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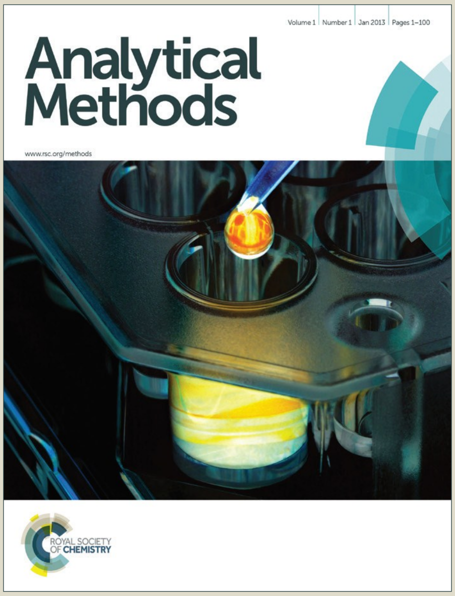

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Use of new magnetic ion-imprinted nanocomposite adsorbent for selective and fast preconcentration and determination of trace nickel by flame atomic absorption spectrometry

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A novel method for selective and fast preconcentration and determination of trace nickel (Ni(II)) in aqueous solution was developed by using magnetic Ni(II)–imprinted chitosan nanocomposite as new adsorbent for solid–phase extraction (SPE) coupled with flame atomic absorption spectrometric determination. The prepared adsorbent was characterized using Fourier transform–infrared spectroscopy (FT–IR), transmission electron microscope (TEM), thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM). The parameters that affect the extraction efficiency of Ni(II) were investigated. The optimum conditions, including sample pH, eluent type and volume, also adsorption and desorption time were obtained. Results indicated that the adsorbent had excellent adsorption selectivity for Ni(II). The analytical performance of the proposed method was evaluated. The enrichment factor for Ni(II) was 92 by using 50 mg of the adsorbent and 200 mL solution. The limit of detection (LOD) and limit of quantification (LOQ) were 0.06 and 0.2 μg L^{-1}, respectively. The intra-day and inter-day relative standard deviations (RSDs, n=6) were 1.5% and 1.8%, respectively. The developed method was successfully applied to the analysis of trace Ni(II) in environmental water, and the recovery for the spiked samples was in the range of 96-112%.

Introduction

Heavy metals are widely distributed in environment due to various industrial processes. One of the heavy metals is nickel (Ni(II)), which can result in serious problems such as nasopharynx, lung and dermatological diseases and malignant tumors.[1] Because of its toxic effects on human health and ecosystem, determination and removal of trace nickel in aquatic environments is of great interest. A number of methods have been applied to the detection of Ni(II) in various matrices, including flame atomic adsorption spectrometry (FAAS), [2,3] graphite furnace atomic absorption spectrometry (GFAAS),[4] inductively coupled plasma–optical emission spectrometry (ICP–OES),[5] and inductively coupled plasma mass spectrometry (ICP–MS).[6] Among these methods, FAAS is the most widely used technique because of its simple operation, low cost and high speed. However, due to low nickel concentrations and matrix influences, direct determination of Ni(II) in environmental samples by FAAS is often difficult or even impossible. Thus, separation and preconcentration procedures such as solvent extraction, ion exchange and coprecipitation are always required. [7-9] Nowadays, solid–phase extraction (SPE) is more common due to its high enrichment factor, low cost, environment friendly and easy operation. [10-13] However, SPE still suffers from interfering compounds which co-extracted with the target analysts when using conventional sorbents such as silica gel and resin. In order to improve extraction selectivity, the use of ion imprinted polymers (IIPs) has become attractive.[14-16] Panjali et al prepared Cd(II)-IIP by a typical polymerization reaction, [17] He et al synthesized Cu(II)-IIP polymer using a sol–gel method. [18] IIPs are highly crosslinked polymers prepared in the presence of a chosen template ion, the removal of which gives a polymer with sorption sites selective towards the particular template ion. [19] The high selectivity that could be obtained by IIPs is due to the selective sites in these polymers. Nevertheless, the slow solid–liquid phase separation rate of the extractant with the solution is one of the biggest problems in IIPs.

