Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Material

Selective extraction and determination of beryllium in real samples using -Amino-5,8-dihydroxy-1,4-naphthoquinone functionalized magnetic MIL-53 as a novel nanoadsorbent

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Magnetite nanoparticles were fabricated based on a previous reported method [1]. In this way, 5.2 g $FeCl_3 \cdot 6H_2O$ and 2.0 g $FeCl_2 \cdot 4H_2O$ were exactly weighted and then transferred to 25 mL 0.4 mol L^{-1} HCl. The mixture of iron salts solution was then added drop by drop into a 250 mL NaOH solution (1.5 mol L^{-1}) under the nitrogen protection and heating at 80 °C during 0.5 h. Afterwards, the magnetic product was isolated from the reaction medium employing a strong magnet (15 × 12 × 5 cm, 1.4 Tesla) and then washed with double distilled water and ethanol, respectively and finally dried in a vacuum oven at 40 °C. In order to coat magnetite nanoparticles with a silica layer, 1.0 g of fabricated particles was added to a solution containing 250 mL DI water, 75 mL ethanol and 4 mL NH_4OH (28%). Thereafter, 4.5 mL TEOS was added drop by drop to the reaction mixture under vigorous stirring and stirred for 10 h at 40 ˚C [2]. Ultimately, Fe_3O_4@SiO_2 NPs were separated by the strong magnet, washed with ethanol and then dried at room temperature [2].

[1] Asgharinezhad AA, Ebrahimzadeh H, Rezvani M, Shekari N, Loni M (2014) A novel 4-(2 pyridylazo) resorcinol functionalized magnetic nanosorbent for selective extraction of Cu(II) and Pb(II) ions from food and water samples. Food Addit Contam 31:1196-1204.

[2] Sadeghi S, Aboobakri E (2012) Magnetic nanoparticles with an imprinted polymer coating for the selective extraction of uranyl ions. Microchim Acta 178:89-97.

Table 1S
Experimental variables and levels of the CCD.

		-α	Level			+α
			Lower	Central	Upper	
Sorption step	A: pH	2.64	4.0	6.0	8.0	9.36
	B: Sorbent amount (mg)	13.2	20.0	30.0	40.0	47.0
	C: Sorption time (min)	3.3	5.0	7.5	10.0	11.7
Elution step	A: Eluent concentration (mol/L)	0.26	0.4	0.6	0.8	0.94
	B: Eluent volume (mL)	0.16	0.5	1.0	1.5	1.84
	C: Elution time (min)	8.3	10.0	12.5	15.0	16.7

Table 2S: The tolerance limit of various ions on the determination of Be(II) ions.

Potentially interfering ion	Tolerable concentration ratio X/Be(II)	Recovery (RSD%)
Na^{+}	15000	99 ± 5
K^{+}	15000	101 ± 4
Mg^{2+}	12000	98 ± 4
Ca^{2+}	12000	99 ± 3
Co^{2+}	1000	97 ± 3.5
Zn^{2+}	750	97 ± 4
Mn^{2+}	750	98 ± 5
Cu^{2+}	1000	95 ± 3
Fe^{3+}	700	99 ± 3
Pb^{2+}	700	99 ± 4.5
Cr^{3+}	500	98 ± 2
Hg^{2+}	1000	96 ± 5
Ni^{2+}	800	95 ± 2
Al^{3+}	200	96 ± 3
Cd^{2+}	800	96 ± 3

Conditions: sample pH = 6.4, sample volume = 100 mL, 5µg of Be(II) ions, uptake time = 6.5 min; eluent = 1.0 mL, 0.6 mol L^{-1} nitric acid solution, elution time = 13.5 min.

X: Concentration of diverse ions.

Table 3S

Comparison of the proposed method with previously reported works for speciation of beryllium.

Method	Instrument	RSD	PF [a]	LOD [b]	Ref.
MIL-53(Fe)/Fe_3O_4@ADHNQ	FAAS	5.8	350	0.07	This work
Octadecyl silica gel-Quinalizarine	FAAS	2.7	200	0.2	[1]
Octadecyl silica gel modified with aluminon	FAAS	<10	330	0.1	[2]
Anion exchange resin III	FAAS	1.2	125	0.045	[3]

[a] $\mu g\ L^{-1}$.

[b] Preconcentration factor.

References:

1. Yamini Y, Hassan J, Mohandesi R, Bahramifar N (2002) Preconcentrationof trace amounts of beryllium in water samples onoctadecyl silica cartridges modified by quinalizarine and itsdetermination with atomic absorption spectrometry. Talanta 56:375
2. Farahmand AR, Yousefi SR, Sheijooni Fumani N, Mirza S,Shamsipur M, Hassan J (2009) Preconcentration of beryllium viaoctadecyl silica gel microparticles doped with aluminon, and itsdetermination by flame atomic absorption spectrometry. MicrochimActa 166:89
3. Castro MA, Robles LC, Lumbreras JM, de Celis B, Aller AJ,Littlejohn D (2009) Determination of beryllium by electrothermalatomic absorption spectrometry using tungsten surfaces andzirconium modifier. Anal Chim Acta 636:158.