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# Molecular Imprinted Membrane with High Flux by Surface Photo-grafting Copolymerization

**LI SHUANG(李爽), ZHANG Fengbao(张凤宝)*, ZHANG Guoliang(张国亮) and WANG Yan(王燕)**

School of Chemical Engineering, Tianjin University, Tianjin 300072, China

**Abstract** Molecular imprinted polymer membranes (MIM) combine the merits of molecular imprint and membrane technology. In this work, a very thin of imprinted polymer that can specifically and selectively absorb the basic template (adenine) was grafted on the surface of polyvinylidene fluoride membrane by photo-grafting copolymerization. Because the molecular imprinted polymer is grafted on the surface of the matrix membrane without blocking the membrane pores, the resultant MIMs have high flux as microfiltration membrane ($0.26\,mol\cdot m^{-2}\cdot h^{-1}$ of template and flux for distilled water was $3.6\,ml\cdot mim^{-1}\cdot cm^{-2}$ at 0.8 MPa). Moreover, the MIMs can absorb/desorb template molecules rapidly. Usually, it only takes several minutes for MIMs to absorb more than 75% of the template (adenine) in aqueous solution. And the influences of the type and amount of the functional monomers, the amount of the cross-linker on the absorption capability are discussed to determine the optimal preparation conditions.

**Keywords** molecular imprinted membrane, photo-grafting copolymerization, adenine

## 1 INTRODUCTION

During the past decades molecular imprinted polymers (MIPs) have shown their wide applications for affinity separation[1], artificial antibody combining site minics[2–4], artificial enzymes[5], and biological sensors[6,7]. MIPs are a kind of highly cross-linked polymeric material with imprinted caves that have specific shape and size with fixedly arranged functional groups. Thus, MIPs can "record" the spatial structure of template[8,9].

Molecular imprinted membranes (MIMs) combine the merits of membrane technology and molecular imprinting, *i.e.* MIMs have high selectivity, and can be applied in continuous operation on a large scale. There are several approaches for preparation of MIMs, such as in-situ polymerization[10–12], phase inversion[13–15], precipitation in membrane pores[16,17], nanosphere composite membranes[18] and photo-grafting co-polymerization[19,20]. However, MIMs preparated by the first four ways have very small flux (less than $10^{-3}\,mol\cdot m^{-2}\cdot h^{-1}$) because they need more highly cross-linked polymers or deposit more imprinted polymers into membrane pores for high selectivity, which results in blocked MIMs pores. MIMs prepared by photo-grafting co-polymerization can overcome these limitations.

Photo-grafting co-polymerization routes can be introduced briefly as follows. Polymeric matrix is coated with photo initiator in advance, for example benzophenone can be excited to singlet state S if it is exposed under the UV, then reverts to triplet state T and the carbonyl of benzophenone turns to hydroxyl by hydrogen-abstraction from the polymeric backbone and leaves free radicals from the polymer surface. These radicals as starters can initiate the graft co-polymerization of the functional monomer and cross-linker to form a thin film of the imprinted polymer on the surface of the polymeric matrix. Because of weak penetrability of UV, photo graft co-polymerization is only limited on the surface or sub-surface of the matrix. Therefore, the intrinsic property of the polymer matrix cannot be impaired. Namely, there is no effect on the internal structure of the polymer matrix membrane and MIMs can maintain the flow property of the matrix membrane.

In this work, MIMs with highly specific selectivity for adenine and high flux as microfiltration membrane ($0.26\,mol\cdot m^{-2}\cdot h^{-1}$) are prepared by photo grafting co-polymerization in the presence of template (adenine), functional monomer (2-acrylamido-2-methyl-1-propane sulfonic acid), cross-linker (*N*, *N*′-methylene-bis-acrylamide) and photo initiator (benzophenone). These MIMs have the highest adsorption for template molecules from its analogues. Moreover, the MIMs are tested to reveal the high rate of absorbing/desorbing template molecules.