Magnetic separation technology can provide a convenient and rapid way for isolation of magnetic particles from solution. So far, magnetic Fe_3O_4 nanomaterials have attracted significant interest due to their unique physical and chemical properties that enable them to be easily removed from a matrix by applying an external magnetic field instead of centrifuging and filtrating.[20, 21]

Chitosan (CTS) possess high contents of amino and hydroxyl functional groups, which has been employed as metal ion chelating agent.[22] So far, diverse chitosan–based materials including magnetic chitosan composites for metal removal have been developed.[23-26]

In the present work, a new adsorbent, magnetic Ni(II)-imprinted chitosan nanacomposite was prepared for selective and fast extraction of Ni(II) from aqueous solutions. The adsorbent was characterized by Fourier transform–infrared spectroscopy (FT–IR), transmission electron microscope (TEM), thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM). The parameters that affect the extraction recovery of Ni(II) such as solution pH, adsorption and desorption time, type and volume of eluent, and coexisting ions were investigated in detail and optimized. Also, the reusability of this sorbent was evaluated. Finally, the adsorbent was applied for preconcentration and determination of trace Ni(II) in different real samples.

Experimental

Reagents

CTS powder was purchased from Shanghai Lanji Scientific Co., LTD, Shanghai, China. $NiSO_4 \cdot 6H_2O$, epichlorohydrin (ECH), $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were obtained from Chengdu Kelon Chemical Reagent Factory, Chengdu, China. Stock standard solution of Ni(II) (1000 mg L^{-1}) was supplied by National Iron and Steel Material Test Center, China. Deionized water was purified with a TKA Smart2 Pure system (Niederelbert, Germany). All other chemicals were of analytical grade.

Apparatus

Determination of metal ions (Ni, Cd, Cu and Pb) was carried out using a Hitachi Z-2000 (Hitachi, Japan) flame atomic absorption spectrometer (FAAS) equipped with a deuterium background correction and an air–acetylene flame (flow rate of acetylene 1.8 L min^{-1}). Hollow cathode lamps (Hitachi, Japan) worked at currents of 6-15 mA were used as the light sources, the wavelengths selected were as follows: Ni 232.0 nm, Cd 228.8 nm, Cu 324.8 nm and Pb 217.0 nm, and the spectral bandpass was 1.3 nm.

IR spectra were recorded on a Vector 22 spectrometer (Bruker, Germany) using KBr pellets. The surface morphological images of the adsorbent were analyzed by a transmission electron microscope (Hitachi HT7700, Japan). The thermal properties of the sample were obtained using a TG 209 thermal gravimeter (Netzsch, Germany). The magnetization of Fe_3O_4 and the sorbent were determined with a WK vibrating sample magnetometer (Physcience Opto-Electronics, Co., Ltd., Beijing, China).

Preparation of magnetic Ni(II)-imprinted chitosan nanacomposite

0.5 g CTS was dissolved in 500 mL of 1% (v/v) dilute acetic acid solution with mechanical stirring. Afterward, to the mixture a 10 mL solution containing 0.25 g $FeCl_3\cdot6H_2O$ and 0.25 g $FeSO_4\cdot7H_2O$ was added, followed by rapid addition of 7 mL ammonia (29%) with vigorous stirring for 0.5 h at 80 ˚C under nitrogen gas protection. After being washed several times with water, the solid was added to a 100 mL solution containing 0.2 g $Ni(NO_3)_2\bullet6H_2O$ with agitation for 15 min. After magnetic separation, the obtained particles were added to 50 mL 5% sodium tripolyphoshate under nitrogen with agitation for 10 min. Then, 0.5 mL ECH was added for cross-linking. The mixture was heated under microwave irradiation with 500 W for 5 min, followed by stirring for 30 min. After that, the mixture was fixed for 2.0 h at room temperature. The resultant material was then rinsed sequentially with 5% EDTA solution, 0.1 mol L^{-1} NaOH, distilled water and acetone, followed by dryness at 60 ˚C.

The magnetic non-imprinted chitosan particles (MNIPs) were prepared in a similar way without Ni(II) imprinting and removal process.

Solid–phase Extraction and determination

50 mg of MIIPs were added to 200 mL nickel containing water sample, and the solution pH was adjusted to pH 7 using 0.1 mol L^{-1} NaOH or HCl solutions. After shaking for 10 min at room temperature, the adsorbent was separated by a magnet and washed with distilled water. The adsorbed Ni(II) ions were eluted with 2 mL of 5% EDTA solution, and the concentration of Ni(II) in the eluent was then determined by FAAS.

