Regulatory Effects of Zn(II) on the Recognition Properties of Metal Coordination Imprinted Polymers

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ABSTRACT: Using a Zn(II)–quercetin complex as a template (quercetin is a kind of flavonoid; flavonoids are important active ingredients of Chinese herbs), we prepared a new kind of metal coordination imprinted polymer (MCIP) in methanol by a molecular imprinting technique. The coordination mode and coordination ratio between quercetin and Zn(II) were studied in differential ultraviolet absorption spectrometry, and the ternary coordination of quercetin, Zn(II), and 4-vinylpyridine was verified by similar methods. The effect of the crosslinking agent dosage on the morphology and network structure of MCIP and its binding capacity were studied by transmission electron microscopy and equilibrium binding experiments. The regulation of different anions and cations on the identification system of MCIP was studied in detail. In addition, the binding characteristics of MCIP were evaluated by Scatchard analysis. The experimental results show that the Zn(II)–quercetin imprinted polymer had selective binding to its template complex, including selectivities to the anions and cations, and a class of homogeneous recognition sites was formed in the polymer within the range of studied concentration. The dissociation constant and most apparent specific adsorption amount of the Zn(II)–quercetin imprinted polymer was calculated to be 0.6983 mmol/L and 78.72 μmol/g, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 258–266, 2010

Key words: chromatography; molecular recognition; TEM

INTRODUCTION

The molecular imprinting technique is a new interdisciplinary subject developed in recent years belonging to the area of host–guest chemistry in supramolecular chemistry, and it plays an important role in the construction of molecular recognition sites in the polymer matrix. As the results of its notable features, such as structure–activity predetermination, specific identification, broad applicability, strong antipoor environmental ability, good stability, and long lifespan, molecularly imprinted polymers prepared by this technique have been widely used in chromatographic stationary phases,[1,2] solid-phase extraction materials,[3] chemical bionic sensors,[4,5] clinical drug analysis, membrane separation technology,[6–8] and so on. Particularly in recent years, its practical applications in the active ingredient isolation of natural products (in particular, the active ingredients of Chinese herbal medicine) have aroused extensive attention.[9,10]

Chinese medicine is a complex system containing a rich diversity of active ingredients; how to extract and separate the active ingredients from the complicated system are important subjects for the acceleration of the process of modernization of Chinese medicine.[11] The molecular imprinting of polymers as an effective and simple separation technique can be used as a new method for screening active ingredients from Chinese medicine. At present, reports using hydrogen-bonding interaction in the preparation and identification process of imprinted polymers are more common; the number of metal coordination interactions remain relatively small.

However, in the study of the biological recognition process, people find that metal coordination interaction plays an important role in the biological system,[12] and the combination of biological or drug molecules with metal ions has a high degree of specificity and mild integration and fault conditions.[13] This may be due to the properties of metal coordination interaction; for instance, the metal coordination bond is stronger than the hydrogen bond and van der Waals force. Such a force is relatively stable in a water–alcohol system, and the space configuration of the metal complex has more specificity.[14] In view of the unique advantages of metal coordination,

research into the preparation of molecularly imprinted polymers by metal coordination interaction has attracted wide attention,[15–17] but its applications in a water–alcohol strong polar solvent environment for the separation or detection of active ingredients from traditional Chinese medicine has been little reported.

Flavonoids are important active ingredients in Chinese herbal medicine, existing widely in a variety of plants and playing an important role in the field of medicine, for instance, in the treatment of cardiovascular diseases, antiliver toxicity, anti-inflammatory effects, and antibacterial and antiviral activities.[18] However, the categories of natural flavonoids in Chinese herbs are numerous, and the structures are very similar, so there are greater difficulties in separation and extraction. In this study, based on the advantages of metal coordination and with Zn(II)–quercetin (Qu) complex as a template (Qu is a kind of flavonoid and easily forms metal coordination), a new kind of metal coordination imprinted polymer (MCIP) was prepared in methanol, and the regulation of different anions and cations on the identification system of MCIP was studied in detail. This study is of great significance in the separation and detection applications of Qu. Meanwhile, studying the role of metal coordination in the molecular recognition process may contribute to a better understanding of the process and mechanism of molecular imprinting and biological identification.

EXPERIMENTAL

Reagents and materials

Qu was of analytical grade available from Shaanxi Huike Botanical Development Co., Ltd. (Shaanxi, China). 4-Vinylpyridine (4-VP) was obtained from Sigma–Aldrich (St. Louis, MO) and was purified by vacuum distillation to remove inhibitor before use. Ethylene glycol dimethacrylate (EGDMA) was analytical grade and was purchased from Shanghai Haiqu Chemical Co., Ltd. 2,2-Azobisisobutyronitrile (AIBN), purchased from Shanghai Hewei Co., Ltd., was chemical grade and was recrystallized in ethanol before use. $Zn(Ac)_2$, $Cu(Ac)_2$, $Ni(Ac)_2$, $ZnCl_2$, and $Zn(NO_3)_2$ were analytical grade and were obtained from Beijing Chemical Works. Tetrahydrofuran, methanol, acetic acid, and ethanol were analytical grade.

