doi:10.1246/cl.2010.478

A Chlortoluron Sensor based on Molecularly Imprinted Sensitive Membranes

Jianping Li* and Fuyang Jiang
College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China

(Received January 20, 2010; CL-100053)

Molecularly imprinted polymer (MIP) was prepared by a reaction among template molecules of chlortoluron, functional monomers of methacrylic acid, and a crosslinker of *N*,*N*′-methylenebisacrylamide. Chlortoluron could be analyzed in the range of 0 to $3.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ with a detection limit of $2.21 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$. Water samples were assayed and recoveries were obtained, ranging from 99% to 102%.

Chlortoluron is one of the most frequently used phenylurea herbicides in agriculture, presenting a long chemical lifetime of more than 200 days in water.[1] Since it exists at very low concentrations and coexists with other herbicides in the environment, the development of a highly selective and sensitive sensor for chlortoluron is very important. However, there are no previous reports of an electrochemical sensor for chlortoluron determination because it is non-electroactive and does not participate directly in the electrochemical process.

Molecular imprinting is a tool for preparing polymeric materials with highly selective recognition and affinity for analytes.[2] Due to their relatively simple synthesis, low cost, and physical and chemical stability, MIPs have been widely explored in the field of analytical chemistry, especially sensors.[3–10] In previous studies, MIP sensors have been extensively used in research on pesticide and herbicide determination which have been widely used during the last decade.[11–14] To the best of our knowledge, no report concerning the determination of chlortoluron by MIP sensors has yet been presented. Here we report an amperometric MIP sensor for chlortoluron determination based on chlortoluron-imprinted poly(methacrylic acid).

During the synthesis of MIPs, methacrylic acid, *N*,*N*′-methylenebisacrylamide, and chlortoluron were mixed and dissolved in doubly distilled water. $(NH_4)_2S_2O_8$ was added as an initiator 12 h later. The bare platinum electrode was dipped into the solution 5 min later, before being air-dried. MIP film prepared in the absence of chlortoluron (abbr. nMIPs) was made using the same conditions.

A standard three-electrode cell connected to a CHI660C (Shanghai, China) was used for electrochemical measurements, which were carried out in the supporting electrolyte of 0.03 $\mathrm{mol\,L^{-1}}$ $K_3[Fe(CN)_6]$ solution containing 0.5 $\mathrm{mol\,L^{-1}}$ KCl at room temperature (25 °C). Cyclic voltammograms (CV) were performed from −0.2 to 0.6 V at a scan rate of $50\,\mathrm{V\,s^{-1}}$, while differential pulse voltammetric (DPV) measurements were performed over a potential range of −0.2 to 0.6 V, at a scan rate of $50\,\mathrm{mV\,s^{-1}}$ and pulse amplitude of 50 mV. Alternating current impedance (AC) were performed at a potential of 0.19 V, over the frequency range of 100 mHz to 100 kHz using an alternating voltage of 5 mV. Prior to each measurement, the MIP sensor was dipped into a chlortoluron solution for 3 min to rebind the template molecules. After each detection, the MIP sensor was immersed in a mixed solution of alcohol and HNO_3 in the equivalent volume (1:1) for 5 min. Then, CV was performed to verify the removal of chlortoluron.

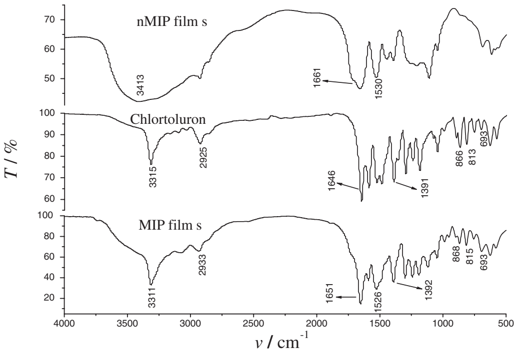

Figure 1. IR of nMIP, MIP, and chlortoluron.