Results and discussion

Characterization of the adsorbent

Fig. 1 shows the FT-IR spectrum of the synthesized MIIPs, magnetic Ni(II)-imprinted chitosan nanaocomposite. The peak at 3462 cm^{-1} is attributed to the peaks of the O-H and N-H stretching. The peaks at 2866 cm^{-1}, 1647 cm^{-1} and 1085 cm^{-1} are assigned to the C-H, C=O and C-OH stretching, respectively. The peaks at 1425 cm^{-1} and 1378 cm^{-1} are mainly related to the C–N stretching. The peak at 562 cm^{-1} represents the Fe-O bond vibration. The thermogram of the prepared adsorbent is represented in Fig. 2, in which the mass loss at around 100 ˚C is due to the loss of water on the sorbent. The thermogram shows a continuous loss in the range of 220– 450 °C, which is associated with the thermal decomposition of the chitosan and epichlorohydrin in the composite adsorbent. TEM image (Fig. 3) shows that the MIIPs possessed uniform spherical shapes, and the average diameter of these nanoparticles was about 20 nm. The magnetic property

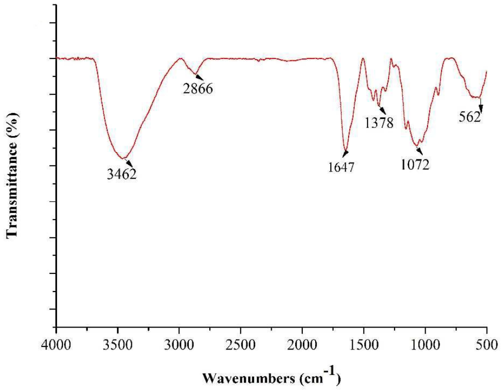

Fig. 1. FT-IR spectrum of MIIPs.

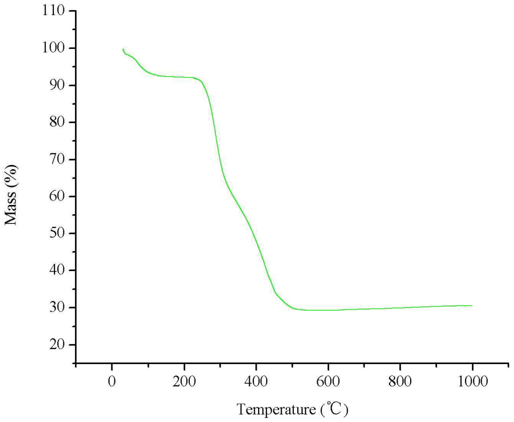

Fig. 2. Thermogram of MIIPs.

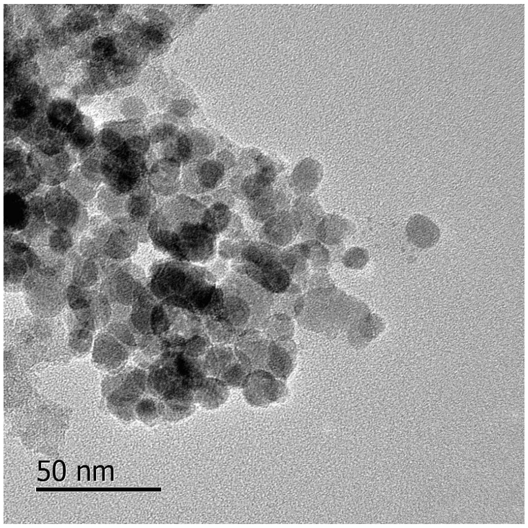

Fig. 3. TEM image of MIIPs.

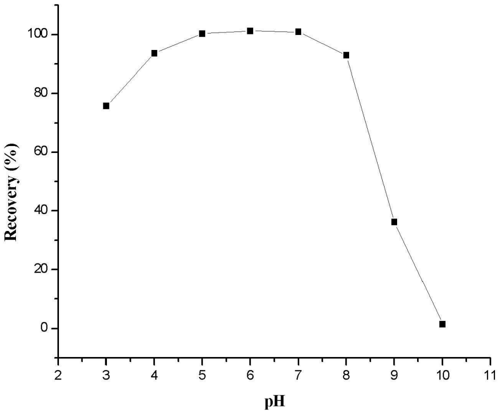

Fig. 4. Effect of pH on recovery of Ni(II).

of the MIIPs was measured with VSM at room temperature. It was found that the greatest saturation magnetization was 15 emu g^{-1}, and its remanence and coercivity were zero. These results indicated that the MIIPs were superparamagnetic.

