent toward a specific compound has been achieved by physical or chemical modification to the surface of the adsorbent. For example, the extent of adsorption of anionic dyes by natural zeolite is limited; upon surface modification with a quaternary amine (hexadecyltrimethylammonium bromide), however, strong adsorption of reactive dyes was observed [1]. Surface modification could enhance selective removal of heavy metals—the extraction efficiency of activated carbon for uranium(VI) ions was effectively improved from 33 to 100% after carbon modification with diarylazobisphenol [2]. The high selectivity of activated carbon was attributed to the favorable interaction between uranium ions and diarylazobisphenol [2]. Mahmoud and co-workers have prepared a highly selective silica surface for extraction of Hg(II) from different water samples [3]. Recently, research on developing selective adsorbents has been directed to molecularly imprinted polymers (MIPs).
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 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 [4]. This polymer is now capable of selectively rebinding the imprint molecule. Both covalent and noncovalent pathways are utilized for preparation of MIPs [5]. The successful preparation of MIPs depends on the monomers, the crosslinkers, and the appropriate polymerization conditions for a particular analyte.

MIPs can function under extreme conditions of pH, temperature, and complex environment [6]. MIPs have been efficiently applied for selective extraction of metals [7] and organic molecules [8]. Moreover, the application of MIPs as stationary phases in chromatographic separation, chiral separation, and preconcentration by solid-phase extraction has been reported in many research papers [4–10].

A very limited number of studies have considered the preparation of MIPs for selective removal or preconcentration of anionic reactive dyes. As an example, Pouci and coworkers have successfully fabricated Sudan I dye imprinted polymer. The prepared polymer was highly selective for extraction of Sudan I dye from food samples [11]. Natural and synthetic dyes are heavily used by many industries including the food, pharmaceutical, cosmetic, textile, and leather industries [12]. The effluents of these industries are highly colored and disposal of these wastes into natural waters causes damage to the environment [12, 13]. Dyes can be classified into three types depending on their chemical structure—cationic, nonionic, and anionic [1]. Anionic dyes are direct, acidic, reactive dyes [12, 13]. It is difficult to remove these dyes from effluents since they are stable to light, heat, and oxidizing agents and are biologically non-degradable [13]. Some classes of dye are harmful to aquatic life even at low concentrations [12–14]. It has been pointed out that less than 1.0 mg L\(^{-1}\) of dye content causes obvious water coloration [15]. Dye concentrations of 10 mg L\(^{-1}\) up to 25 mg L\(^{-1}\) have been cited as being present in dyehouse effluents [15]. After mixing with other water streams, the concentration of dyes is diluted. The concentration of dyes could be at \(\mu\)g L\(^{-1}\) levels in textile wastewater [16]. Usually, reactive dyes are used for dyeing wool, cotton, Nylon, silk, and modified acrylics [17]. Generally speaking, adsorption of reactive dyes is modest on most surfaces except expensive activated carbons [18]. Accordingly, finding other less expensive adsorbents for extraction/preconcentration of reactive dyes is an essential task for environmental and analytical chemists.

In this work, methacrylic acid and methyl methacrylate were used as functional monomers to fabricate two reactive dye-imprinted-polymers. The polymers are tested for selective extraction and pre-concentration of the imprinted dye from water and wastewater. Textural characteristics, and thermogravimetric and differential scanning calorimetric analysis were carried out to characterize the prepared MIPs. The studied dyes (Fig. 1) are synthetic colorants widely used in fabrics coloring and poorly adsorbed (compare with cationic dyes) on a wide range of adsorbents [17, 18].

**Experimental**

**Instruments**

Dye content was measured by using a double-beam spectrophotometer (Cary 50 UV-Vis spectrophotometer). A digital pH meter (WTW, Inolab, Germany) was used for pH measurements. IR spectra were recorded in the range (400–4000 cm\(^{-1}\)) for the polymers by means of an FTIR spectrophotometer (Perkin–Elmer, Nicolet model). Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were carried out using a TGA-50H.

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Fig. 1 The chemical structure of Cibacron reactive dyes
Preparation of highly selective solid-phase extractants

Three reactive dyes with many industrial applications were selected, namely C.I. reactive blue 2; C.I. reactive red 4; C.I. reactive yellow 2 (Aldrich Chemicals). Figure 1 depicts the chemical structures of the dyes. As a template for preparing MIPs, C.I. reactive red 4 was selected.