Main apparatus

All ultraviolet–visible (UV–vis) spectra and adsorption experiments were performed with a UV-1200 UV–vis spectrophotometer (Beijing Rayleigh Analytical Instrument Corp., Beijing, China). An H-7650 transmission electron microscope (Hitachi, Ltd.,

Japan) was used to observe the morphology of the imprinted polymer. To synthesize, prepare, and process the products, many other instruments were used, a WE-1 thermostat water-bath oscillator (Tianjin Honour Instruments, Inc., China), an SK5200 ultrasonic vibration generator (Shanghai Kudos Ultrasonic Instrument Co., Ltd., China), a TG16-WS (1650D) supercentrifuge (Shanghai Luxiangyi Centrifuge Instrument Co., Ltd., China), and Soxhlet extractor.

Synthesis of the MCIPs

Qu (0.4 mmol) and $Zn(Ac)_2$ (0.4 mmol) were dissolved in 6 mL of a tetrahydrofuran/methanol mixed solution (1 : 3 v/v) with ultrasonic oscillation for 2 h; then, 4-VP (1.2 mmol) was added to the solution. After 2 h of oscillation, certain amounts of crosslinker [EGDMA; the molar ratios of print molecule to crosslinker were 1 : 20 (P_1), 1 : 30 (P_2), and 1 : 40 (P_3), respectively] and initiator (AIBN) 20 mg were added. The solution was degassed in a sonicating bath and deoxygenated with a stream of nitrogen for 10 min. Then, the ampule was placed into an ice-bath apparatus for 20 min and sealed *in vacuo*. The polymerization was carried out in a constant-temperature water bath at 60°C for 24 h. The resulting rigid polymers were ground to pass through a 74-μm sieve. Fine particles were removed by decantation in acetone. The resulting particles were placed in a Soxhlet extractor and washed with a 20 vol % acetic acid/methanolic solution until the template could no longer be detected in the elution; then, they were washed with a 0.1 mmol/L EDTA solution to remove the residual metal ions in the polymers. Finally, the particles were washed with pure methanol and dried to a constant weight *in vacuo* at 60°C. As a control, the nonimprinted polymers (P_4 and P_5) in the absence of the template molecule or metal ions were prepared and treated with a similar method.

Ultraviolet (UV) spectrum analysis

To study the coordination relations between Qu and Zn(II), a series of solutions were prepared with a fixed concentration of Qu (0.025 mmol/L) and various amounts of Zn(II) in methanol. The ratios of the molar concentration between Qu and Zn(II) among this set of solutions were 1 : 0, 1 : 0.2, 1 : 0.4, 1 : 0.6, 1 : 0.8, 1 : 0.9, 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5. Then, the solutions were shaken for about 3 h to obtain sufficient interaction. The changes in absorbance and the difference absorption spectra of these solutions were determined on the UV spectrometer under a wavelength range of 200–600 nm.

To verify the ternary coordination of Qu, Zn(II), and 4-VP, we kept the concentration of 4-VP and the

coordination ratio of Qu/Zn(II) (1 : 1) unchanged and gradually increased the concentration of the Zn(II)–Qu complexes. The UV absorption spectrum changes of 4-VP were determined with a similar method to that described previously.

Transmission electron microscopy (TEM) characterization of the MCIPs

The MCIPs with a certain degree of fineness were put into ethanol to prepare suspensions of appropriate concentrations and scattered for 15 min in the ultrasonic oscillator. Then, a professional copper net was used to quickly dredge the powder samples. After the volatile ethanol was removed absolutely, the samples could be observed by TEM.

Kinetic approach to the polymers' specific adsorption on Qu

Three equivalent portions of MCIPs with masses of 50 mg were put into a group of Qu/Zn(II) solutions, the molar ratio between Qu and Zn(II) in solution was 1 : 1, and the concentrations of Qu in all of solutions were the same (2 mmol/L). The equilibrium binding capacities of Qu at different times were determined by UV–vis spectrophotometry.[17] The experimental steps were as follows: the 25-mL conical flasks filled with 5-mL solutions were placed in a shaking bed and oscillated at room temperature. Then, the solutions at different times were transferred to the centrifuge tubes, respectively. After 15 min of high-speed centrifugation, supernatant liquor (3 mL) was injected in a 50-mL volumetric flask and then diluted to a certain size. Under a certain wavelength (258 nm), UV–vis spectrophotometry was used to determine the equilibrium concentration of Qu in the solutions. According to the changes in the Qu concentration before and after specific adsorption, the binding amount of the polymers to Qu (Q) could be calculated with the following equation:

$$Q = (c_0 - c_t) \times V/m \qquad (1)$$

where c_0 is the initial concentration of Qu (mmol/L), c_t is the equilibrium concentration of Qu at different time intervals (mmol/L), and V (mL) and m (g) are the volume of the Qu solution and the weight of the dry polymer used for the specific adsorption experiment, respectively.