## 2 EXPERIMENTAL

Following the established procedure in the literature[19], the details of the present experiment is outlined as follows.

### 2.1 Materials

Polyvinylidene fluoride (PVDF) microfiltration membranes (Durapore) with pore size 0.22 μm were

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* To whom correspondence should be addressed.

purchased from Millipore. Methacrylic acid (MAA) and $N$, $N'$-methylene-bis-acrylamide (MBAA) was obtained from Tianjin Chemical Reagent Research Laboratory. 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was purchased from Aldrich. Benzophenone (BP) was obtained from Tianjin Yuanhang Chemical Reagent Limited. Adenine, hypoxanthine, guanine and adenosine were all purchased from Sigma. All other chemicals and solvents were obtained from commercial sources. All materials were used as received without further purification.

### 2.2 Selectivity of functional monomers

$10^{-5}$ mol·L$^{-1}$ of adenine in methanol was mixed with $5 \times 10^{-5}$ mol·L$^{-1}$ of MAA and $5 \times 10^{-5}$ mol·L$^{-1}$ of AMPS separately and vibrated for 4 h. Then the UV spectra of these two mixtures $S_{T1}$, $S_{T2}$ were measured by a double-beam UV-vis spectraphotometer (TU-1901). The sepctra of the mixtures are compared with the superimposition of the spectra of single compounds (template, functional monomer).

### 2.3 Preparation of the photo-grafting molecular imprinted membranes

Circular PVDF membranes ($\phi$25 mm) were weighed and coated with photo initiator BP by soaking in 0.15 mol·L$^{-1}$ of BP in methanol for 30 min. After drying at 40℃ in vacuum, the resultant PVDF membranes were immersed in a monomer solution containing $10^{-2}$mol·L$^{-1}$ of adenine, certain concentration of the functional monomer and MBAA as cross-linker, and $5 \times 10^{-3}$ mol·L$^{-1}$ of BP to avoid the loss of BP from the coated PVDF membranes. After 10 min, membranes were exposed under the high pressure UV mercury lamp (1000 W) for 17 min. The resultant membranes were extracted with methanol in a Soxhlet apparatus for 24 h followed by 0.1 mol·L$^{-1}$ of HCL and distilled water until the absorbency of the washing solution at 260 nm is less than 0.004. After drying, membranes were weighed again. The mass difference is the net mass of grafted co-polymer ($G_g$). The preparation of blank membranes was the same as MIMs except for no adenine.

### 2.4 Characterization of MIMs

In order to affirm whether the imprinted polymer can attach to the surface of the PVDF membranes or not, Transmission Fourier transform (FR) IR spectra of the initial PVDF membranes and MIMs were taken by a spectrometer NEXUS (Thermo Nicolet).

Scanning electron microscopy (SEM) measured by a XL 30 ESEM (PHILIPS) was used for observing the surface and the cross-sectional images of initial PVDF membranes and MIMs. These images could show the differences between pore structure of initial PVDF membranes and MIMs.

The flux of water was determined by the water volume through MIM at 0.8 MPa divided by the time needed and the area of MIM ($\phi$25 mm).

### 2.5 Determination of the absorption capability of MIMs

5 ml of $10^{-5}$ mol·L$^{-1}$ adenine, hypoxanthine, guanine and adenosine aqueous solution were respectively filtered through MIMs fixed in membrane holders ($\phi$25 mm) at 1 ml·min$^{-1}$. The initial solution and permeation were respectively measured at 260 nm, 249.5 nm, 248.5 nm, 257 nm, using UV-vis spectrophotometer (Leng Guang 752). The differences between these data were calculated for absorption amount $q = (c_0 - c)V/G_g$ mol (the absorbed molecule)/mg (grafted co-polymer), in which $c_0$ is the concentration of initial solution (mol·L$^{-1}$); $c$ is the concentration of permeation (mol·L$^{-1}$); $V$ is the volume of solution through MIM (ml); $G_g$ is the amount of grafted copolymer on the surface of the MIM (mg).

