Optimization of Molecularly Imprinted Poly (MAA-*co*-AM) Composite Membranes for Evaluation of Chlorimuron-Ethyl Herbicide

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Several experimental conditions, such as reaction solvent, extraction solvent, extraction time and crosslinker were evaluated and optimized in the preparation molecularly imprinted composite membranes using chlorimuron-ethyl herbicide as the template. The structures and the thermal stability of molecularly imprinted composite membranes were characterized by infrared spectroscopy and thermogravimetric analysis. The static equilibrium binding properties of the membranes to chlorimuron-ethyl and the swelling property of the membrane in different solvents were tested. The Scatchard plot revealed that one class of binding sites was mainly produced in the imprinted composite membrane in the studied concentration range of chlorimuron-ethyl herbicide.

Key Words: Molecularly imprinted composite membrane, Chlorimuron-ethyl, Preparation, Sulfonylurea herbicides.

INTRODUCTION

Owing to the current fascination with designable materials, much attention has been focused on the molecularly imprinted technology[1-3], in which the non-covalent method, reported by Mosbach and Ramstro¨m in 1981[4], relying on the weak interaction between the functional monomer and the template as well as the convenient operation, has been paid more and more attention[5-8]. Molecularly imprinted membrane is a new research field in the last decades along with the development of the molecular recognition polymer material. Molecularly imprinted membrane has the advantage of continuous performance during separation, which is not available for the chromatographic separation. Preparation of molecularly imprinted membranes to simulate biological membranes has an important significance in biological inorganic chemistry, organic chemistry and environmental chemistry[9-14].

Chlorimuron-ethyl (CAS No. 90982-32-4), also called as: ethyl 2-[N-[N-(4-chloro-6-methoxypyrimidin-2-yl) carbamoyl] sulfamoyl] benzoate, DPX-E6025 (Dupont), classic (Dupont), Classic 25DF, HIT25VP and so on, is one of the sulfonylurea herbicides that was developed by America Dupont company in the early 1980s. Chlorimuron-ethyl has the characteristics of controlling broadleaf weeds, high activity, high selectivity and high miscibility etc and has been used as the main chemical herbicide in soybean fields. But because of its high stability and long period of decomposition, the residue of chlorimuron-ethyl in soils may cause both serious damage to stubble-sensitive crops and soil environmental pollution[15]. Testing chlorimuron-ethyl in soil, water and soybean has been become very important.

In order that the molecularly imprinted membrane with molecular recognition function could be applied to the analysis of chlorimuron-ethyl residual, the molecularly imprinted composite membrane and the non-imprinted composite membrane hosting chlorimuron-ethyl molecules were prepared following the surface imprinting method by UV photo-copolymerization using porous filter paper as support, acrylamide and/or methacrylic acid as functional monomer and chlorimuron-ethyl as template molecular in this study. The experimental conditions, such as the ratio of methacrylic acid and acrylamide, the crosslinker, the reaction and the extraction solvents, the extraction time and the equilibrium time were evaluated and optimized. The structures and the thermal stability of the composite membranes were characterized by infrared spectroscopy and thermogravimetric analysis. Static equilibrium binding properties of the membranes to chlorimuron-ethyl and the swelling property of the membrane in different solvents were tested.

The results could provide the theoretical basis to the preparation of chlorimuron-ethyl-templated composite membranes for testing its residue in water, soil or soybean, which is significant in the control of food safety and environmental pollution.

EXPERIMENTAL

Chlorimuron-ethyl was obtained from Jintan Yangtze Agricultural Institute of Chemistry (Jiangsu, China). Its molecular structure was shown in **Scheme-I**. Methacrylic acid (MAA) and acrylamide were purchased from Tianda Chemical Reagent (Tianjin, China). 2,2'-Azobisisobutyronitrile were purchased from Beijing Chemical Reagent Company (Beijing, China) and EGDMA was from Sigma-Aldrich (Shanghai, China). EGDMA and methacrylic acid were distilled to remove the inhibitors. 2,2'-Azobisisobutyronitrile and acrylamide were recrystallized prior to use. Microporous filter membrane (PVDF, aperture: 1.2 μm) was bought from Automatic Science Instrument (Tianjin, China) and was used as the membrane support. All the other chemicals were of the analytical or the HPLC grade and used without further disposal. Doubly deionized water (DDW) was used throughout. Solutions for HPLC were filtered through a 0.45 μm membrane filter.
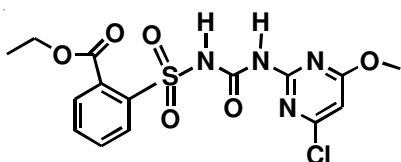
Scheme-I: Molecule structure of chlorimuron-ethyl