Specific isothermal adsorption experiments with the polymers

In this process, 11 equivalent portions of polymers for a mass of 50 mg were put into a group of Qu/Zn(II) solutions with gradient concentrations of

0.2–5.0 mmol/L. Conical flasks (25 mL) filled with 5-mL solutions were placed in a shaking bed and oscillated 5 h at room temperature. The equilibrium binding capacity of Qu at different concentrations was determined by UV–vis spectrophotometry in accordance with the determination method in the prestep experimental procedure.

RESULTS AND DISCUSSION

Study of the coordination behavior between Qu and Zn(II) by UV spectrophotometry

The groups that can absorb UV–vis light in organic molecules are limited to certain functional groups (also known as *chromophores*), and in general, these chromophores contain valence electrons with a lower excitation energy and are unsaturated groups that can cause electron transitions. Qu had two absorption peaks in the methanol solution at 258 and 370 nm; these belonged to the n–π^* (A ring) electronic transition and the π–π^* (B ring) electronic transition, respectively, and corresponded to the composition of two chromophores: the absorption band (I) at 370 nm was generated by the cinnamoyl chromophore, and the absorption band (II) at 259 nm was generated by the benzoyl chromophore. Because the types of hydroxyls in the Qu molecule were phenolic hydroxyl or enol hydroxyl, the 3-hydroxyl-4-ketone in the C ring, 3′,4′-dihydroxyl in the B ring, and 5-hydroxyl-4-ketone as electron donors easily formed coordination with the metal ions.[18] The structure of Qu is shown in Figure 1.

In the experiments, the tested solution samples were prepared at a fixed content of Qu with gradually augmentation of the concentration of Zn(II). This series of mixed solutions were scanned on a UV spectrometer. As shown in Figure 2, with increasing concentration of Zn(II), the absorption band (I) mainly changed and showed a redshift from 370 to 426 nm, the absorption intensity at 370 nm decreased gradually, and the absorption intensity at 426 nm increased gradually. When the molar ratio between Zn(II) and Qu was greater than 1 : 1, to continue to increase the concentration of Zn(II), the maximum absorption wavelength and the absorbance of Qu had almost no change. Also, an equal absorption point appeared at 391 nm. Therefore, we inferred that Zn(II) and Qu produced coordinate interaction, and the coordination ratio calculated between them was 1 : 1 by the molar ratio method.

According to the structure of Qu and the changes in the UV spectrum, we deduced that it was the 3-hydroxyl-4-ketone involved in the metal coordination. After coordination, the cinnamoyl conjugated system extended, the density of electron clouds
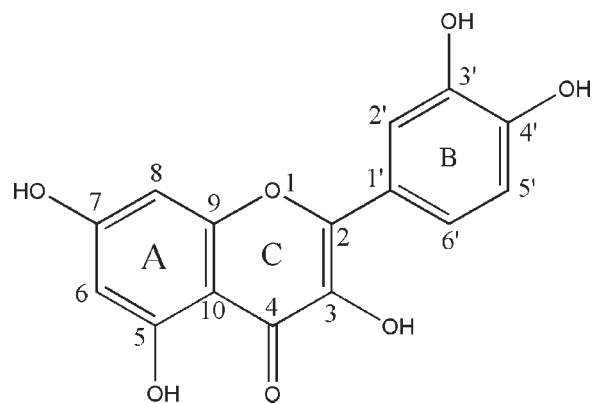
Figure 1 Chemical structure of Qu.

decreased, the π-electron mobility increased, and a lower energy was just required for the transition of electronic energy levels. Consequently, the significant redshift of the spectrum of band I happened. However, 3′,4′-dihydroxyl and 5-hydroxyl-4-ketone were not involved in the coordination because the coordination abilities of the coordination sites of the Qu molecule in neutral solutions were as follows: 3-hydroxyl-4-ketone < 3′,4′-dihydroxyl < 5-hydroxyl-4-ketone,[19] and 3-hydroxyl-4-ketone was mainly involved in coordination because the acidity of the 3-hydroxyl proton was stronger than that of the 5-hydroxyl proton, and after 3-hydroxyl-4-ketone was involved in the coordination, the steric hindrance of the complex hindered the 5-hydroxyl involved in the coordination. 3′,4′-dihydroxyl leaned toward the formation of the complex in an alkaline environment, and the complex formed was very unstable; to take part in the coordination, both H⁺'s of 3′,4′-dihydroxyl must have been dissociated, and the existence of a small amount of acid and trace water could inhibit the two adjacent phenolic hydroxyls from taking part in coordination.[18]
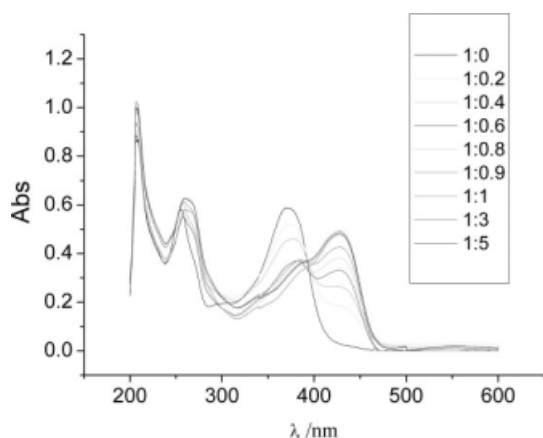
Verification of the ternary coordination of Qu, Zn(II), and 4-VP