Optimization of SPE conditions

Effect of sample pH

Sample pH is generally one of the most critical parameters for adsorption of metals on ion imprinted polymer. The effect of sample pH was tested in the range of 3-10. Fig.4 shows the dependence of extraction recovery of Ni(II) on sample pH. This pH dependency could be attributed to the facts that at lower pHs, the amino groups are protonated and thus could not coordinate to Ni(II) ions and at higher pHs, the precipitation of Ni(II) ions would reduce the recovery. As can be seen, the best pH for adsorption of Ni (II) on the MIIPs is 5.0–7.0. Because the pH of natural samples is usually around 7.0, this pH was chosen as optimum for further experiments.

Effect of eluent

The effect of type, concentration and volume of eluent on the extraction recovery of Ni (II) was examined. Considering Fe_3O_4 will be dissolved in strong acid medium, conventional solutions such as HCl and HNO_3 solutions were not suitable as the eluents for elution of Ni (II) from the MIIPs. Instead, EDTA in different concentrations was used to elute Ni (II) ions from this magnetic nanocomposite. It was found that the extraction recovery for Ni (II) increased along with the increase of EDTA concentration from 1% to 5%, and then kept almost unchanged up to 10%. Therefore 5% EDTA solution was adopted as the eluent. The effect of volume of this eluent on the recovery was also examined, and it was shown that 2 mL of this solution could efficiently elute off the adsorbed Ni (II) ions.

Effect of adsorption and desorption time

The effect of time on extraction recovery for Ni(II) in both adsorption and desorption steps was investigated. 100 mL of solutions containing 10 μg L^{-1} Ni(II) were adjusted to pH 7.0 and 30 mg of the MIIPs was introduced to the solutions and then shaken for different times. As it can be seen from Fig.5, the recovery increased drastically at the initial adsorption stage from 1 to 10 min. After 10 min, the recovery showed little changes due to the reach of adsorption equilibrium. Based on these results, 10 min was employed as the optimal adsorption time.

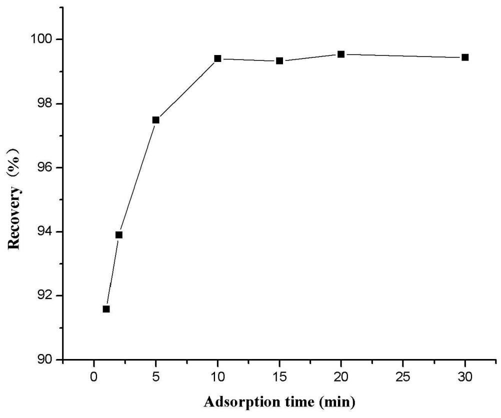

Fig. 5. Effect of adsorption time on recovery of Ni(II).

In order to investigate the optimum desorption time, various times were examined in the range of 1 to 10 min. According to measurements (data not shown), 2 min was found to be sufficient for quantitative elution of nickel ions from the imprinted polymer.

Adsorbent selectivity

To investigate the selectivity of Ni(II) adsorption on the prepared MIIPs and NIIPs, Cd(II), Cu(II) and Pb(II) were chosen as the competitive metal ions. These ions were treated with the MIIPs and NIIPs. After adsorption equilibrium, the concentration of each ion remaining in the solution phase was measured by FAAS. The selectivity coefficient (α) of Ni(II) with respect to Cd(II), Cu(II) and Pb(II) for the same sorbent (MIIPs or NIIPs) was calculated according to the following equations

$$\alpha = K_{\mathrm{Ni}}/K_{\mathrm{M(\boxed{?})}} \qquad (1)$$

$$K = Q/C_{\mathrm{e}} \qquad (2)$$

where K is the distribution coefficient and M(II) represents Cd(II), Cu(II) or Pb(II), Q is the adsorbed amount of each ion onto the MIIPs or NIIPs and C_{e} is the remaining concentration of each ion in the solution. In order evaluate the adsorption affinity of recognition sites to the imprinted ion (Ni(II)), a relative selectivity coefficient (β) for MIIPs with respect to NIIPs is introduced, which is obtained by Eq. (3):