Stock solutions of the dyes (500 mg L\(^{-1}\)) were prepared by dissolving 0.500 g of each dye in 15 mL triply distilled water and then diluting to 1.0 L. Dye solutions of different concentration were prepared from stock solutions by appropriate dilution with distilled water. Adjustment of the pH of the solutions was always carried out before final dilution. Methacrylic acid (MA), methyl methacrylate (MMA), 2,2’-azobisisobutyronitrile (AIBN), acetic acid, and methanol were obtained from Aldrich. The monomers and the cross-linker were all carefully purified prior to polymerization by passing them through an activated basic alumina column to remove inhibitors. They were then stored under inert atmosphere. The solvent for polymerization (the porogen) was obtained as ultra-pure solvent; accordingly, it did not require purification.

Synthesis of red dye-imprinted polymers (MIP-1 and MIP-2)

Two types of red dye-imprinted polymers, based on methacrylic acid and methyl methacrylate as monomers, were prepared. Methacrylic acid (0.7 g, 8.0 mmol), ethylene glycol dimethacrylate (EGDMA, 8.0 g, 40.0 mmol), reactive red dye (2.5 g, 2.5 mmol), and AIBN (103 mg, 0.63 mmol) were completely dissolved in 50 mL chloroform in a two-necked round-bottomed flask. The resulting solution was purged with pure nitrogen gas and sonicated for 10.0 min. The mixture was then incubated under a flow of nitrogen at 50 °C for 20 h. The resulting solid polymer was crushed into powder and then sieved into small particle sizes. To leach the template molecule from the polymer, the particles were subjected to Soxhlet extraction with 200 mL acetic acid–ethanol 1:1 (v/v) for 48 h. The polymer particles were removed from the solution, washed several times with ethanol, dried at 80 °C for 24 h, and sieved before characterization analyses and adsorption tests. The polymer obtained from this procedure was referred to as MIP-1. The Soxhlet extraction was necessary to leach imprinted red dye from the polymer matrix. Under the best leaching conditions, approximately 90% of the imprinted dye was removed from the polymer matrix. To check if there was any bleed of the template, another Soxhlet extraction cycle (using acetic acid–ethanol 1:1 v/v) was carried out for 5 h. The extraction solution was checked and found to be free from red dye. The earlier preparation procedure was repeated using methyl methacrylate (0.7 g, 7.0 mmol) as monomer and the polymer obtained was referred to as MIP-2. For both MIP-1 and MIP-2, blank polymers (BPs) were identically synthesized but without adding red dye to the mixture.

Adsorption and selectivity studies

To study competitive adsorption of the dyes 100 mL solution containing 100 mg L\(^{-1}\) of each dye was mixed with 100 mg of the MIPs or BPs (particle size range 50–74 μm) in a 250-mL volumetric flask. The mixture was sealed and agitated in a temperature-controlled shaker (GFL 1083, Germany) for 24 h. The equilibration time (24 h) for adsorption of the dyes by the polymers was determined from earlier kinetic studies. A much longer time (over three days) was needed to achieve dye adsorption equilibrium on activated carbon [18]. pH of solutions was adjusted to 4.0 before adsorption studies using 0.1 mol L\(^{-1}\) acetic acid–sodium acetate buffer solution. At the end of the equilibration time, the mixtures were carefully filtered to separate solid particles and the amounts of the dyes remaining were quantified as discussed below. The concentration of the dyes in ternary dye solutions was estimated using the modified Beer’s law for a solution containing three absorbing species [18]. The absorbance of the solutions at the maximum wavelength of each dye was obtained and following equations were simultaneously solved to find concentrations of the dyes:

\[
A(\text{at } 604 \text{ nm}) = \varepsilon_{604}^{\text{RB}} C_{\text{RB}} + \varepsilon_{604}^{\text{RR}} C_{\text{RR}} + \varepsilon_{604}^{\text{RY}} C_{\text{RY}} \quad (1)
\]

\[
A(\text{at } 516 \text{ nm}) = \varepsilon_{516}^{\text{RB}} C_{\text{RB}} + \varepsilon_{516}^{\text{RR}} C_{\text{RR}} + \varepsilon_{516}^{\text{RY}} C_{\text{RY}} \quad (2)
\]