The stock solutions of chlorimuron-ethyl was prepared at a concentration of 0.08 g/L in acetonitrile and diluted to the final concentration with acetonitrile when used.

Instrumentation and analytical conditions: The high performance liquid chromatography analysis of the samples in this study was performed on a LC-15C system (SHIMADZU, Japan) with UV-VIS detector. The analysis of the sulfonylurea herbicide by HPLC was optimized according to the paper[16,17]. The samples were performed at 230 nm on a XDB C_{18} column (5 μm, 250 mm × 4.6 mm) at the flow rate of $1.0 \text{ mL} \times \text{min}^{-1}$. The operated mobile phase was ACN/DDW (50 : 50, v/v), in which pH of water was adjusted to 2.5 with phosphoric acid. The injection volume of all the samples was 20 μL and the column temperature was the room temperature.

The powder from molecularly imprinted composite membrane and the non-imprinted composite membrane prepared according to the following process and the template were placed on the ATR crystal and firmly fastened by clips. The infrared spectra of molecularly imprinted composite membrane (MAA : AM = 0 : 1, 3 : 2), non-imprinted composite membrane (MAA : AM = 0 : 1, 3 : 2) and chlorimuron-ethyl were obtained by Varian 640-IR Fourier infrared spectrometer (American).

The TGA of molecularly imprinted composite membrane was determined after dried and extracted (MAA : AM = 4 : 1) and that of the PVDF filter paper were carried out on Pyris6 apparatus (PerkinElmer, American) in atmospheric oxygen at a heating rate of 10 ºC/min.

Preparation of molecularly imprinted composite membranes and non-imprinted composite membranes: The membranes were prepared *via* photo-copolymerization with microporous filter paper as membrane support between two even and transparent glass plates (20 cm × 10 cm). 0.2 mmol

of the template chlorimuron-ethyl, free-radical initiator (AIBN), the monomer (AM and/or MAA) and the cross-linker (EGDMA) were dissolved in acetonitrile in a 50 mL conical flask. The compositions of the reagents were shown in Table-1. After sonicated for 15 min and deoxygenated with nitrogen for 5 min, the reagent was spread on the microporous membrane. Then the microporous membrane was deposited between two glass plates immediately. The air bubble between the glass plates and microporous membrane was carefully removed by placing a constant weight on the glass plates. The polymerization was carried out at 30 ºC under a 1000 W UV lamp at 365 nm for 12 h. The composite membranes were intensively extracted with acetonitrile-acetic acid (9 : 1, v/v) for 6 h firstly after the polymerization completed to remove the unreacted polymerization reagents and chlorimuron-ethyl from the membranes and then extracted with methanol for 2 h to remove rest acetic acid. The membranes were preserved in acetonitrile for 12 h and were dried to constant weight for the future usage. Non-imprinted composite membranes were prepared according to the same procedure, in which chlorimuron-ethyl was not added in the reaction system.