### 2.6 Regeneration of MIMs

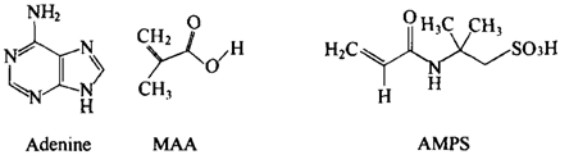
MIMs which absorbed adenine can be used for absorption experiment again just by washing MIMs with 0.1 mol·L$^{-1}$ of HCL and distilled water for several times.

## 3 RESULTS AND DISCUSSION

### 3.1 Determination of functional monomer

The strength of the non-covalent bonds depends on the polarity of media. The polar media combines with the templates by hydrogen bonds, etc. Because of preparation and following recognition of MIPs utilize the non-covalent bonds between the functional monomers/polymer and the template molecule by hydrogen bonds, hydrophobic interactions, etc., that can hardly react in polar media, the two processes are mostly performed in apolar media. But the strong ionic interaction is an exception. In this study, p$Ka_1$ and p$Ka_2$ of adenine (Fig. 1) as the template are 4.20 and 9.87[21], respectively. So, adenine can react with acids by ion interaction and hydrogen bonds (Fig. 2). The p$Ka$ of MAA and AMPS (Fig. 1) as functional monomers are 4.65 and < 1, respectively. They both have acid group and AMPS is a strong acid, so they can react with adenine.

In order to determine the strength of the complexes formed with the template and functional monomers, the absorbencies of the complexes and single compounds were measured by a double-beam UV-vis spectraphotometer (Fig. 3).




Adenine MAA AMPS

**Figure 1 Template and functional monomers**

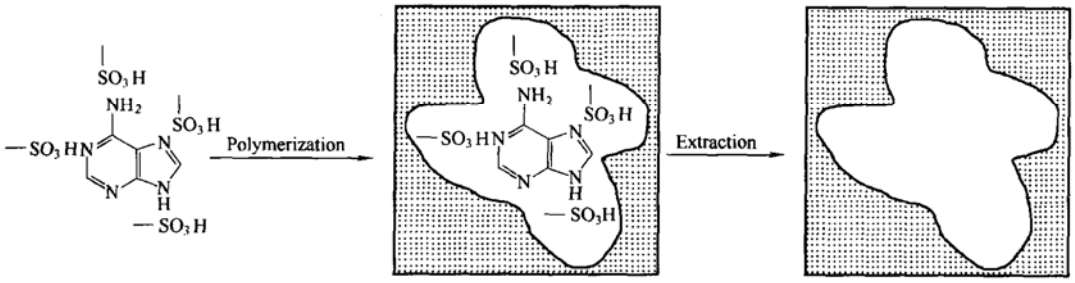
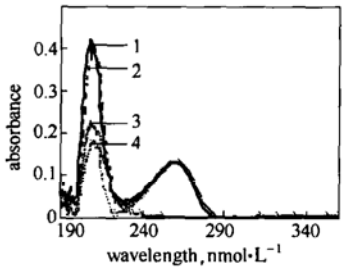
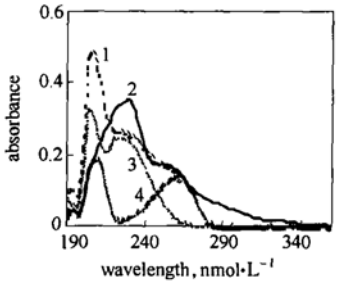



**Figure 2 Preparation of molecular imprinted membranes**




(a)
1—mixture; 2—theoretical sum;
3—MAA; 4—adenine




(b)
1—theoretical sum; 2—mixture;
3—AMPS; 4—adenine

**Figure 3 UV spectra for template (adenine $10^{-5}$ mol·L$^{-1}$), functional monomers** (A: MAA; B: AMPS, $5 \times 10^{-5}$ mol·L$^{-1}$) **in methanol and the complexes formed with them**

When template and functional monomer form complexes, the absorbance of complexes is different from the superimposition of the absorbencies for the two separate compounds. If the absorbance of the complexes coincides with the superimposition, the strength of the reaction between template and functional monomer is very weak or no reaction.