\[
A(\text{at } 406 \text{ nm}) = \varepsilon_{406}^{\text{RB}} C_{\text{RB}} + \varepsilon_{406}^{\text{RR}} C_{\text{RR}} + \varepsilon_{406}^{\text{RY}} C_{\text{RY}} \quad (3)
\]

where \(A\) is the solution’s absorbance at the indicated wavelength and \(\varepsilon\) and \(C\) are the molar absorptivity (at the indicated wavelength) and the molar concentration of the dye in the mixture. RB denotes reactive blue, RR denotes reactive red, and RY denotes reactive yellow. The values of \(\varepsilon\) were previously determined using the simple version of Beer’s law at pH 4 [18]: \(\varepsilon_{406}^{\text{RB}} = 2\,266, \varepsilon_{406}^{\text{RR}} = 2\,840, \varepsilon_{406}^{\text{RY}} = 46\,500, \varepsilon_{516}^{\text{RB}} = 2\,760, \varepsilon_{516}^{\text{RR}} = 12\,170, \varepsilon_{516}^{\text{RY}} = \text{zero}, \varepsilon_{604}^{\text{RB}} = 5\,960, \varepsilon_{604}^{\text{RR}} = 140 \text{ and } \varepsilon_{604}^{\text{RY}} = \text{zero}. \) The earlier absorptivities changed slightly (approx. 1%) over the pH range 3–11, therefore, the earlier absorptivities were used for simultaneous determination of dyes over the mentioned pH range.
The following important constants were obtained from competitive adsorption studies:

Percentage extraction ($E, \%$) of the dyes by the polymer:

$$E, \% = \frac{Q_{ads}}{Q_{total}} \times 100$$  \hspace{1cm} (4)

where $Q_{ads}$ is the amount of dye taken by the polymer at equilibrium and $Q_{total}$ is the total amount of the dye introduced in the solution.

Distribution ratio ($K_d$):

$$K_d = \frac{Q_{ads}}{C_{dye}}$$  \hspace{1cm} (5)

where $C_{dye}$ is the amount of dye left in the solution after extraction. $K_d$ value >> 1.0 indicates favorable extraction.

Selectivity coefficient of dyes ($S_{red \ dye/dye}$):

$$S_{red \ dye/dye} = \frac{(K_d)_{red \ dye}}{(K_d)_{dye}}$$  \hspace{1cm} (6)

High values of $S_{red \ dye/dye}$ indicate the adsorbent is very selective for red dye removal and the imprinting process is successful.

General procedure for preconcentration/separation of red dye from water and textile wastewater

The MIP was tested as a solid-phase extractant for red dye (the imprinted solute) that was present at trace levels ($\mu$g L$^{-1}$) in water and wastewater. The variables that affect SPE were studied and optimized. These variables include: mass of MIP, pH, preconcentration time, elution time, type of eluent, and volume of dye solution. A portion of solution containing 2–90 $\mu$g of red dye was diluted to 1.0 L and the final pH was adjusted to 4.0. A sample (250 mg) of the MIP was added to this solution and the mixture was stirred for 15 min. The amount of dye preconcentrated by the MIP was eluted for 10 min with 10 mL 0.1 mol L$^{-1}$ HCl solution. The final pH of the elution solvent was adjusted to 4 and the dye content was determined as outlined earlier in this section.

Results and discussion

Application of MIP technology to prepare adsorbents selective toward organic molecules has been studied by many researchers. The chemical nature of templates (the imprinted molecules) considered in the published papers are:

1. slightly polar, moderate molar mass (100–200 g mol$^{-1}$) with no ionizable functional groups [19–22];
2. highly polar, moderate molar mass (100–200 g mol$^{-1}$) with one ionizable functional group [11, 23, 24]; and
3. highly polar, moderate molar mass (100–200 g mol$^{-1}$) with two ionizable functional groups [25].

As can be noted, the reported studies considered relatively small molecules with slight polarity containing a small number of ionizable groups. In this work, a template of high molar mass (approx. 1000 g mol$^{-1}$), high polarity, and containing four ionizable sulfonate functional groups was studied. The common factor between this study and the published studies is that the typical polymerization process was applied for the synthesis of methacrylic acid and methyl methacrylate-based MIP [19–22] but a new template was utilized (reactive red). In addition, application of methyl methacrylate as monomer is not common for preparing MIPs.