TABLE-1 COMPOSITION OF POLY (MAA-CO-AM) MEMBRANES					
Membranes	Chlorimuron-ethyl (mmol)	MAA (mmol)	AM (mmol)	EDGMA (mmol)	AIBN (mg)
MICM (1:0)	0.2	1	0	5.0	10
MICM (4:1)	0.2	0.8	0.2	5.0	10
MICM (3:2)	0.2	0.6	0.4	5.0	10
MICM (2:3)	0.2	0.4	0.6	5.0	10
MICM (1:4)	0.2	0.2	0.8	5.0	10
MICM (0:1)	0.2	0	1	5.0	10
NICM (1:0)	-	1	0	5.0	10
NICM (4:1)	-	0.8	0.2	5.0	10
NICM (3:2)	-	0.6	0.4	5.0	10
NICM (2:3)	-	0.4	0.6	5.0	10
NICM (1:4)	-	0.2	0.8	5.0	10
NICM (0:1)	-	0	1	5.0	10

Adsorption experiments of molecularly imprinted composite membrane and non-imprinted composite membrane to chlorimuron-ethyl: Binding properties of molecularly imprinted composite membrane and non-imprinted composite membrane to chlorimuron-ethyl were studied by the static equilibrium binding experiment. Chlorimuron-ethyl-imprinted and non-imprinted membranes were weighted (about 0.10 g) and then equilibrated with 5 mL of $0.08 \text{ g} \times \text{L}^{-1}$ chlorimuron-ethyl solution for 12 h at 20 ºC. The final volume of the solution was fixed to 10 mL with acetonitrile and then the concentration was estimated by HPLC. The equilibrium adsorption capacity of chlorimuron-ethyl ($Q, \mu g \times g^{-1}$) were calculated according to eqn. (1)[18]: $Q = V (C_0 - C_i)/m$, where V is the volume of solution (mL); C_0 and C_i is the initial and balanceable concentration of the sulfonylurea herbicides in acetonitrile solution ($mg \times L^{-1}$), respectively.

Binding characteristics of molecularly imprinted composite membrane: In order to investigate the binding performance to chlorimuron-ethyl of the molecularly imprinted composite membrane, binding isotherm was determined in the $0.5\text{-}5.0 \text{ mmol} \times L^{-1}$ range of chlorimuron-ethyl. 0.04 g

Molecularly imprinted composite membrane was placed into a conical flask and mixed with 3 mL of a known concentration of substrate. The flask was oscillated in a constant temperature bath oscillator at 20 ℃ for 12 h. The concentration of free substrate (C_e) in the solution was determined using HPLC. The amount of substrate bound to the membrane was calculated according to eqn. (1). The obtained data were plotted according to the Scatchard eqn. (2)[19]: $Q/C_e = (Q_{max}-Q)/K_d$, where K_d is the equilibrium dissociation constant and Q_{max} an apparent maximum number of binding sites.

Studies of swelling property of the membranes: The swelling properties of molecularly imprinted composite membrane and non-imprinted composite membrane in different solvent were studied. As static swelling experiment, molecularly imprinted membrane and NIM were soak in different solvents to evaluate the swelling property (δ) as eqn. (3)[20]: $\delta = [(V_2-V_1)/V_1] \times 100$ %, where V_1 and V_2 were the volume of membrane before and after infusion, those were estimated according to the ratio of the mass change to the water density (1.0 g/mL).

RESULTS AND DISCUSSION

Optimization of experimental conditions and studies of recognition mechanism: To optimize the experimental conditions, a variety of factors impacting on the results were evaluated.

Determination of reaction solvent: In polymerization, chlorimuron-ethyl should be dissolved in reactant mixture firstly and then be spread on the filter paper and glass plates. Therefore, the solubility of chlorimuron-ethyl in the solvent and the workability of the solution were the key of reaction process. So the relevant experiments to different solvent systems were carried on respectively.

Results showed that the solubility of chlorimuron-ethyl in dichloromethane and dichloromethane:dimethylformamide (4:1) was very well. But the volatility of the two kinds of solvent is high so that the desired membranes were not able to be prepared perfectly. Chlorimuron-ethyl dissolved in methanol, tetrahydrofuran or acetonitrile:water (1:1) difficultly. However, in the solvent acetonitrile, chlorimuron-ethyl could be dissolved sufficiently and the reaction could be carried out smoothly. Finally, acetonitrile was chosen as the solvent in the study.

Studies of extraction solvent and extraction time: The extraction solvent and the extraction time was determined. The extraction solvent acetonitrile: acetic acid (9:1) was economical and effective in the extraction of chlorimuron-ethyl. The result showed the extraction time of 6 h was sufficient and fit. After extracted with acetonitrile: acetic acid (9:1) and then with methanol for 2 h, membranes were preserved in acetonitrile for 12 h so as to ensure all template molecules could be extracted completely.