Figure 3 shows that when using MAA as functional monomer, the absorbance of the mixture of MAA and adenine was the same as that of the superimposition. While using AMPS, comparing with the superimposition, the absorbance of the mixture shifted. Obviously, the interaction between AMPS and adenine is stronger than that of MAA and adenine. So in the following experiments, AMPS as the functional monomer was chosen.

### 3.2 Photo-grafting MIMs preparation and characteristics

After matrix PVDF membranes coated with BP were immersed in monomer solution and then exposed under the UV, the BP on the surface of the membranes were excited to singlet state S and then reverted to triplet T. Here, the carbonyls of BP abstracted a hydrogen atoms from the surface of the PVDF membrane, and turned to hydroxyl, leaving free radicals on the membrane surface[22] (Fig. 4).

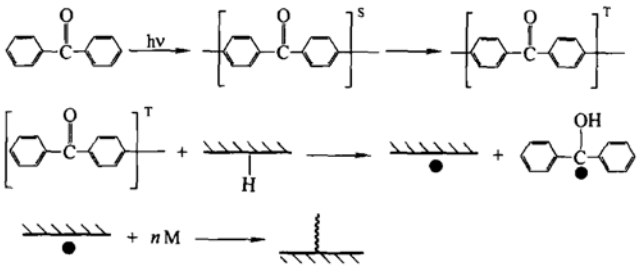
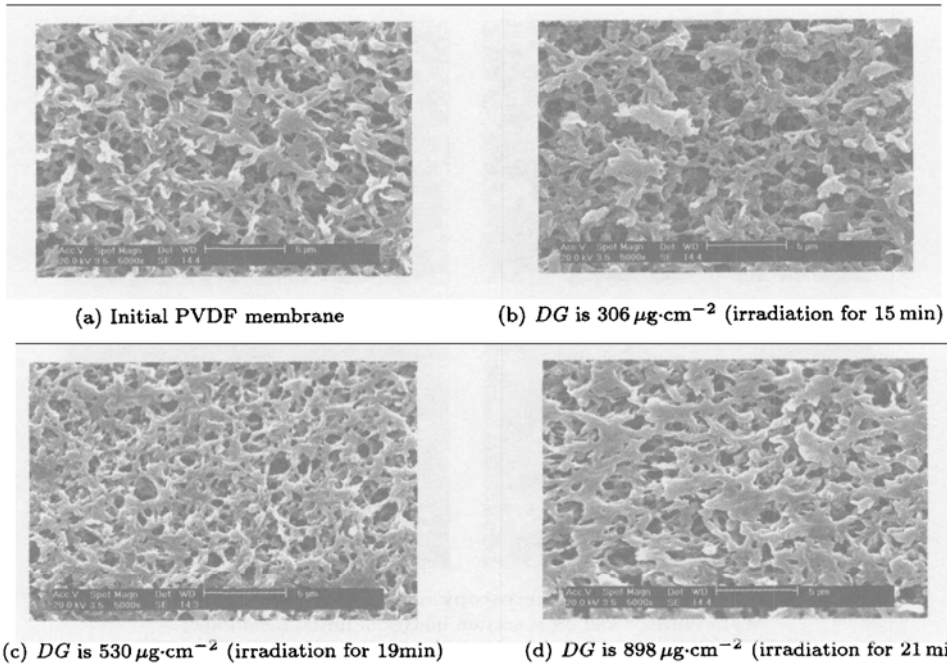