The infrared spectroscopy (IR) studies of chlortoluron, MIP, and nMIPs were performed using a Nicolet Nexus 470 FT-IR spectrometer. As shown in Figure 1, for nMIPs, the peak at $1530\,\mathrm{cm^{-1}}$ represents the absorption band of the –N–H bending which was at $1526\,\mathrm{cm^{-1}}$ for MIP, the peak at $3413\,\mathrm{cm^{-1}}$ represents the stretching vibration of –OH, and the peak at $1661\,\mathrm{cm^{-1}}$ corresponds to –C=O stretching vibrations of H_2N–C=O which was a binding site of MIP to –COOH of methacrylic acid. For chlortoluron, the peak at $1391\,\mathrm{cm^{-1}}$ represents the stretching vibration of –C–N; the peaks at 866 to $693\,\mathrm{cm^{-1}}$ arise from the bending of $–C_6H_6$; the peaks at 3315 and $2925\,\mathrm{cm^{-1}}$ represent the stretching vibration of –N–H and $–CH_3$; the peak at $1646\,\mathrm{cm^{-1}}$ corresponds to the stretching vibrations of C=O. MIP after rebinding presents the –C–N stretching vibration band of chlortoluron at $1392\,\mathrm{cm^{-1}}$ and the bending of the $–C_6H_6$ from 868 to $693\,\mathrm{cm^{-1}}$.

CV was used to elucidate the imprinting processes. As shown in Figure 2, the decrease of current from a to b could be attributed to film which has been produced and covered at the surface of the Pt electrode. The increase of currents from b to c could be attributed to the removal of chlortoluron from the MIPs film. The decrease of currents from c to d could be attributed to chlortoluron rebound to the film. This may be explained by the interaction between chlortoluron and the MIP film, which determines the electron transfer of the $[Fe(CN)_6]_3^-/[Fe(CN)_6]_4^-$ ion pair on the electrode surface.

AC impedance of imprinting is shown in Figure 3. The increased resistance from a to b could be attributed to the film which was produced and covered the surface of the Pt electrode. The decrease of resistance from b to c could be attributed to the template (chlortoluron) which has been removed from the MIPs film. The increased resistance from c to d could be attributed to chlortoluron rebound to the film.

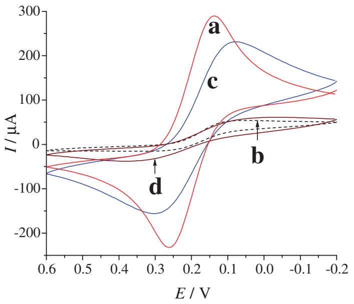

Figure 2. CVs of MIP-modified electrode: a, Pt electrode; b, MIPs electrode before removing chlortoluron; c, MIPs electrode after removing chlortoluron; d, MIPs electrode after rebinding.

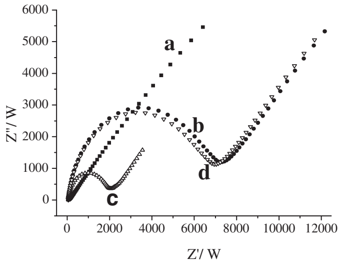

Figure 3. AC impedance of MIP-modified electrode: a, b, c, and d all have the same meanings as in Figure 2.

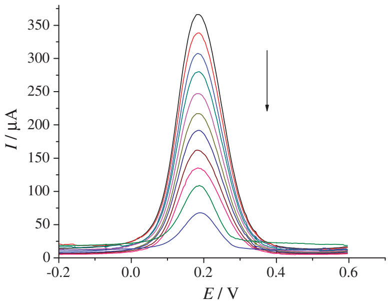

Figure 4. DPV response of chlortoluron concentration.

Figure 4 shows the dependence of the oxidation current on chlortoluron concentration. Due to the increasing number of binding sites in the film which were occupied by chlortoluron molecules, the peak current decreased with the increase of chlortoluron concentration. The oxidation peak currents were linear with chlortoluron concentration in the range of 0 to $3.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. The detection limit was $2.21 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ at a signal-to-noise ratio of 3.

