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A new simple extraction method for the extraction of hesperitin from wastewater

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Uniform hesperitin magnetic molecularly imprinted polymers (HES-MMIPs) were successfully synthesized, and present good extraction activity, selection and reusability in the extraction of wastewater.

Fe_3O_4 nanomaterials, as convenient recyclable materials, were widely used for the synthesis of polymer absorbents due to their good monodispersibility, magnetic responsiveness and chemical stability.^{1–3} To extract and obtain targets from complex mixtures, some recognition parts such as some molecular functional groups are usually modified on the surface of Fe_3O_4 nanospheres.^{4–6} In addition, non-crystalline SiO_2 has been modified onto the surface of Fe_3O_4 nanospheres,^{7,8} leading to enhanced dispersibility and improvement in the modification of molecular functional groups. Molecularly imprinted polymers (MIPs) display good recognition activity for extraction and have a certain resistance to the extraction conditions, such as temperature, components, and pH. Therefore, MIPs were widely used for separation for fluorescence polarization assays,⁹ chemical sensors,¹⁰ and in recognition and separation,¹¹ drug delivery and controlled release,¹² and catalysis.¹³ In addition, magnetic MIPs could be quickly re-collected *via* a magnetic field in the extraction process.¹⁴

Hesperitin was one of important flavonoid medicines, which is widely used in cholesterol,¹⁵ cardiovascular,¹⁶ and nerve therapies.¹⁷ Once it is excreted into environmental water, it leads to waste, and has some negative effects on human health and the environment. Therefore, it is very important and significant to develop good sensitive and active methods for the separation of hesperitin (HES) from wastewater. In this study, HES magnetic molecularly imprinted polymers (HES-MMIPs) were synthesized through adding recognition for the polymer onto the surface of the magnetic core–core structure

($\text{Fe}_3\text{O}_4@ \text{SiO}_2$) material, and further were used for the extraction of hesperitin from wastewater.

XRD patterns of the as-obtained Fe_3O_4 and HES-MMIPs are presented in Fig. 1. Analysis with JADE software indicates that the diffraction peaks could be indexed as cubic Fe_3O_4 (JCPDS Card No. 79-0418) with cell constants of $a = 8.3985 \text{ \AA}$, $b = 8.3985 \text{ \AA}$, and $c = 8.3985 \text{ \AA}$, which are consistent with the reported values.¹⁸ Additionally, there are no other peaks occurring in the image for HES-MMIPs, indicating that the SiO_2 and MIPs were non-crystalline. The relative decrease in the diffraction peak intensity of Fe_3O_4 compared to HES-MMIPs indicated that the SiO_2 and MIPs have gradually modified the surface of the Fe_3O_4 nanospheres.

To further demonstrate the existence of SiO_2 and MIPs successfully coated onto the Fe_3O_4 , FT-IR measures were carried out as shown in Fig. 2. The obvious adsorption peaks at 578 cm^{-1} , 1090 cm^{-1} , and 1701 cm^{-1} were the characteristic peaks of Fe–O, O–Si–O and O–C=O, respectively. Additionally, a certain intensity increase was found due to the response functional of the EDMA. TEM images could provide further insight into the microstructural details. The morphology of the HES-MMIPs was observed

Fig. 1 XRD patterns of the Fe_3O_4 and HES-MMIPs.

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Fig. 2 FT-IR spectrum of as-obtained samples; inset: TEM image of HES-MMIPs.

and is shown in the inset image of Fig. 2. The last obtained HES-MMIPs still showed preferable dispersibility with the size of *ca.* 280 nm, and the coating was *ca.* 20 nm thick.

As we know, the kinetic rate is an important indicator of the sorbent. To further study the adsorption models of the HES-MMIPs, a study of the kinetic rate of the HES-MMIPs was carried out.^{19,20} In Fig. 3, it is shown that the process of adsorption of hesperitin by HES-MMIPs was more prone to be

Fig. 3 Adsorption kinetics of the HES-MMIPs: (a) pseudo-first order; and (b) pseudo-second order.

Table 1 Adsorption kinetic constants of HES-MMIPs

Order-equation	K	Q_e ($\mu\text{mol g}^{-1}$)	R^2
Pseudo-second	0.0036	67.80	0.99
Pseudo-first	-0.0025	10.89	0.78

in accordance with the second-order kinetic equation, indicating that the process is controlled by chemical adsorption. Moreover, the maximum amount of hesperitin was $67.80 \mu\text{mol g}^{-1}$ (Table 1).

To further study the adsorption properties of the HES-MMIPs, the adsorption isotherm curves were obtained. In Fig. 4, it is shown that the adsorption amount increased as the hesperitin concentrations increased both for HES-MMIPs and MNIPs. But at the same concentration, the adsorption amount for HES-MMIPs was obvious higher than for MNIPs, and this might be due to their special adsorption behavior, as a special molecular-imprinted hole matched well with hesperitin.