**Figure 4 Photo-grafting co-polymerization initiated by BP**

When monomer solution containing BP only without MBAA or AMPS was exposed under the UV, no change on the mass of membranes was detected, even irradiated for 40 min. However, adding PVDF membranes coated with BP to the monomer solution, membranes mass increased remarkably after 17 min irradiation. Namely, the change of mass was not owing to deposition of the polymer into the membrane pores. It was the result of photo-grafting co-polymerization initiated with free radicals left *via* hydrogen-abstraction of BP from PVDF membrane backbone and coated the surface of PVDF membrane with a very thin film of imprinted polymers. The degree of graft (*DG*) increased with prolongation of irradiation time or raiseing of monomer concentration (Tables 1 and 2). Too long irradiation time resulted in a large number of homopolymers that could block the membrane pores (Fig. 5). After repeated experiments, 17min was determined as the optimal irradiation time.



(a) Initial PVDF membrane (b) $DG$ is 306 $\mu g \cdot cm^{-2}$ (irradiation for 15 min)

(c) $DG$ is 530 $\mu g \cdot cm^{-2}$ (irradiation for 19min) (d) $DG$ is 898 $\mu g \cdot cm^{-2}$ (irradiation for 21 min)

**Figure 5 Scanning electron microscopy for initial PVDF membrane and MIMs with varied $DG$**

**Table 1 DG with varied concentrations of MBAA**

| MBAA$\times 10^{-3}$, mol·L$^{-1}$ | $DG$, $\mu g \cdot cm^{-2}$ |
|---|---|
| 100 | 159 |
| 300 | 347 |
| 400 | 523 |

AMPS 50 × $10^{-3}$ mol·L$^{-1}$, adenine $10^{-2}$ mol·L$^{-1}$, BP 5 × $10^{-3}$ mol·L$^{-1}$ in methanol, irradiation for 17 min

**Table 2 DG with varied irradiation time**

| $t$, min | $DG$, $\mu g \cdot cm^{-2}$ |
|---|---|
| 12 | 0 |
| 17 | 347 |
| 22 | 918 |

AMPS 50 × $10^{-3}$ mol·L$^{-1}$, adenine $10^{-2}$ mol·L$^{-1}$, MBAA 0.3 mol·L$^{-1}$, BP 5 × $10^{-3}$ mol·L$^{-1}$ in methanol

$DG = \frac{G_g - G_0}{A}$, $G_g$—mass of MIM, $G_0$—mass of initial PVDF membrane, $A$—area of membrane

When blank membranes and MIMs were photo-grafting co-polymerized with functional monomer (AMPS) and cross-linker (MBAA), the IR spectra of them should have strong amide I band (carbonyl) at 1665 cm$^{-1}$ and amide Ⅱ band (N-H) at 1535 cm$^{-1}$ because of the amides in AMPS and MBAA. On the contrary, there were not the two bands disappeared for the initial PVDF membranes (Fig. 6).

The SEM photos (Fig. 7) of initial PVDF membrane and MIM showed that there was no change on the structure of membrane pores after photo-grafting co-polymerization. As expected, imprinted polymers were grafted onto the surface of PVDF membranes to form a very thin coating film without blocking the pores. The MIMs displayed high flux as microfiltration membranes.

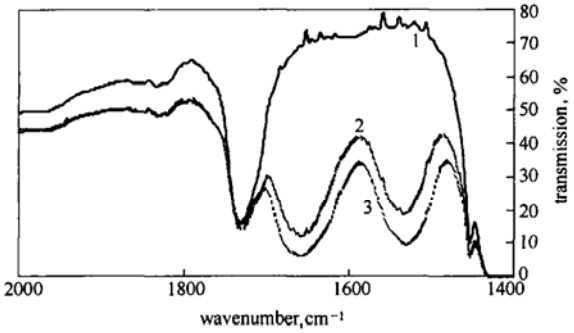



**Figure 6 IR spectra of initial PVDF membranes and MIMs**

(AMPS 50 × $10^{-3}$ mol·L$^{-1}$, MBAA 0.3 mol·L$^{-1}$, adenine $10^{-2}$ mol·L$^{-1}$, BP 5 × $10^{-3}$ mol·L$^{-1}$ in methanol, irradiation for 17 min)