Determination of crosslinker: Different crosslinkers (N-MAM, TMPTA, EDGMA) were studied impacting on the preparation of membrane. TMPTA could mixed with monomer and the reaction solvent easily, but the membrane, prepared with TMPTA as crosslinker, had high adhesiveness to glass

plates so that it could be tore off the glass plates after sonicated for about 50 min. Because N-MAM is water soluble crosslinker, several kinds of solvent were tried and the results showed N-MAM was not fit in this reaction. EDGMA could be dissolved in the reaction system and the adhesiveness was moderate between the membrane and the glass plates so as to facilitate the preparation of the composite membranes. So EDGMA was determined to be as cosslinker in this study.

Studies of recognition mechanism: In chlorimuron-ethyl molecules, sulfonyl oxygen, carbonyl oxygen and heterocyclic ring nitrogen are able to form many hydrogen bonds with hydroxyl group or amino group of methacrylic acid and acrylamide easily because of their free electron pairs. Amino hydrogen of sulfonylurea maybe also attract carbonyl oxygen of methacrylic acid and acrylamide to form hydrogen bonds. Lots of hydrogen bonds made chlorimuron-ethyl molecules stationary in the reaction system and then special cavities were formed after extraction.

A representative scheme for the formation of chlorimuron-ethyl molecularly imprinted composite membrane and the recognition mechanism of molecularly imprinted composite membrane were presumed and reported in Fig. 1.

Adsorption properties of chlorimuron-ethyl on molecularly imprinted composite membranes and non-imprinted composite membranes: To plot the calibration curves, standard solutions of chlorimuron-ethyl (concentrations between 2.0 mg × L^{-1} and 40.0 mg × L^{-1}) were prepared. 20 µL of each of the standard solutions was injected into the HPLC under the chromatography conditions described above.

The results of binding properties of molecularly imprinted composite membrane (a) and non-imprinted composite membrane (b) to chlorimuron-ethyl were shown in Fig. 2. All the data were presented as middle data and the standard deviation ranged from 1.45 to 18.49 (n = 5).

The result showed that the amounts of chlorimuron-ethyl bound by molecularly imprinted composite membrane increased as the ratio of methacrylic acid and acrylamide climbing up to 4:1 and the best binding capacity (361.9 µg × g-membrane^{-1}) was the membrane in which MAA/AM was 4:1. It was found that all of the binding amounts of molecularly imprinted composite membrane were more than 209.0 µg × g-membrane^{-1}, which were higher than those of the non-imprinted composite membrane.