$$\beta = \alpha_{\mathrm{MIIPs}}/\alpha_{\mathrm{NIIPs}} \qquad (3)$$

The values of K, α and β are summarized in Table 1. As can be seen, the α values of the MIIPs for Ni(II)/Cd(II), Ni(II)/Cu(II) and Ni(II)/Pb(II) were 4.9, 3.0 and 4.1, which were 2.3, 5.6 and 2.2 times (corresponding to the β values) greater than those of the MNIPs, respectively. These results indicate that the MIIPs exhibited high selectivity for Ni(II), and an obvious imprinting effect was achieved. Although Cd(II), Cu(II) and Pb(II) have the same charge number as Ni(II), their shape and size did not completely match the imprinted cavities of the MIIPs. Consequently, the adsorption of these ions onto the MIIPs was significantly lower than the adsorption of Ni(II).

Matrix effect

Sample pretreatment methods for determination of trace metal ions can be strongly affected by the matrix constituents of samples. In order to evaluate the effect of matrix ions on extraction recovery of Ni(II) using the MIIPs adsorbent, solutions of 10 μg L^{-1} of Ni(II) containing coexisting ions (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Cl^{-}, NO_3^{-} and SO_4^{2-}) were treated according to the above mentioned SPE procedure. The tolerable amounts were defined as the maximum concentration could cause a change of less than 5% in signal compared to the signal without any interference. As shown in Table 2, relatively high concentrations of alkaline and alkaline earth metals, common anions, and most transition metals had no significant interferences with the analysis of Ni(II) at pH 7. These results reveal that the presented method is selective toward Ni(II) ion and can be applied to various natural samples containing Ni(II) at low concentrations.

Analytical performance

Under the optimum experimental conditions, the calibration curve for Ni was linear in the concentration range from 0.5 to 50 μg L^{-1} ($R^2 = 0.9998$). The limit of detection (LOD) and the limit of quantification (LOQ)

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Table 1 The selectivity parameters of MIIPs and MNIPs

Metal ions	K_{MIIPs} (L g^{-1})	K_{NIIPs} (L g^{-1})	α_{MIIPs}	α_{NIIPs}	β
Ni (II)	5.38	0.13	–	–	–
Cd(II)	1.10	0.06	4.9	2.1	2.3
Cu(II)	1.78	0.24	3.0	0.5	6.0
Pb(II)	1.31	0.07	4.1	1.9	2.2

Table 2 The tolerance limit of coexisting ions in the determination of Ni(II) in a solution containing 10 μg L^{-1} Ni(II)

Interfering ions	Tolerable concentration ratio X/Ni	Recovery (%)
K^+	5000	96.2
Na^+	5000	95.0
Ca^{2+}	2500	94.1
Mg^{2+}	2500	95.2
Cu^{2+}	800	98.7
Cd^{2+}	800	95.7
Pb^{2+}	600	95.1
Zn^{2+}	200	96.2
Fe^{3+}	1000	94.8
Al^{3+}	2000	95.4
Cl^-	20000	95.8
NO_3^-	20000	98.7
SO_4^{2-}	12000	99.3

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for Ni(II), defined as the concentration corresponding to three and ten times the standard deviation of ten replicate measurements of the blank solution, were found to be 0.06 and 0.2 μg L^{-1}, respectively. The precision of the method was studied by six replicate experiments at the same Ni(II) concentration (10 μg L^{-1}), which yielded an intra-day RSD of 1.5% and an inter-day RSD of 1.8%, respectively. The enrichment factor (EF), evaluated by the ratio of slopes of the calibration curves with and without preconcentration procedure using 200 mL sample solution, was found to be 92. The above figures of merit are summarized in Table 3, which demonstrates that the proposed analytical approach has high sensitivity and good reproducibility for Ni(II) determination.

Adsorbent reuse

Reusability is one of the key factors in the application of solid-phase extraction materials. The stability of the MIIPs as solid-phase adsorbent was investigated by successive adsorption and elution cycles of solutions of 10 μg L^{-1} Ni(II) under the optimum conditions, which was estimated by monitoring the change in extraction recovery of Ni(II). Results showed that after 6 adsorption–desorption cycles, there was no significant decrease in the recovery. Therefore, the MIIPs can be reused 6 times for solid-phase extraction.