1—initial PVDF membranes; 2—MIMs; 3—blank membranes

### 3.3 Influence of the functional monomer concentration on MIMs absorption capability

The data from Table 3 indicated that the binding capability for the template of the MIMs and blank membranes became higher when increasing the concentration of the functional monomer, and the specific factor $\beta$ (absorption ratio of MIM and blank membrane) reached to the maximum 2.65 when the ratio of AMPS and the template was 5:1 (molar ratio). With too low AMPS concentration, MIMs contained inadequate action sites formed by the functional monomer and the template, and the absorption of the MIMs for

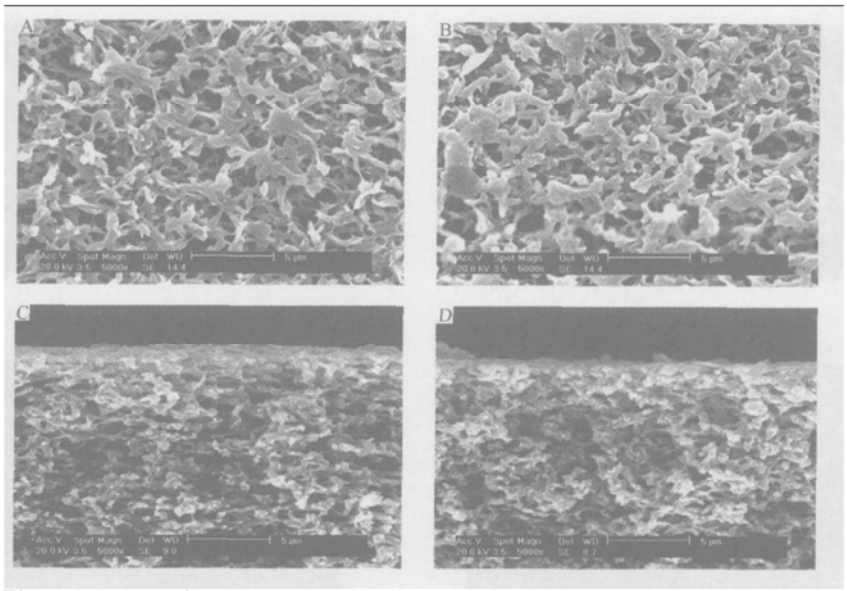


**Figure 7 Scanning electron microscopy of the initial membrane and MIM**
A, C—surface and cross section images of initial membrane;
B, D—surface and cross section images of MIM ($DG = 347\,\mu g \cdot cm^{-2}$)

template was weak. As AMPS were too much, besides some AMPS surrounding around the template, the redundant irregularly distributed into the imprinted polymers, which benefited for non-specific sorption and allowed $\beta$ to decrease.

**Table 3 Absorption by MIMs at varied functional monomer concentration**

| AMPS$\times 10^3$ mol·L$^{-1}$ | Blank membrane$\times 10^9$ mol·mg$^{-1}$ | MIMs$\times 10^9$ mol·mg$^{-1}$ | $\beta$ |
|---|---|---|---|
| 30 | 1.8146 | 3 | 1.05 |
| 40 | 2.9264 | 7.034 | 2.40 |
| 50 | 3.8548 | 10.217 | 2.65 |
| 60 | 6.1922 | 10.9625 | 1.77 |

adenine $10^{-2}$ mol·L$^{-1}$, MBAA 0.3 mol·L$^{-1}$, BP 5 × $10^{-3}$ mol·L$^{-1}$ in methanol, irradiation for 17 min

### 3.4 Influence of the cross-linker concentration on absorption capability

For effective performance of MIPs, it is necessary to find the optimum amount of cross-linker, because that the ideal molecular imprinted polymers not only have desired rigidity that can fix the functional groups to correct sites and retain the cavities spatial configuration, but also have proper flexibility that enables rapid kinetic equilibrium for adsorption.