The reproducibility of the sensor was evaluated by detecting the peak current of $9 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ chlortoluron in 10 mL of $K_3[Fe(CN)_6]$ solution ($0.03\,\mathrm{mol\,L^{-1}}$) five times. Prior to detection, template-removing treatments of the sensor were carried out, through which we obtained the following results: 279.8, 273.2, 276.8, 274.1, and 277.3 μA. In addition, a relative standard deviation (RSD) of 1.0% was calculated, indicating good reproducibility.

Interference experiments were performed to verify the specificity of the MIP film sensor toward chlortoluron. Compounds which have similar chemical structure, difenoxuron, neburon, isoproturon, and fluometuron, were then added into the supporting electrolyte, respectively. When difenoxuron was lower than $50\,\mathrm{\mu mol\,L^{-1}}$, neburon lower than $25\,\mathrm{\mu mol\,L^{-1}}$, fluometuron $18\,\mathrm{\mu mol\,L^{-1}}$, or isoproturon $12\,\mathrm{\mu mol\,L^{-1}}$, the current changes were lower than 10%, which could be deemed as no interference to the determination of $0.5\,\mathrm{\mu mol\,L^{-1}}$ chlortoluron. In view of the above facts, the recognition sites formed in the polymerized film have the capability to distinguish the target molecules through their size, shape, and functional group distribution.

To ensure stability, the sensor was dipped in doubly distilled water at 4 °C after each use. No apparent decrease in response to $9.0 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ chlortoluron was found after 2 weeks. Over the next week, the current response decreased by about 8% and by about 15% after a month, compared to the initial response. This suggests that the sensor could work for about a month.

Farmland water was analyzed and no chlortoluron was found. Standard addition was performed to assess the accuracy by adding 6.0×10^{-7}–$1.2 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ chlortoluron. Recoveries ranged from 99.4% to 102.3%, and the RSDs were less than 2.8%, which can be indicators of good recovery and practicability.

The financial support from the NSFC (No. 20665003) is gratefully acknowledged.

References

1 L. Poulain, G. Mailhot, P. W. W. Chung, M. Bolte, *J. Photochem. Photobiol., A* **2003**, *159*, 81.
2 K. Haupt, K. Mosbach, *Chem. Rev.* **2000**, *100*, 2495.
3 M. C. Blanco-López, M. J. Lobo-Castañón, A. J. Miranda-Ordieres, P. Tuñón-Blanco, *TrAC, Trends Anal. Chem.* **2004**, *23*, 36.
4 S. A. Piletsky, A. P. F. Turner, *Electroanalysis* **2002**, *14*, 317.
5 M. Pesavento, G. D'Agostino, R. Biesuz, G. Alberti, *Electroanalysis* **2009**, *21*, 604.
6 X. Kan, Q. Zhao, Z. Zhang, Z. Wang, J. Zhu, *Talanta* **2008**, *75*, 22.
7 J. Li, J. Zhao, X. Wei, *Sens. Actuators, B* **2009**, *140*, 663.
8 Y. T. Wang, Y. X. Zhou, J. Sokolov, B. Rigas, K. Levon, M. Rafailovich, *Biosens. Bioelectron.* **2008**, *24*, 162.
9 K. Reimhult, K. Yoshimatsu, K. Risveden, S. Chen, L. Ye, A. Krozer, *Biosens. Bioelectron.* **2008**, *23*, 1908.
10 G. P. González, P. F. Hernando, J. S. D. Alegría, *Biosens. Bioelectron.* **2008**, *23*, 1754.
11 A. L. Jenkins, R. Yin, J. L. Jensen, *Analyst* **2001**, *126*, 798.
12 R. Shoji, T. Takeuchi, I. Kubo, *Anal. Chem.* **2003**, *75*, 4882.
13 A. V. Juarez, L. M. Yudi, *Electroanalysis* **2009**, *21*, 767.
14 K. P. Prathish, V. Vishnuvardhan, T. P. Rao, *Electroanalysis* **2009**, *21*, 1048.