In the experiments, we kept the concentration of 4-VP and the complex ratio of Qu/Zn^{2+} (1 : 1) unchanged and gradually increased the concentration of the Zn(II)–Qu complexes, the UV absorption spectrum changes of 4-VP are shown in Figure 3.

As shown in Figure 3, when the Zn(II)–Qu complexes were added to the 4-VP methanol solution, the absorption intensity of 4-VP at 205 nm decreased significantly, and with the increasing concentration of Zn(II)–Qu complexes, the absorption wavelength at 205 nm showed a redshift, and the absorption intensity increased. Also, the absorption intensity at 242 nm decreased gradually, and the maximum absorption wavelength at 242 nm also showed a redshift. When the molar ratio between 4-VP and the Zn(II)–Qu complexes reached 1 : 1, the maximum absorption wavelength was up to 265 nm and showed a redshift of 23 nm. The experiments indicated that the ternary coordination of Qu, Zn(II), and 4-VP was formed.

We deduced from the UV spectrum analysis that the synthetic route and recognition mechanism of the imprinted polymer were as follows (Fig. 4).

Effect of the crosslinker dosage on the morphology and specific adsorption properties of MCIPs

In the preparation of the imprinted polymer, to fix the template molecules and specific locations of the functional monomer groups interacting with the template molecules in the polymer matrix and maintain the three-dimensional configuration space of polymer holes, an imprinted polymer with a certain rigidity was required. After the template molecules were eluted, the imprinted polymer could maintain the original shape and size of holes; that is, it could maintain the stability and rebinding capacity of the
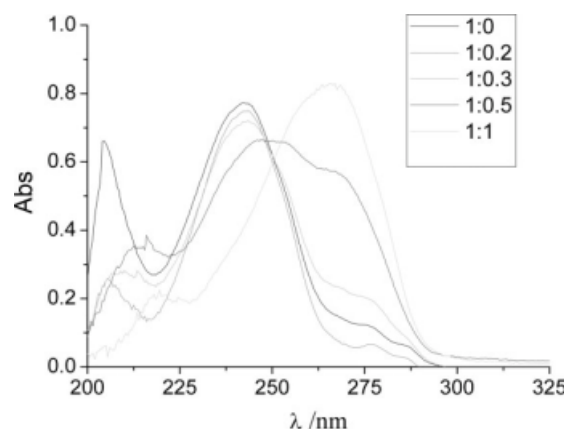

Figure 2 UV–vis spectra of Qu samples with different molar ratios of Qu to Zn(II) in methanol solutions (λ = wavelength).

Figure 3 UV–vis spectra of 4-VP samples with different molar ratios of 4-VP to the Zn(II)–Qu complex in methanol solutions (λ = wavelength).
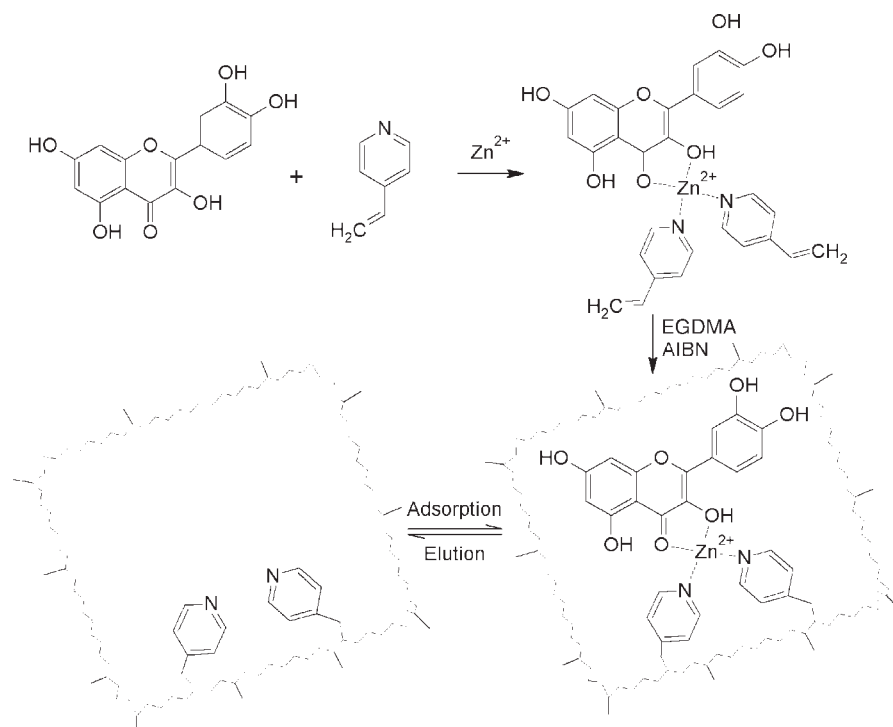
Figure 4 Graphical synthetic routes of the imprinted polymer and its recognition mechanism. EGDMA, ethylene glycol dimethacrylate.