The data of Table 4 indicated that the MIMs with very few (at 0.1 mol·L$^{-1}$) or much (at 0.4 mol·L$^{-1}$) of cross-linker had lower selectivity factor for the template. For very low MBAA concentration (at 0.1 mol·L$^{-1}$), the resultant imprinted polymers had weak rigidity and could not immobilize functional groups to the correct action sites or retain the shape of cavities formed by imprinting. As the deviation of the functional groups, the shape of imprinted cavities and the spatial arrangement of the functional groups could not complement with the template molecules. Therefore, the specific absorption of MIMs was weakened and non-specific binding was enhanced, namely the specific factor β dropped. While the concentration of MBAA was too high, the imprinted cavities were wrapped into the highly cross-linking polymers and the amount of accessible affinity sites was reduced. It was difficult for absorbed molecules to enter the cavities. In this case, non-specific absorption could be decreased but the specific binding was also restrained remarkably. The compromise concentration in this study is 0.3 mol·L$^{-1}$ and the specific factor $\beta = 2.65$.

**Table 4 Absorption at varied cross-linker concentration**

| MBAA$\times 10^3$ mol·L$^{-1}$ | Blank membranes$\times 10^9$ mol·mg$^{-1}$ | MIMs$\times 10^9$ mol·mg$^{-1}$ | $\beta$ |
|---|---|---|---|
| 100 | 7.71 | 13.367 | 1.734 |
| 300 | 3.85 | 10.217 | 2.654 |
| 400 | 3.46 | 5.35 | 1.546 |

adenine $10^{-2}$ mol·L$^{-1}$, AMPS 0.05 mol·L$^{-1}$, BP 5 × $10^{-3}$ mol·L$^{-1}$ in methanol, irradiation for 17 min

### 3.5 Selective absorption capability of MIMs for the template

A series of analogues with similar chemical structure as adenine (hypoxanthine, guanine, adenosine, in Fig. 8 was used to examine the selective absorption capability of the MIMs in rapid filtration experiments. Obviously, MIMs have very low absorption for hypoxanthine, guanine and adenosine, and the specific binding of adenine was very efficient (Fig. 9). For guanine

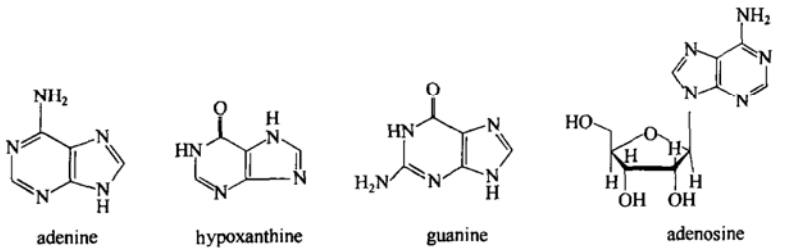



**Figure 8 the structure of adenine, hypoxanthine, guanine and adenosine**

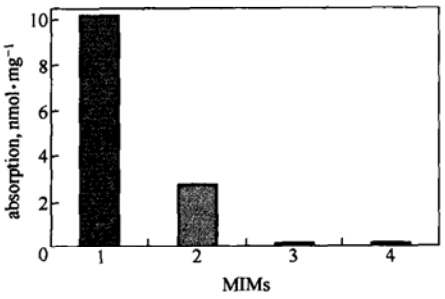



**Figure 9 Absorption of MIMs for the analogues**
1—adenine; 2—adenosine; 3—guanine; 4—hypoxanthine

and hypoxanthine, they cannot coincide with the imprinted cavities because their functional groups are at different sites from adenine. Although adenosine have the same arrangement of action sites, its large side chain prevent adenosine from getting into the cavities perfectly, that results in weak absorption too. Here, it can be concluded that adenine molecule imprinted membranes have formed cavities that have the shape and desired arrangements of functional groups perfectly complementary with adenine and can efficiently and selectively binding adenine. On the contrary, the analogues are absorbed only by non-specific binding.