Table 3 Analytical characteristics of the proposed method

Parameters	Ni
Linear dynamic range (μg L^{-1})	0.5—50
R^2	0.9998
LOD (μg L^{-1})	0.06
LOQ (μg L^{-1})	0.2
Enrichment factor	92
Intra-day RSD (%, n=6)	1.5
Inter-day RSD (%, n=6)	1.8

Samples analysis

To evaluate the capability of the proposed method for analysis of real samples with different matrices containing various amounts of Ni(II), four environmental water samples were analyzed and the results are presented in Table 4. In order to evaluate the accuracy of the analytical results, the water samples were spiked with Ni(II) at different concentration levels. Recoveries of Ni were in the range of 96–112% with

RSDs of 0.2%–3.2%. These results indicate the suitability of the MIIPs for selective SPE and determination of Ni(II) in environmental water samples.

Comparison with other methods

In order to explain the advantages of the synthesized MIIPs, a comparison between this present work and other previously reported methods for detection of Ni(II) was done in Table 5, in terms of LOD, extraction time, recovery and RSD. All of these methods employ SPE for sample preconcentration, followed by FAAS determination. However, the adsorbents used for SPE are different, including Ni(II)–imprinted polymer obtained by bulk polymerization, [2] aminothioamidoanthraquinone-modified silica, [22] dithioxamide-modified activated carbon, [23] modified ionic liquid-coated nanometer titanium dioxide, [24] 4-(2-Thiazolylazo)resorcinol-modified carbon nanotubes, [25] dithizone-modified nanoporous fructose [26] and magnetic Ni(II)–imprinted chitosan nanocomposite. It is

Table 4 Analytical results of Ni (II) in environmental water samples

Sample	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	RSD (%)
River water	0	0.52	–	2.2
	0.50	1.08	112	1.4
Lake water	0	nd [a]	–	–
	0.50	0.51	102	1.7
Well water	0	2.20	–	1.5
	2.5	4.90	108	1.5
Spring water	0	nd [a]	–	–
	0.50	0.51	102	1.3

[a] Not detected (i.e., below the limit of quantification).

Table 5 Comparison with other previously reported techniques

Adsorbent	Extraction time (min)	LOD (μg L^{-1})	Recovery (%)	RSD (%)	Reference
Ni(II)–imprinted polymer	----	0.2	98-100	3.4	2
Aminothioamidoanthraquinone-modified silica	100	2.9	98-102	2.0	22
Dithioxamide-modified activated carbon	330	0.8	98	<2	23
Modified ionic liquid-coated nanometer titanium dioxide	50	0.8	97-106	2.0	24
4-(2-Thiazolylazo)resorcinol -modified carbon nanotubes	18	4.3	95-102	<5	25
Dithizone-modified nanoporous fructose	25	0.5	97-99	2.3	26
magnetic Ni(II)–imprinted chitosan nanocomposite	10	0.1	96–112	1.8	This work

evident that compared to the existing techniques, the proposed method has the lowest LOD, the shortest extraction time, and comparable recovery and RSD.

Conclusions

In this paper, a new nanostructured MIIPs, magnetic Ni(II)-imprinted chitosan nanocomposite was successfully synthesized. Application of this adsorbent was investigated in solid-phase extraction of Ni(II) ions from aqueous samples. Combined with FAAS, a sensitive, fast, reliable and environmentally friendly method for determination of Ni(II) was developed and applied to environmental water samples with satisfactory results. Due to its superparamagnetism, high selectivity and preconcentration factor of the resulting MIIPs, trace Ni(II) ions at μg L^{-1} levels can be rapidly and easily separated from a relatively large volume sample, and then are analyzed accurately and precisely. Therefore, the MIIPs could be a powerful alternative to the previously reported SPE sorbents for Ni(II) and is suitable for detection of nickel content below the detection limit of FAAS in environmental waters.

Acknowledgements

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References

1 M.G.A. Korn, E.S.B. Morte, D.C.M.B. dos Santos, J.T. Castro, J.T.P. Barbosa, A.P. Teixeira, A.P. Fernandes, B. Welz, W.P.C. dos Santos, E.B.G.N. dos Santos, M. Korn, *Appl. Spectrosc. Rev.*, 2008, **43**, 67–92.

2 M. Behbahani, M. Taghizadeh, A. Bagheri, H. Hosseini, M. Salarian, A. Tootoonchi, *Microchim. Acta*, 2012, **178**, 429–437.