recognition sites. Also, the imprinted polymer needed a certain degree of flexibility to make the template molecules enter into the polymer holes and achieve rapid integration, which was necessary for binding kinetics and could make the combination between the template molecules and binding sites reach a balance rapidly. On the basis of these two points and with the effect of the crosslinker dosage on the crosslinking degree and pore structure of the imprinted polymer taken into account, it was essential to optimize the dosage of crosslinker.

TEM revealed the internal relevance between the macroscopic properties and microscopic features of the materials. The effect of the crosslinker dosage on the morphology and network structure of MCIP was studied by TEM, and the effect of the microstructure of the polymer on the binding capacities was studied by the equilibrium binding experiments.

When the three groups of TEM images in Figure 5 are compared, one can see that the MCIPs that were synthesized with different dosages of crosslinker had different morphologies. When the dosage of crosslinker was too much, a large packing structure was easily formed, as shown in Figure 5(c), and the kinetic curve in Figure 6(b) indicated that the specific adsorption capacity of P_3 increased slowly and did not easily reach saturation in a short period of time; this may have been due to the higher concentration of the solution obtained in this case. When the polymerization occurred, the viscosity increased rapidly, and the porogen was not enough to enter

into the polymer network to form the structure of a pore channel. It affected the extent of the template–monomer complex packaged in the matrix. We inferred that the imprinting points had a serious degree of embedding in this material matrix, which may have been detrimental to the process of mass transfer. Also, when a lesser amount of crosslinker was used, as shown in Figure 6(a), the materials exhibited a loose structure, and the polymerization degree of the product was lower; the kinetic curve in Figure 6(c) indicates that the specific adsorption of P_1 increased quickly and easily reached saturation in a short period of time, but the saturated specific adsorption amount was lower. This was because the concentration of the reaction solution may have been too dilute, the radical polymerization reacted at a slower rate, and the polymerization degree of the product may have been lower. The loose structure of material with a large specific surface area made the polymer binding sites easy to reach. As the template molecules avoided driving in the deep part of the imprinted polymer matrix, a high specific adsorption speed was obtained. However, the lower polymerization degree weakened the stiffness of the imprinted polymers, and they exhibited poor mechanical strength and were easily crushed. In this way, it was inevitable that too many imprinted cavities were damaged in the process of grinding, which decreased the number of imprinted sites and the amount of saturated adsorption at the same time. However, a moderate amount of crosslinker
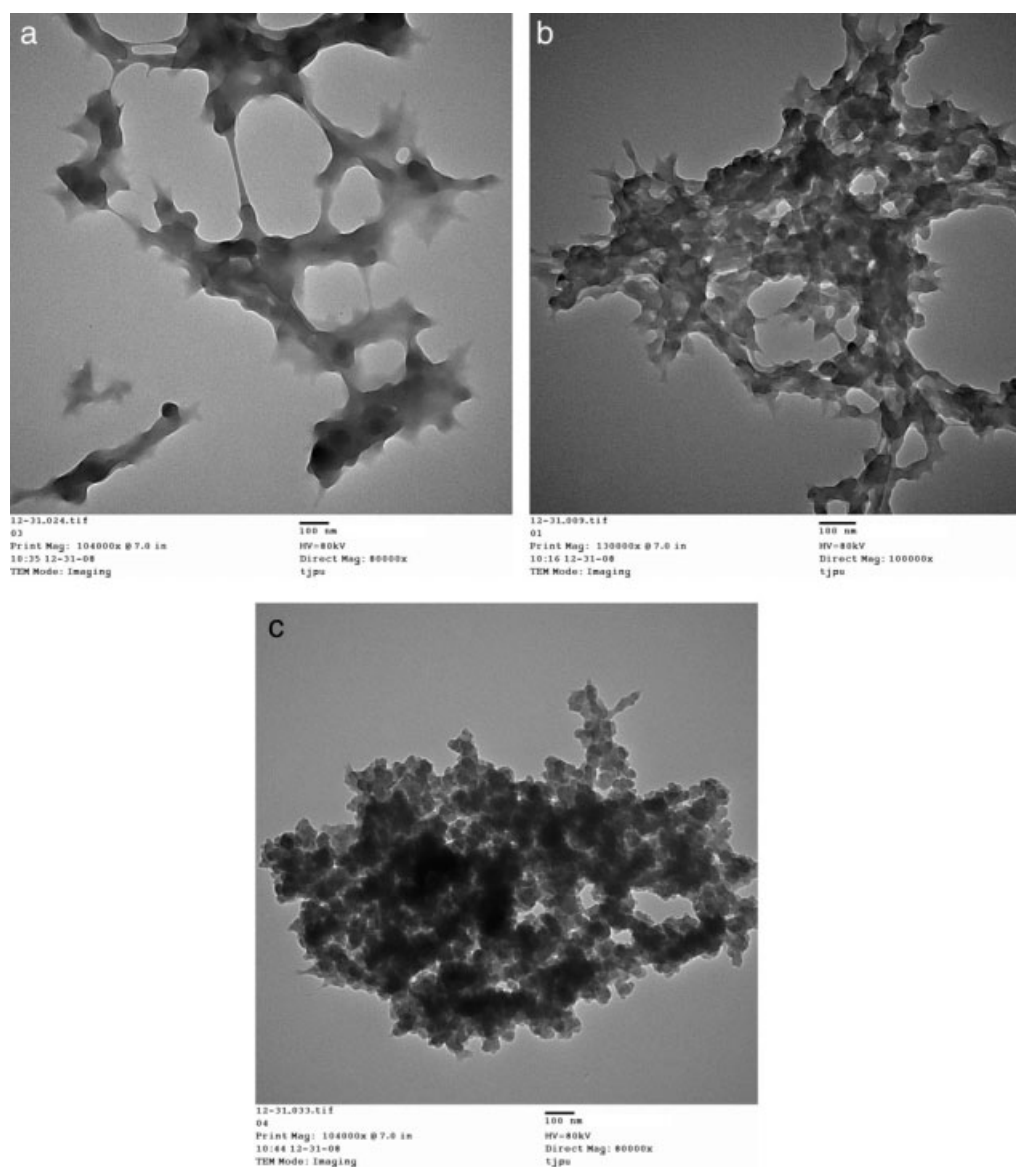
Figure 5 TEM images of MCIPs prepared in different amounts of the crosslinker: (a) P_1 (molar ratio of the print molecules to the crosslinker = 1 : 20), (b) P_2 (molar ratio of the print molecules to the crosslinker = 1 : 30), and (c) P_3 (molar ratio of the print molecules to the crosslinker = 1 : 40).