Molecularly imprinted composite membrane with the most adsorption amount were copolymer with certain ratio of methacrylic acid and acrylamide. This may be because amide group has stronger hydrogen bonding ability in polar solvents and the monomer methacrylic acid can form intramolecular hydrogen bond[21,22]. Along with the increasing of acrylamide, the amounts of the effective hydrogen bond that could form specific recognition sites increased. Due to the special functional groups in chlorimuron-ethyl molecule, hydrogen bonds can be formed among different groups of chlorimuron-ethyl and the hydroxyl or carbonyl groups of methacrylic acid and/or the carbonyl or amino groups of acrylamide. So it could be found there was a best proportion of methacrylic acid and acrylamide in the molecularly imprinted composite membrane (MAA:AM = 4:1) that had bigger binding capacity.
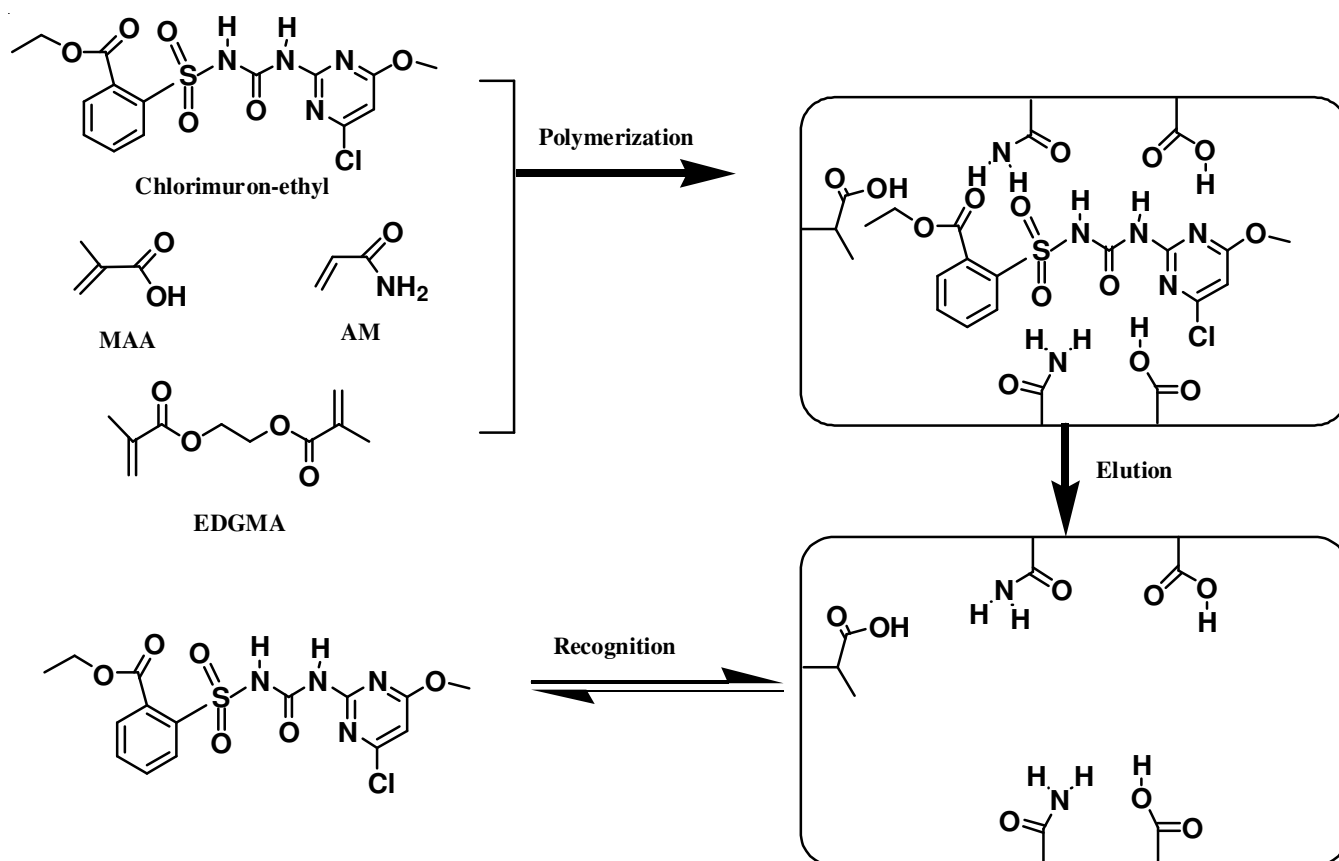
Fig. 1. Formation and the recognition mechanism of chlorimuron-ethyl molecularly imprinted polymer membranes
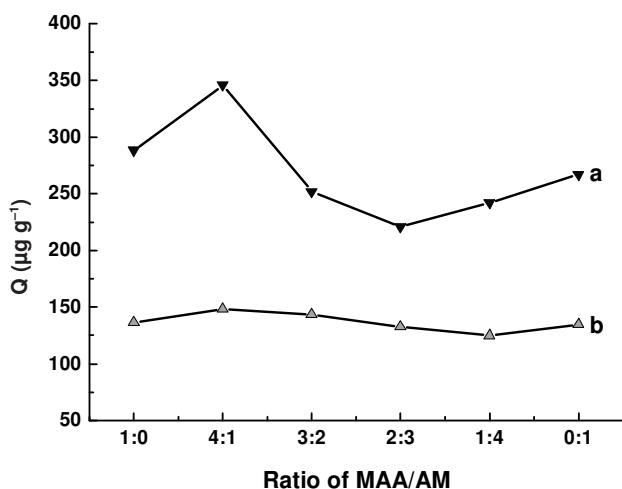