Scatchard plot analysis was used and calculated by the following formula:

$$Q/C = (Q_{\max} - Q)/K_d$$

where K_d ($\mu\text{mol mL}^{-1}$) is the equilibrium binding sites dissociation constant, $Q_{\max}$ ($\mu\text{mol g}^{-1}$) is the apparent maximum amount of binding sites, and C ($\mu\text{mol mL}^{-1}$) is the equilibrium concentration of hesperitin in the solution.

In Fig. 5, it can be seen that there are two different linear slopes in the adsorption (0.10 – $5.00 \mu\text{mol mL}^{-1}$), indicating that there are two different binding sites in the HES-MMIPs, a higher affinity site and a lower affinity site. As shown in Table 2, the binding capacities of the HES-MMIPs at the higher affinity site and lower affinity site of the HES-MMIPs were $55.65 \mu\text{mol g}^{-1}$ and $24.38 \mu\text{mol g}^{-1}$, respectively. The differences might be caused by the different combinations of 2-Vpy and hesperitin.

The selective adsorption and reusability were also preliminarily studied in this study (Fig. 6). We have found that the HES-MMIPs have obvious selective adsorption ($64.70 \mu\text{mol g}^{-1}$) compared to the MNIPs. Moreover, HES-MMIPs showed a certain decrease with the reuse of the sorbents, but the re-adsorption is still over 95%.

Fig. 4 Adsorption isotherm curves of HES-MMIPs and MNIPs.

Fig. 5 Scatchard curve of HES-MMIPs.

Table 2 Scatchard analysis results of HES-MMIPs

Binding site	Linear equation	K_d ($\mu\text{mol mL}^{-1}$)	Q_c ($\mu\text{mol g}^{-1}$)
Higher affinity	$Q/C = 55.65 - 1.07Q$	0.935	52.00
Lower affinity	$Q/C = 24.38 - 0.099Q$	10.10	246.26

Fig. 6 Selection and high-efficiency of the sorbent.

These results indicate that the HES-MMIPs are good sorbents and could be used in practical extraction processes.

In summary, HES-MMIPs were successfully prepared through a simple multi-step method. In the extraction process of hesperitin, they showed good high-efficiency, target-selection and reusability. The adsorption process followed the second-order kinetic equation. This study should extend to other herbal medicine extracts, due to the value of the basic theory and practical applications.

Experimental

All of the chemicals were of analytical grade and were used without further purification, and deionized water was used in all experiments. As previously described,⁸ the Fe_3O_4 nanospheres prepared were modified with SiO_2 . MPS was introduced to graft double bonds onto the surface of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ to form polymerizable sites with ethylene glycol dimethacrylate (EDMA)

and 2, 2'-azoisobutyronitrile (AIBN) in the next reaction process. Briefly, 0.25 mmol hesperitin, 1.5 mmol 2-vinylpyridine (2-Vpy), and 50 mL methanol in the three-neck flask, was added to 0.20 g $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -MPS, EDMA and AIBN (w/w, 1%) under stirring for 24 h at 60 °C in a N_2 atmosphere. After the polymerization, the mixture was dispersed in ethanol and the target was collected using a magnet. Then the obtained sample was washed with the mixture solution of methanol/acetic acid (6 : 4, v/v) using Soxhlet extraction to remove the template molecules. Finally, the sample was dried in a vacuum oven at 60 °C for 12 h. In comparison, the magnetic molecularly non-imprinted polymers (MNIPs) were also prepared in a similar way but without the addition of hesperitin.

In the isothermal adsorption activity test process, 20 mg HES-MMIPs (or MNIPs) and 10 mL of different concentrations of hesperitin methanol solution were poured into 15 mL quartz comparison tubes to mix *via* constant temperature oscillator shaking for 10 min. Then, the sorbents were separated using the magnet. Before the analysis of the absorbance of the liquid supernatant, particles should be removed using a 0.25 μm filter. Then the filtrates were analyzed by checking the absorbance at room temperature to obtain the concentration of the hesperitin.

The details of the selection experiment for HES-MMIPs are as follows: 20 mg HES-MMIPs (or MNIPs) and 10 mL of 1.5 $\mu\text{mol L}^{-1}$ of different methanol solutions (hesperitin, HES; apigenin, API; chlorogenic acid, CHA; or rutin, RUT) were poured into 15 mL quartz comparison tubes to mix *via* constant temperature oscillator shaking for 10 min. Then, the sorbents were separated using the magnet. Before the analysis of the absorbance of the liquid supernatant, particles should be removed using a 0.25 μm filter. Then the filtrates were analyzed by checking the absorbance at room temperature to obtain the concentration of the hesperitin.

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