seemed to provide appropriate conditions for the formation of an adequate construction on microscopic morphology. As shown in Figure 6(b), the polymer presented irregular three-dimensional mesh patterns. Those pore channels running through the material were very useful. On one hand, they greatly increased the surface area of the material and reduced the number of embedded imprinting points in the imprinted polymers, so as to enhance the accessibility of the binding site. On the other hand, they provided a passing medium for in-house channels. This was conducive to the achievement of combination and specific adsorption. As the kinetic curve in Figure 6(a) shows, the specific adsorption performance of the imprinted polymer was more

stable, and it had a high specific adsorption capacity.

Identification system of the series of polymers

In the experiments, the equilibrium adsorption capacity of the series of polymers to the Zn(II)–Qu complexes or Qu at different initial concentrations (range = 0.2–5 mmol/L) were determined with an equilibrium binding experiment method. The adsorption isotherms drawn from the experimental data are shown in Figures 7 and 8.

As shown in the two figures, the adsorption of polymers adhered to the rules of monolayer adsorption of the Langmuir model.[20] From the comparison
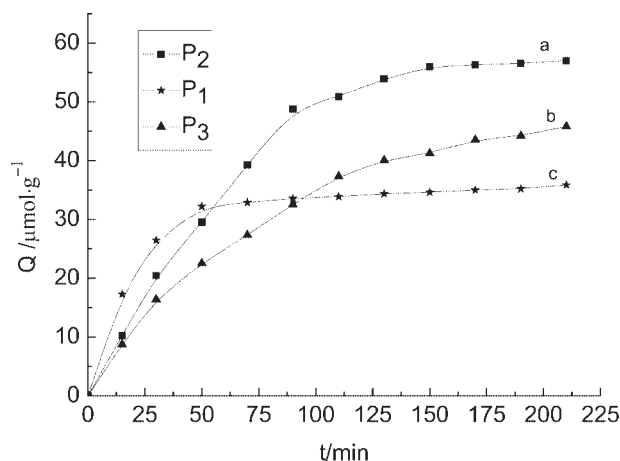
Figure 6 Kinetic curves of the specific adsorption (Q) for MCIPs (t = time).