Fig. 2. Binding properties of MIM (a) and NIM (b) to chlorimuron-ethyl

The results also showed the binding capacity of the non-imprinted composite membrane to chlorimuron-ethyl were lower with little change than that of molecularly imprinted composite membrane. This indicated that the molecularly imprinted composite membrane with special cavities interacted more easily with template than normal membranes. Moreover, because the surface of non-imprinted composite membrane was more compact than that of molecularly imprinted composite membrane and there were not fit cavities in non-imprinted composite membrane to the template so that the interaction between non-imprinted composite membrane and samples limited on the surface of non-imprinted composite membrane

mainly. So it was concluded that the non-imprinted composite membrane had little binding capacity to these herbicides compared with molecularly imprinted composite membrane.

Analysis of the FT-IR: While the copolymerization finished, a thin and transparent layer of copolymer was coated on the microporous support. FT-IR spectra of chlorimuron-ethyl, non-imprinted composite membrane and molecularly imprinted composite membrane (MAA:AM = 0:1, 3:2) after the templates extracted were carried out and shown in Fig. 3 so that the polymerization and the binding mechanism between the imprinting sites and the template molecules were confirmed.

The main characteristics observed was the presence of carbonyl stretching vibration absorption band at 1732 cm^{-1} in the IR spectra, corresponding to the carbonyl groups of PAM and P (MAA-*co*-AM) copolymer chains and chlorimuron-ethyl. It was found that the intensity of N-H stretching vibration absorption bands of molecularly imprinted composite membrane (b) and (c) spectra at 3299 cm^{-1} was lower than that of the non-imprinted composite membrane (d) and (e). The N-H stretching vibration absorption bands results from acrylamide in the membranes. Because chlorimuron-ethyl molecules could interact with amino groups of acrylamide and occupy a certain space in molecularly imprinted composite membrane (b) and (c) during the polymerization, this implied that there were many cavities generated after the template molecules were extracted, leading to the decreasing of amino groups in molecularly imprinted composite membrane. At the same time, it was found that there was stretching vibration absorption band at 3647 cm^{-1} corresponding to free hydroxyl

group in molecularly imprinted composite membrane (c). The O-H stretching vibration absorption bands results from methacrylic acid in the membranes. Because chlorimuron-ethyl molecules could interact with hydroxyl groups of methacrylic acid and occupy a certain space in molecularly imprinted composite membrane (b) and (c) during the polymerization, this implied that there were many cavities generated after the template molecules were extracted, leading to the increasing of free hydroxyl groups in molecularly imprinted composite membrane. So it was concluded that P (MAA-*co*-AM) membranes and massive cavities were produced during the preparation of molecularly imprinted composite membrane. In these cavities, the interactions between the functional sites of the copolymers and the templates were formed *via* hydrogen bonding of the free COOH groups and $CONH_2$ groups.
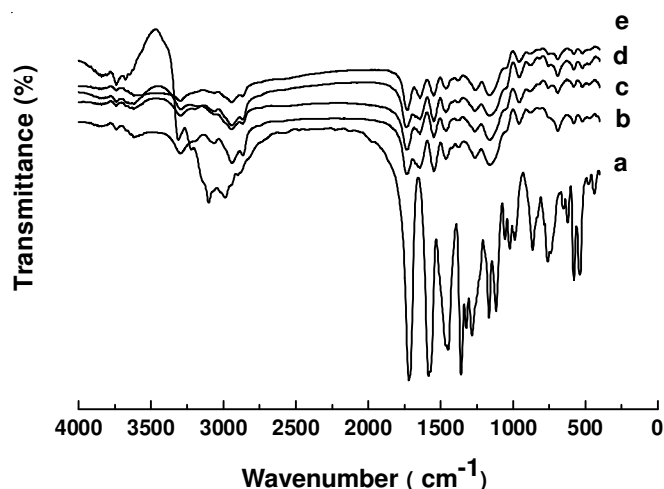