In the first step of polymerization via methacrylic acid, strong chemical interactions (mainly hydrogen bonding) between the carboxylic acid group of the monomer and the sulfonate groups ($-SO_3H$) located on the dye were created. Upon crosslinking by EGDMA, a strong backbone of the polymer is formed where the red dye molecules are entrapped. By leaching of the red dye molecules from the polymer matrix, a molecularly imprinted polymer material is generated.

Characterization of the MIPs

Evidence of molecular imprinting and the effect of imprinting on the structural properties of the prepared polymers were investigated using FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and N$_2$-adsorption analysis. As will be shown later, polymer MIP-1 had high extraction power and excellent selectivity for red dye compares with the other polymers, therefore, characterization studies were restricted to this polymer.

FTIR observation of MIP-1 and BP-1

The FTIR spectra of MIP-1 and its corresponding blank were recorded over the range 4000–400 cm$^{-1}$. FTIR analysis can provide much useful information regarding the nature of surface functional groups created on the polymer surface. The characteristic bands of the carboxylic acid group (1163, 1393, 1460, 1515, 1540, 1645, 1714, 1740, and 3445 cm$^{-1}$) were clearly observed in the spectra of both polymers. A high similarity between MIP-1 and its blank polymer was noted which supported the fact that both polymers have the same backbone, and carboxylic acid groups are created on the surface of both polymers. It seems that there is no external dye attached to the polymer.
because the main FTIR bands of the dye (1137, 1051, and 616 cm\(^{-1}\) arising from the strong vibrations of the –SO\(_3\)H group) were not detected in the spectrum of MIP-1.

**Thermogravimetric analysis**

The thermal stability of the prepared polymers and the effect of imprinting on polymer stability were studied using thermogravimetric analysis. The thermogravimetric curves of MIP-1 and its BP are depicted in Fig. 2. Generally, the thermogravimetric plots showed a similar pattern and both polymers are not decomposed up to 260 °C. This observation indicates that the stability of polymer particles is unchanged by imprinting. Both polymers are entirely decomposed prior to reaching 500 °C. Similar observations were noted for MIP-2 and its BP.

**Differential scanning calorimetry**

Crystallinity of both MIPs and the BPs was assessed by use of DSC. The DSC scans of the MIP materials were different from those of the blanks. The scan of MIP-1 showed similar transition peaks as that for the template-free polymer, but with higher \(T_m\) values. This could be attributed to the different structure of the dye MIP. The different structural features of the imprinted materials were also observed in the DSC scan of MIP-2. A new transition temperature was observed at approximately \(T_m=415\) °C in addition to the original ones at approximately 276 and 460 °C. The appearance of this transition could be because of the creation of new ordered segments in the polymer structure upon imprinting [26].

**Surface area and pore-size analysis**

It seems that textural analyses are more indicative of the effect of imprinting on polymers compared with the earlier methods. Table 1 shows the surface area and pore size analysis values for MIPs and BPs.

### Table 1 Textural characteristics of MIPs and BPs

<table>
<thead>
<tr>
<th>Property</th>
<th>BP-1</th>
<th>MIP-1</th>
<th>BP-2</th>
<th>MIP-2</th>
</tr>
</thead>
</table>
| Specific surface area (m\(^2\) g\(^{-1}\))
| \(a\)                          | 122.6 | 293.2  | 155.3 | 355.3  |
| Total pore volume (cm\(^3\) g\(^{-1}\))
| \(b\)                          | 0.092 | 0.312  | 0.102 | 0.421  |
| Average pore diameter (nm)
| \(c\)                          | 2.10  | 2.42   | 2.01  | 2.15   |

\(a\) Multipoint BET method [17]

\(b\) Calculated from N\(_2\) adsorbed at \(P/P_0=0.95\) [17]

\(c\) BJH method [17, 18]

As can be noted from Table 1, there is a large increase in surface area and pore volume for both polymers after imprinting. It seems that imprinting has created a larger surface area and pore volume in MIP-2 than in MIP-1. This may explain the high adsorption capacity of MIP-2 for dyes, as will be shown soon. The average pore diameters for all polymers are in the range 20–25 Å, indicating that mesoporous polymers were obtained in the current study.