of the three binding isotherms of P_2, P_4, and P_5 in Figure 7, with increasing initial concentration of Zn(II)–Qu complexes, the adsorption capacities of the three polymers to Qu increased. However, the combination amount of Qu on P_2 was always greater than those on P_4 and P_5, obviously. Also, it was saturated in a high concentration range. Thus, it showed a better binding ability. In many receptor binding assays,[21] as the curve of a nonselective combined volume to the initial concentration increases linearly, it is difficult to reach saturation as a rule. Therefore, we inferred that adsorption of P_4 and P_5 to Qu was nonselective, and P_2 exhibited selective adsorption. Meanwhile, the maximum binding capacity of P_2 to Qu, shown in Figure 8, was less than that of P_2, shown in Figure 7. Comparing the synthesis process of the three polymers, we prepared P_2 using the Zn(II)–Qu complexes as templates. Qu, Zn(II), and 4-VP formed the ternary coordination in the presence of Zn(II). P_2 demonstrated its ability to identify the template through the metal coordination interaction; that is, the identification system of P_2 was the Zn(II)–Qu complexes rather than simply Qu. In other words, Zn(II) had regulation on the identification of P_2. This was because many specific structure holes with fixed three-dimensional shapes and positions of functional groups matching the Zn(II)–Qu complexes were formed during the synthesis process in the presence of Qu and Zn(II). These imprinted holes with active binding sites in them caused good ability to selective binding on the MCIPs.

At the same time, as shown in Figure 8, although the imprinted polymer P_4 was prepared with Qu as the template molecule, its binding capacity of Qu was far less than that of P_2, as shown in Figure 7. This was because, when Qu was used as the template molecule, it was necessary to form the stable complex through the noncovalent bond interaction
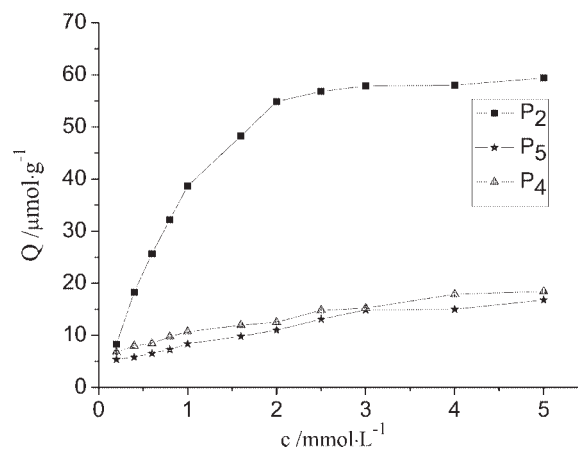
Figure 7 Adsorption (Q) of the series of polymers to the Zn(II)–Qu complex with different values of the initial concentration (c). P_2 was prepared with the Zn(II)–Qu complex as the template, P_4 was prepared with the Qu molecule as the template, and P_5 was prepared in the absence of the template molecule and metal ions. The molar ratio of the print molecules to the crosslinker for the three polymers was 1 : 30.

(e.g., hydrogen bond, electrostatic interaction) between Qu and 4-VP by self-organization in solution before polymerization. The strength of the noncovalent bond directly impacted the stability of the complex formed between the template molecule and the functional monomer and further affected the imprinting effect of the imprinted polymer. Therefore, the selection of solvents is crucial to the preparation process of noncovalent imprinted polymers, and some organic solvents (e.g., toluene, chloroform, acetonitrile) with low polarities and weak impacts on the noncovalent bond are often chosen, but strong polar solvents (e.g., a water–alcohol system) are less used because of their greater impact on hydrogen bonding and electrostatic interaction. In the experiments, the binding capacity of Qu on P_4, shown in Figure 8, was far lower than that on P_2,
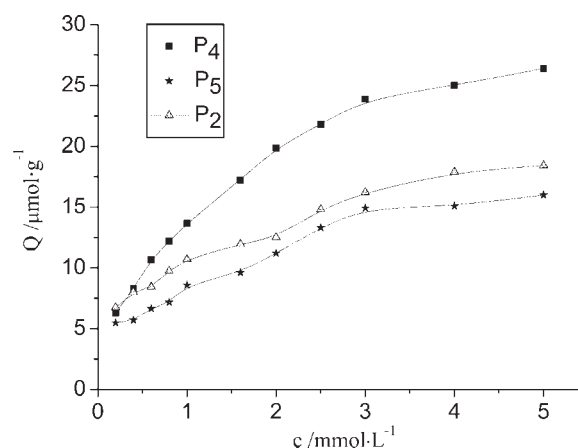

Figure 8 Adsorption (Q) of the series of polymers to Qu with different values of the initial concentration (c).

shown in Figure 7; the reason may have been that in methanol solvent, the strong polarity of solvent interfered with or damaged the hydrogen bonding or electrostatic interaction between Qu and 4-VP. The experimental results further verify that the metal coordination bond was stronger than the hydrogen bonds, van der Waals force, electrostatic attraction, hydrophobic force, and so on and was more stable in the water–alcohol system. In view of the unique advantages of the metal coordination, it is more suitable to prepare the imprinted polymer in strong polar solvents. This also proves that the properties of interaction forces between the imprinted molecule and functional monomer, which is presented as a supramolecular complex in the course of synthesis, played an important role in the specific identification and strong affinity.