Fig. 3.   FT-IR spectrum of nicosulfuron imprinted and non-imprinted membranes after extraction. (a) FT-IR spectra of chlorimuron-ethyl, (b) chlorimuron-ethyl-imprinted membranes (MAA:AM = 0:1), (c) chlorimuron-ethyl-imprinted membranes (MAA:AM = 3:2) (d) non-imprinted membranes (MAA:AM = 0:1) (e) non-imprinted membranes (MAA:AM = 3:2)

The peaks in the region of 1449 cm^{-1} and 1584 cm^{-1} were characterized the stretching vibration of C=C in benzene rings of chlorimuron-ethyl molecules. Moreover,it could be found there was an absorption peak at 1117 cm^{-1} corresponding to C-O-C band in chlorimuron-ethyl molecule. The absorption bands mentioned above did not appear in the spectra of membranes. Consequently, all chlorimuron-ethyl molecules could be extracted completely in the process.

Thermogravimetric analysis: Thermogravimetric analysis (TGA) of filter paper and that of the imprinted membranes was shown in Fig. 4. An obvious difference was found between them. The TGA of filter paper (a) showed a weight loss in two stages. At the first stage between 29 ºC and 110 ºC, it showed about 1.22 % loss in weight. This corresponded to the loss of adsorbed and bound water. Then the quick weight loss started at 358 ºC and continued up to 436 ºC, during which there was 70.44 % of weight loss resulted from the degradation of the sole component of filter paper. However, the TGA of imprinted membranes after extraction (MAA: AM = 4:1) (b) was different and three stages of distinct weight loss between 26 ºC and 620 ºC were observed. The first stage

ranged between 30 ºC and 110 ºC with 2.63 % of the adsorbed and bound water weight loss. The second stage of weight loss started at 286 ºC and continued up to 382 ºC, during which there was 26.48 % of weight loss due to the degradation of P(MAA-*co*-AM). There was 43.46 % weight loss in the third stage from 382 to 465 ºC that contributed to the decomposition of the filter paper. So, it is evident that imprinted membranes were generated onto filter paper and could change the stability of filter paper at higher temperature.
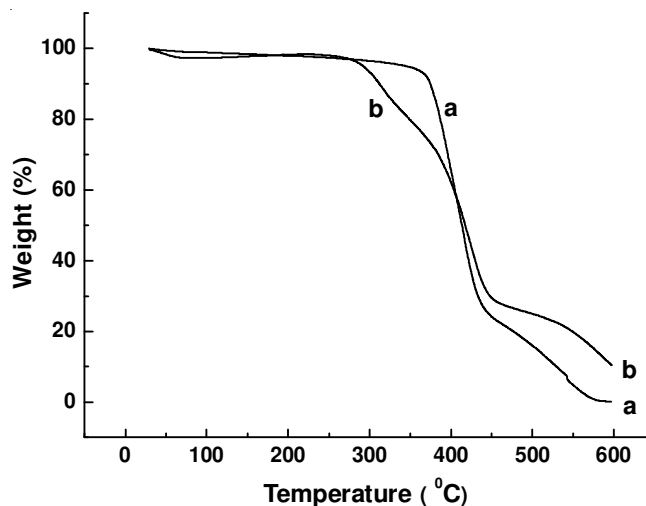

Fig. 4.   Thermogravimetric analysis of filter paper (a) and imprinted membranes after extraction (MAA:AM = 4:1) (b)

Binding characteristics of molecularly imprinted composite membrane: In order to investigate the binding performance for chlorimuron-ethyl in the resultant molecularly imprinted composite membrane (MAA:AM = 4:1), we determined the binding isotherm (Fig. 5) in the 0.5-5.0 mmol × L^{-1} range of chlorimuron-ethyl. The obtained data were plotted according to the Scatchard equation as shown in Fig. 6.