**Effect of solution pH on dye adsorption by MIP-1**

In fact, \(pH\) has a large influence on the extent of adsorption of solutes from solution. Accordingly, determination of the optimum \(pH\) at which maximum adsorption occurs is essential to utilize the maximum capacity of the polymer. Therefore, adsorption of red dye by MIP-1 and BP-1 was investigated at \(pH\) 3.0, 4.0, 6.0, 8.0, and 10.0. The conditions used for the adsorption tests, and the uptake results, are given in Table 2.

It was found that under acidic conditions (\(pH<6.0\)), better adsorption of red dye was achieved. The best adsorption value was observed at a solution \(pH\) of 4.0. Therefore, \(pH\) 4 was taken as the optimum \(pH\) for red dye adsorption or extraction from solution. The preferential adsorption of red dye at this \(pH\) could be attributed to the preferred H-bonding interactions between undissociated

### Table 2 Comparison of adsorption capacities for red dye at different \(pH\) values

<table>
<thead>
<tr>
<th>(pH) of dye solution</th>
<th>Initial dye concentration (ppm)(a)</th>
<th>Final dye concentration (ppm)(b)</th>
<th>Adsorption capacity (mg dye g(^{-1}) polymer)(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>101.0</td>
<td>26.5</td>
<td>74.5</td>
</tr>
<tr>
<td>4.0</td>
<td>102.0</td>
<td>21.3</td>
<td>80.7</td>
</tr>
<tr>
<td>6.0</td>
<td>100.0</td>
<td>29.1</td>
<td>70.9</td>
</tr>
<tr>
<td>8.0</td>
<td>103.0</td>
<td>35.2</td>
<td>67.8</td>
</tr>
<tr>
<td>10.0</td>
<td>99.0</td>
<td>45.6</td>
<td>53.4</td>
</tr>
</tbody>
</table>

\(a\) Mass of polymer 100 mg, volume of solution 100 mL, temperature 25 °C, and agitation time 24 h. For acidic solutions, 0.1 mol L\(^{-1}\) acetic acid buffer solution was used for \(pH\) adjustment; phosphate buffer (0.1 mol L\(^{-1}\)) was used to adjust the \(pH\) of basic solutions

\(b\) Average from three trials (RSD < 5.0% in all cases)
carboxylic acid groups on polymer surface and sulfonated groups of the dye. In contrast, the poor adsorption observed under basic conditions is attributed to repulsion between carboxylate polymer surface groups and the dissociated sulfonated dye groups. It is worth mentioning that the $pK_a$ values for surface carboxylic acid groups and sulfonated groups were in the range 5–6 [17, 18].

Effect of polymer imprinting on red dye adsorption, and selectivity studies

The percentage extraction, distribution ratio, and selectivity coefficients for red dye removal by the polymers are summarized in Table 3.

From Table 3, the following observations can be made.

1. For both polymers, better extraction of the red dye was observed after imprinting. This, in turn, indicates that imprinting has increased the selectivity of the polymer toward red dye among other dyes. The extraction capacity of MIP-1 was 79.2% which is approximately twice as high as that for MIP-2. It seems that imprinting (for both polymers) has a small effect on extraction of blue and yellow dyes, which confirms that molecular cavities and specially-designed active sites that are created by molecular imprinting are very selective for red dye even in the presence of other competing dyes.

2. The magnitude of the distribution values usually indicates the favorability of the adsorption process—higher values of the distribution ($K_d > 1.0$) indicates favorable adsorption, and the solute favorably migrates from the solution to the surface of the adsorbent. As can be seen in Table 3, MIP-1 has outstanding retention capacity for red dye, with a $K_d$ of 3.76 compared with the other extractants ($K_d < 1.0$). The distribution value for red dye on MIP-1 is six times higher than on MIP-2; this is indicative of the high extraction power of MIP-1 for red dye even in the presence of other interfering dyes or other solutes.