Scatchard analysis

In studying the molecular imprinting technique, the Scatchard model is often used to evaluate the specific adsorption characteristics of molecularly imprinted polymers. The data of P_2 obtained from isothermal adsorption experiments were plotted according to the Scatchard equation as follows[22,23]:

$$Q/[c] = (Q_{max} - Q)K_d \qquad (2)$$

where K_d is the equilibrium dissociation constant of the binding sites (mmol/L), Q is the amount of template molecules bound to the polymer (μmol/g), Q_{max} is the apparent maximal combination amount of binding sites (μmol/g), and $[c]$ is the equilibrium concentration of template molecules in solution (mmol/L).

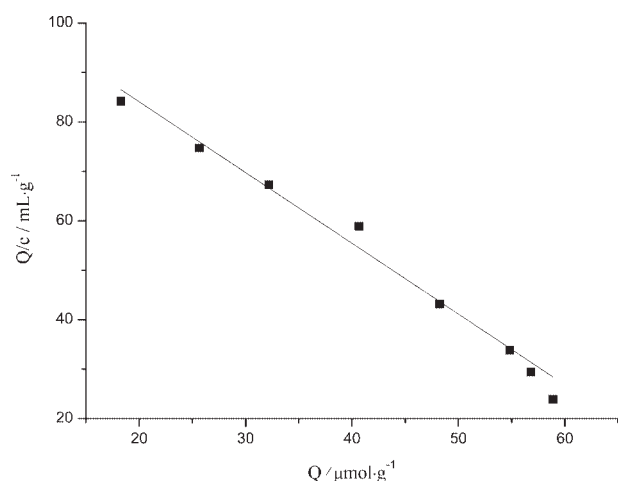According to the Scatchard equation, the relation curve between $Q/[c]$ and Q becomes almost straight,

Figure 9 Scatchard plots for estimating the binding property of MCIPs (c = concentration; Q = adsorption).

TABLE I
Effects of Cations and Anions on the Binding Capacity of an MCIP

MCIP	Binding capacity (μmol/g)				
	$Zn(Ac)_2$	$Cu(Ac)_2$	$Ni(Ac)_2$	$ZnCl_2$	$Zn(NO_3)_2$
P_2	56.64	17.83	15.25	26.39	22.46

as shown in Figure 9. The linear equation is as follows:

$$y = -1.432x + 112.72659 \qquad (3)$$

K_d and Q_{max} of P_2 were calculated to be 0.6983 mmol/L and 78.72 μmol/g, respectively, according to the slope coefficient and intercept in linear eq. (3). This suggests that P_2 formed a class of equivalent binding sites within the range of studied concentration and exhibited a uniform binding capacity to Qu in the presence of Zn(II). These results came from the template effect in the process of molecular imprinting, and the imprinted polymer exhibited specific adsorption on the Zn(II)–Qu complexes. Moreover, we verified that the coordination site of the Qu molecule was 3-hydroxyl-4-ketone rather than 3′,4′-dihydroxyl and 5-hydroxyl-4-ketone; this was consistent with the UV spectral analysis results.

Effects of cations and anions on the binding capacity of MCIPs

To further verify the high selectivity of MCIPs, the effect of cations and anions on their binding capacity was studied.

As shown in Table I, compared with Zn(II), although Cu(II) and Ni(II) were also easily involved in the coordination with Qu, the binding capacity of P_2 to Qu was significantly greater in the $Zn(Ac)_2$ medium than in the other mediums. Comparing the radius of these ions—Cu (II) = 0. 072 nm, Ni (II) = 0. 070 nm, and Zn (II) = 0. 074 nm–we could see there was little difference between them. This suggested that it was the geometry that determined the selective binding capacity of P_2 rather than the radius of metal ions. The imprinted polymer P_2 exhibited a high degree of selectivity to Qu only in the Zn(II)–Qu system. When Zn(II) was replaced with other metal ions, the geometry of the ternary complex was inconsistent with that left after the template molecule eluted from the polymer; this resulted in a reduced binding capacity of the imprinted polymer.

When the anions were replaced with Cl^- or NO^{3-}, as shown in Table I, P_2 did not exhibit effective selective binding to Qu, which may have been attributed to the difference in the binding strength of the

cations and anions, or anions were also involved in the process of molecular imprinting in the preparation of MCIP. The imprinted holes were formed by Zn(II), Ac⁻, and Qu. Because of the differences of the anions in size and geometry, the binding capacity of the imprinted polymer decreased when the anions were replaced with other anions.

CONCLUSIONS

As shown by the experimental results, the selective recognition of MCIPs to ligands could be regulated by metal ions. This characteristic was consistent with the requirements of biosensors or the identification and control system of an artificial enzyme. In addition, because the selective recognition of MCIPs to ligands was achieved by metal coordination bonding, the polymers could be used in some systems (e.g., molecular recognition in a water–alcohol solvent system) in which hydrogen bonds are easily damaged or interfered with. In this study, an MCIP with a specific recognition to Qu was prepared with a Zn(II)–Qu complex as a template; this has good application prospects in the fields of the separation and detection of Qu from complex samples.

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