It was found that the Scatchard plot was linear indicating that the binding sites in molecularly imprinted composite membrane are uniform with respect to the affinity for chlorimuron-ethyl. Because there was one distinct section within the plot, which can be regarded as straight line, it revealed that one
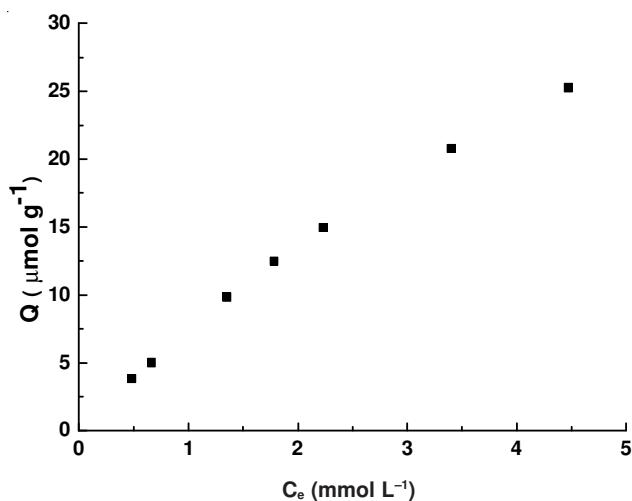

Fig. 5. Binding isotherm of MICM (MAA:AM = 4:1)

class of binding sites was mainly produced in molecularly imprinted composite membrane in the studied concentration range of chlorimuron-ethyl. The equilibrium dissociation constant K_d and the apparent maximum number Q_{max} can be calculated to be 9.71 mmol L^{-1} and 80.36 µmol g^{-1} of dry molecularly imprinted composite membrane from slope and intercept of its Scatchard plot.
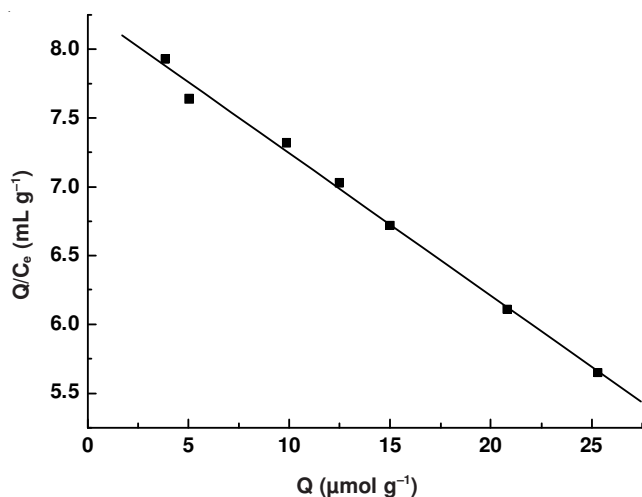

Fig. 6. Scatchard plot to estimate the binding nature of MICM (MAA:AM = 4:1)

Studies of swelling property of molecularly imprinted composite membrane: The swelling properties of molecularly imprinted composite membrane (MAA:AM = 4:1) in different solvent were studied. Adopting static swelling method, molecularly imprinted composite membrane was soaked in water, acetonitrile or DMF for 72 h. According to eqn. (3), the swelling properties of molecularly imprinted composite membrane in water, acetonitrile and DMF were 42.53, 4.06 and 49.81 % respectively. The results showed the major change in the inner structure of molecularly imprinted membrane did not happen and separation property was stable in acetonitrile. So, molecularly imprinted membrane could be used in aceto-nitrile solution system for long time.

Conclusion

In this study, several main experimental conditions of membranes were optimized in preparation of novel composite chlorimuron-ethyl-imprinted membranes using chlorimuron-ethyl as the template molecule. The results of binding experi-ments of showed that molecularly imprinted composite membrane (MAA:AM = 4:1) had the best binding capacity to chlorimuron-ethyl.

The structures and the thermal stability of membranes were characterized by infrared spectroscopy and thermogravi-metric analysis. The thermal stability of molecularly imprinted composite membrane was higher than that of filter paper at higher temperature. According to the results, the possible interactions between the template and the imprinted composite membranes were suggested, in which part of COOH groups and $CONH_2$ groups of membranes participated in the linkage. The Scatchard plot revealed that one class of binding sites was mainly produced in molecularly imprinted composite membrane in the studied concentration range of chlorimuron-ethyl.

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