3. Upon imprinting, the selectivity coefficient increases from 0.77 to 17.1 relative to blue dye and from 0.73 to

### Table 3 Percentage extraction, distribution ratio, and selectivity coefficients of the prepared polymers

<table>
<thead>
<tr>
<th>Dye</th>
<th>Extraction CP-1</th>
<th>MIP-1</th>
<th>CP-2</th>
<th>MIP-2</th>
<th>Distribution CP-1</th>
<th>MIP-1</th>
<th>CP-2</th>
<th>MIP-2</th>
<th>Selectivity CP-1</th>
<th>MIP-1</th>
<th>CP-2</th>
<th>MIP-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>24.3</td>
<td>79.2</td>
<td>14.0</td>
<td>38.2</td>
<td>0.32</td>
<td>3.76</td>
<td>0.16</td>
<td>0.61</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Blue</td>
<td>15.4</td>
<td>18.4</td>
<td>13.8</td>
<td>19.6</td>
<td>0.18</td>
<td>0.22</td>
<td>0.15</td>
<td>0.23</td>
<td>0.77</td>
<td>17.1</td>
<td>1.07</td>
<td>2.65</td>
</tr>
<tr>
<td>Yellow</td>
<td>16.8</td>
<td>21.3</td>
<td>15.2</td>
<td>19.4</td>
<td>0.19</td>
<td>0.27</td>
<td>0.18</td>
<td>0.23</td>
<td>0.73</td>
<td>13.9</td>
<td>0.89</td>
<td>2.65</td>
</tr>
</tbody>
</table>

$^a$ Adsorption conditions: mass of polymer 100 mg, initial dye concentration 100 ppm, pH 4.0, volume of solution 100 mL, agitation time 24 h, temperature 25 °C

### Table 4 Effect of pH, mass of extractant, preconcentration time, elution time, and volume of solution on extraction of red dye by MIP-1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Percentage extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of extractant (mg)$^a$</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>68.6</td>
</tr>
<tr>
<td>200</td>
<td>&gt;99</td>
</tr>
<tr>
<td>300</td>
<td>&gt;99</td>
</tr>
<tr>
<td>500</td>
<td>&gt;99</td>
</tr>
<tr>
<td>pH$^b$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>85.3</td>
</tr>
<tr>
<td>4</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td>76.3</td>
</tr>
<tr>
<td>10</td>
<td>52.7</td>
</tr>
<tr>
<td>Preconcentration time (min)$^c$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>72.6</td>
</tr>
<tr>
<td>20</td>
<td>&gt;99</td>
</tr>
<tr>
<td>30</td>
<td>&gt;99</td>
</tr>
<tr>
<td>70</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Elution time (min)$^d$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>56.7</td>
</tr>
<tr>
<td>15</td>
<td>&gt;99</td>
</tr>
<tr>
<td>20</td>
<td>&gt;99</td>
</tr>
<tr>
<td>30</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Volume of solution$^e$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>&gt;99</td>
</tr>
<tr>
<td>50</td>
<td>&gt;99</td>
</tr>
<tr>
<td>100</td>
<td>&gt;99</td>
</tr>
<tr>
<td>250</td>
<td>&gt;99</td>
</tr>
<tr>
<td>1000</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Dye content and volume of eluent were 20 μg and 10 mL, respectively, in all experiments. Results are averages from three trials (RSD < 3.0% in all cases)

$^a$ pH 4.0, preconcentration time 20 min, elution time 15 min, volume of solution 1000 mL

$^b$ mass of MIP-1 200 mg, preconcentration time 20 min, elution time 15 min, volume of solution 1000 mL

$^c$ mass of MIP-1 200 mg, pH 5.0, elution time 15 min, volume of solution 1000 mL

$^d$ mass of MIP-1 200 mg, pH 5.0, preconcentration time 20 min, volume of solution 1000 mL

$^e$ mass of MIP-1 200 mg, pH 5.0, preconcentration time 20 min, elution time 15 min
13.9 relative to yellow dye. This indicates reasonable preconcentration of red dye by MIP-1 from solutions containing blue and yellow dyes which have similar chemical structures (Fig. 1).

Analytical studies

Optimization of preconcentration/separation of red dye from solution

Five experimental variables that affect red dye extraction by MIP-1 were investigated and optimized. These variables and their ranges are summarized in Table 4.