### 3.6 Regeneration

The MIMs can be utilized repetitively by washing MIMs with 0.1 mol·L$^{-1}$ HCL and distilled water. From Fig. 10, after simple regeneration, MIMs can bind adenine again and still display high absorption.

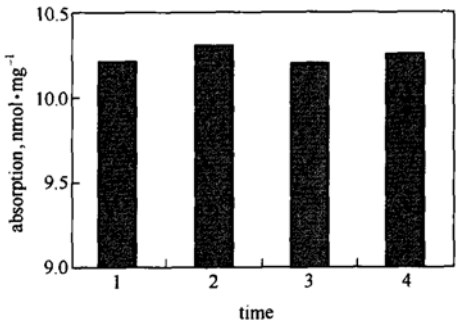



**Figure 10 Regeneration of MIMs**

### 3.7 Comparison with the other methods

MAA is one of the most common functional monomers using hydrogen bond that could be weaken in polar media[23,24]. At the same time, in the natural molecular recognition systems, enzyme/substrate, antigen/antibody and donator/acceptor mostly act in polar media. AMPS as a strong acid combine the basic template by ion interaction and the resultant MIMs show better adsorption capability in polar media.

Compared with other methods (flux less than $10^{-3}$ mol·m$^{-2}$h$^{-1}$)[12–16], for example, the work of Dzgoev and Hampt, who filled the pores of a polypropylene microfiltration membrane with about 15 mg·cm$^{-2}$ and who consequently obtained a MIM with negligible permeability. MIMs prepared by photo-grafting co-polymerization have high flux as microfiltration membrane ($\approx$ 0.26 mol·m$^{-2}$·h$^{-1}$ of template and flux for distilled water was 3.6 ml·mim$^{-1}$·cm$^{-2}$ at 0.8 MPa) that were nearly not influenced by modification, and can be used to rapid separation

Because ion interaction of the functional monomer/the template and high flux, this MIMs can reach absorption/desorption equilibrium within 5 minutes. But this process usually takes other MIMs several hours at least[16–18].

## 4 CONLUSIONS

PVDF membranes were functionalized via photo grafting co-polymerization in methanol with an imprinted polymer, specific for adenine. The thin-layer molecular imprinted polymer was grafted on the surface of PVDF membranes coated with a hydrogen-abstraction type photoinitiator. As the MIPs film did not block the pore which was showed in SEM photos and the flux of water (3.6 ml·mim$^{-1}$·cm$^{-2}$ at 0.8 MPa). So the resistance of mass transfer was weakened and MIMs could rapidly absorb/desorb template molecules, usually only a few minutes. It was also shown MIMs provided the highest selective binding of adenine from aqueous solution ($10.217 \times 10^{-9}$ mol·L$^{-1}$) company with the other analogues ($2.71 \times 10^{-9}$ mol·L$^{-1}$ for adenosine and no absorption for guanine or hypoxanthine). It was very convenient to regenerate MIMs by washing with 0.1 mol·L$^{-1}$ HCl and water for several times and still display high absorption.

## NOMENCLATURE

| | |
|---|---|
| $A$ | area of membrane |
| $c$ | concentration of permeation, $mol \cdot L^{-1}$ |
| $c_0$ | concentration of the initial solution, $mol \cdot L^{-1}$ |
| $DG$ | degree of graft, $mg \cdot cm^{-2}$ |
| $G_g$ | amount of grafted co-polymer on the surface of the MIM, mg |
| $G_0$ | amount of initial membrane |
| $q$ | amount of solute absorbed on membrane, $nmol \cdot mg^{-1}$ |
| $V$ | volume of solution through MIM, ml |
| $\beta$ | specific factor |

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