3 M. Soylak, A. Recep, *Atom. Spectrosc.*, 2014, **35**, 79–84.

4 S. Scaccia, *Talanta*, 2005, **66**, 805–808.

5 D. Bakircioglu, Y. B. Kurtulus, S. Yurtsever, *Food chem.*, 2013, **138**, 770-775.

6 I.S. Trujillo, E.V. Alonso, A.G. de Torres, J.M.C. Pavón, *Microchem. J.*, 2012, **101**, 87-94.

7 H. Bagheri, M. Saraji, M. Naderi, *Analyst*, 2000, **125**, 1649–1654.

8 N. Rajesh, B. Deepthi, A. Subramaniam, *J. Hazard. Mater.*, 2006, **144**, 464–469.

9 R.S. Praveen, G.R.K. Naidu, T.P. Rao, *Anal. Chim. Acta*, 2007, **600**, 205–213.

10 L. Elci, M. Soylak, A. Uzun, E. Buyukpatir, M. Dogan, *Fresenius J. Anal.Chem.*, 2000, **368**, 358-361.

11 J.P. Zhou, X.G. Ma, Y.F. Dang, Y. Chen, *J. Anal. At. Spectrom.*, 2014, **28**, 1692–1697.

12 Y. Wang, H. Chen, J.Tang, G.Ye, H. Ge, X. Hu, *Food Chem.*, 2015, **181**, 191-197.

13 J.F. Chen, X.G. Ma, *Food Anal. Method.*, 2014, **7**, 1083-1089.

14 M. Shamsipur, B. Hashemi, S. Dehdashtian, M. Mohammadi, M. B. Gholivand, A. Garau,, V. Lippolis, *Anal. Chim. Acta*, 2014, **852**, 223-235.

15 M. Saraji, H Yousefi, *J. Hazard. Mater.*, 2009, **167**, 1152–1157.

16 O. Sayar, N. A.Torbati, H. Saravani, K. Mehrani, A. Behbahani, H. R. M. Zadeh, *J. Ind. Eng. Chem.*, 2014, **20**, 2657–2662.

17 Z. Panjali, A.A. Asgharinezhad, H. Ebrahimzadeh, S. Karami, M. Loni, M. Rezvani, S. J. Shahtaheri,

Anal. Methods, 2015, **7**, 3618-3624.

18 H. He, D. Xiao, J. He, H. Li, H. He, H. Dai, J. Peng, *Analyst*, 2014, **139**, 2459-2466.

19 A Bhaskarapillai, SV Narasimhan, *RSC Adv.*, 2013, **3**, 13178-13182

20 M. Behbahani, A. A. Akbari, M. M. Amini, A. Bagheri, *Anal. Methods*, 2014, **6**, 8785-8792.

21 S.Y. Xu$_a$, C.J. Guo, Y.X. Li, Z.R. Yu, C.H. W, Y.W. Tang, *J. Hazard. Mater.*, 2014, **264**, 34–41.

22 E. Guibal, C. Milot, J.M. Tobin, *Ind. Eng. Chem. Res.*, 1998, **37**, 1454–1463.

23 M. J. C. Calagui, D.B. Senoro, C. C Kan, J. W. L. Salvacion, C. M. Futalan, M. W. Wan, *J. Hazard. Mater.*, 2014, **277**, 120–126.

24 W.S.W. Ngah, L.C. Teong, M.A.K.M. Hanafiah, *Carbohydr. Polym.*, 2011, **83**, 1446–1456.

25 X. Liu, Q. Hu, Z. Fang, X. Zhang, B. Zhang, *Langmuir,* 2008*,* **25**, 3-8.

26 D.H.K. Reddy, S.M. Lee, *Adv. Colloid Interfac.*, 2013, **201***,* 68-93.

27 W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, *Talanta*, 2007, **71**, 1075-1082.

28 M. Ghaedi, F. Ahmadi, M. Soylak, *J. Hazard. Mater.*, 2007, **147**, 226-231.

29 M. Amjadi, A. Samadi, *Colloid Surface A*, 2013, **434**, 171-177.

31 Z. A. Alothman, M. Habila, E. Yilmaz, M. Soylak, *Microchim. Acta*, 2012, **177**, 397-403.

32 M. Behbahani, M. Najafi, M. M. Amini, O. Sadeghi, A. Bagheri, M. Salarian, *Microchim. Acta*, 2013, **180**, 911-920.

Graphic Abstract

Selective and rapid preconcentration of trace Ni(II) in environmental water by solid-phase extraction using magnetic Ni(II)–imprinted nanocomposite as adsorbent.