A set of solutions (volume 1.0 L) containing 20 μg red dye was prepared and pH was adjusted between 3 and 10 by use of appropriate buffer solution. These solutions were then subjected to the preconcentration procedure (section “General procedure for preconcentration/separation of red dye from water and textile wastewater”). The results are given in Table 4. Extraction of the red dye is constant and maximum within the pH range 4–6 whereas modest extraction power was observed at pH<4 and pH>6. Accordingly, in all subsequent studies pH was adjusted to 4.0. The minimum weight needed for quantitative extraction of red dye per liter solution was 200 mg. Therefore, 200 mg MIP-1 was used for preconcentration of trace levels of red dye from solution. As can be noted from Table 4, constant stirring for 20 min was enough to preconcentrate 20 μg present in a 1.0-L sample using 200 mg MIP-1 particles. Moreover, 15 min seems to be enough for stripping the adsorbed red dye from the MIP-1 surface and achieving the maximum recovery. Preconcentrating 20 μg red dye from solutions raging from 25 to 1000 mL in volume was quantitative in all cases using 200 mg adsorbent. The optimum experimental conditions considered for each experiment are given below Table 4. Under the optimum conditions described in Table 4, the calibration plot was linear over the concentration range 2–100 μg red dye in 1.0 L sample solution. Five replicate determinations of 30 μg red dye in 1 L solution gave a satisfactory RSD (2.5%). The detection limit corresponding to three times the standard deviation of blank was found to be 1.5 μg L⁻¹. All statistical results were based on averages from triplicate trials for each standard solution in the indicated range.

Selective preconcentration of red dye from real water samples

This study was undertaken in order to evaluate the potential application of the MIP for selective preconcentration of polar reactive dyes present in natural waters. To achieve this, samples (1000 mL adjusted to pH 4) of tap water and treated textile wastewater were spiked with trace amounts of reactive dyes (20 μg) and subjected to the optimized extraction procedure. The results from extraction/preconcentration of red dye from different water matrices using MIP-1 are summarized in Table 5.

Using MIP-1, selective preconcentration of red dye was established with a preconcentration factor of approximately 100. This preconcentration factor can be further improved to 200 by simply doubling the sample volume, however, this practice will increase the time of analysis. In fact, the matrices tap water and wastewater seem to affect the selective-extraction power of MIP-1 for red dye. The dissolved inorganic and organic matter in natural water systems played a role in reducing (slightly) the selective efficiency of MIP-1. It should be mentioned that the MIP-1 is not expensive compared to activated carbon, nanotube activated carbon, or anionic exchanger resins. Moreover, MIP-1 offers high selectivity for reactive dyes which is not available when the aforementioned expensive adsorbents are used.

Conclusions

An extractant for selective removal of anionic reactive red dye from a mixture of dyes has been made by using molecular imprinting technology. The extractant enabled selective uptake of red dye only in the presence of blue and yellow dyes, which have similar chemical natures to red dye. The polymeric extractant was employed for selective preconcentration, with a preconcentration factor of 100, of red dye at 20 μg L⁻¹ from different water samples, for example tap water and treated textile wastewater. The detection limit for determination of red dye by the proposed analytical method was 1.5 μg L⁻¹. Adopting similar preparation conditions to MIP-1, similar MIPs for blue and yellow dyes could be obtained and applied for selective extraction of these polar solutes from textile wastewater.

Table 5 Preconcentration of red dye from tap water and treated textile wastewater⁴

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preconcentration factor</th>
<th>Red dye detected (mg L⁻¹)</th>
<th>Recovery (RSD)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>99.3</td>
<td>1.96</td>
<td>99.3 (3.5)</td>
</tr>
<tr>
<td>Tap water</td>
<td>94.6</td>
<td>1.87</td>
<td>94.6 (4.5)</td>
</tr>
<tr>
<td>Wastewater</td>
<td>90.8</td>
<td>1.81</td>
<td>90.8 (4.6)</td>
</tr>
</tbody>
</table>

⁴ Conditions: dye content 20 μg, pH 4, mass of MIP-1 200 mg, sample volume 1000 mL, preconcentration time 20 min, elution time 15 min, eluent 0.1 mol L⁻¹ HCl, eluent volume 10 mL.

⁵ Results are averages from three trials for distilled and tap waters and four trials for textile wastewater.
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References