

**Ultrasound-assisted dispersive magnetic solid phase extraction based on metal-organic
framework/1-(2-pyridylazo)-2-naphthol modified magnetite nanoparticles composite for
speciation analysis of inorganic tin**

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Instrumentation

Tin was determined by a Varian Zeeman spectra atomic absorption spectrometer (Varian Company, USA), Model 220 Z, equipped with a personal computer for the record of the absorbance signal/profile. Deuterium background correction was employed in order to correct non-specific absorbance. A tin hollow cathode lamp with wavelength of 224.6 nm with a spectral bandwidth of 0.7 nm and a pyrolytic graphite coated graphite tube was used too. In all tests, 20 μL sample along with 5 μL $\text{Mg}(\text{NO}_3)_2$ (1000 mg/L) and $\text{Pd}(\text{NO}_3)_2$ (1000 mg/L in 0.1% v/v in HNO_3) as matrix modifier was injected [1]. The operating conditions of the instrument are listed in Table 1S [1]. Ar with 99.995% purity (Roham Gas Company, Tehran, Iran) was employed as protective and purges gas. An ultrasonic bath (35 kHz, 320 W, Sonorex, Germany) was used in the sorption and desorption process. The pH of the solutions were measured at 25 ± 1 °C with a digital Metrohm 827 pH meter (Herisau, Switzerland, www.metrohm.com) equipped with a combined glass-calomel electrode. A Bruker IFS-66 FT-IR spectrophotometer (Karlsruhe, Germany, www.brukeroptics.com) was used for FT-IR spectra recording. Scanning electron microscopy (SEM) was conducted using an SEM (KYKY-3200, Beijing, China) instrument. Magnetic properties of nanocomposites were measured by a vibrating sample magnetometer (VSM) model AGFM/VSM 117 3886 (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) with a magnetic field strength of 1 Tesla and at room temperature. Elemental contents of nanocomposite were determined by an elemental analyzer model Thermo Finnigan Flash EA112 (Okehampton, UK). The specific surface area of MIL-101(Cr)/MNPs@SiO₂@PAN sorbent was obtained using a Micromeritics ASAP 2010 analyzer (Norcross, GA, USA) at 77 K using the BET method.

Real sample pretreatment

Food samples and reference material

Canned tuna fish, canned cherry, and tomato paste samples were purchased from local supermarkets in Tehran, Iran. Briefly, 1.0 g of each food sample or certified reference material was placed in a digestion cell and 6 mL HNO₃ (65% w/w) and 2 mL H₂O₂ (30% w/w) were added to the sample. Digestion was carried out according to following procedure: samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [1]. After digestion, the solution was cooled to room temperature, filtered into a 250 mL volumetric flask and diluted with ultrapure water.

Mineral and drinking water sample (Tehran, Iran) were filtered into cleaned polyethylene bottles. Each sample was divided to two equal portions and the pH of them was adjusted to 6.8 before the extraction procedure.

References

- [1] O.D. Uluozlu, M. Tuzen, Carrier element-free coprecipitation and speciation of inorganic tin in beverage samples and total tin in food samples using N-Benzoyl-N,N-diisobutylthiourea and its determination by graphite furnace atomic absorption spectrometry. *LWT-Food Sci. Technol.* 63 (2015) 1091-1096.

Table 1S

Operating condition of ETAAS for determination of tin.

Step	Temperature (°C)	Time (s)		Argon gas flow rate (mL min ⁻¹)
		Ramp	Hold	
Injection of modifier	60	5	20	250
Injection of sample				
Drying	120	5	20	250
Drying	170	15	20	250
Ashing	1500	10	20	250
Atomization	2500	0	5	0 (read)
Cleaning	2600	1	5	250

Table 2S

The recovery of Sn(IV) ions in the presence of potentially interfering ions.

Potentially interfering ions	Tolerable concentration ratio X/Sn(IV)	Recovery (%)
K ⁺	100000	101.0 ± 3.5
Na ⁺	100000	99.8 ± 3.8
Co(II)	1000	97.6 ± 2.7
Al(III)	1000	99.0 ± 3.4
Ca(II)	50000	98.2 ± 4.4
Mn(II)	1000	99.0 ± 5.0
Cd(II)	700	96.5 ± 2.9
Cu(II)	750	94.9 ± 2.0
Zn(II)	1000	97.2 ± 3.4
Pb(II)	250	98.3 ± 2.7
Cr(III)	1000	99.5 ± 3.0
Fe(III)	600	95.7 ± 4.5
Hg(II)	500	98.0 ± 2.7

^a Recovery^b standard deviation (n = 3)Conditions: sample pH = 6.8, Sn(IV) concentration = 0.5 µg L⁻¹, sorption time = 6.5 min ultrasonication; eluent volume = 0.75 mL 1.25 mol L⁻¹ HCl solution, elution time = 3.0 min ultrasonication.^c Concentration of potentially interfering ions.

Fig. 1S: Effect of the sorbent type on the extraction recovery of Sn(IV) at pH = 6.8.

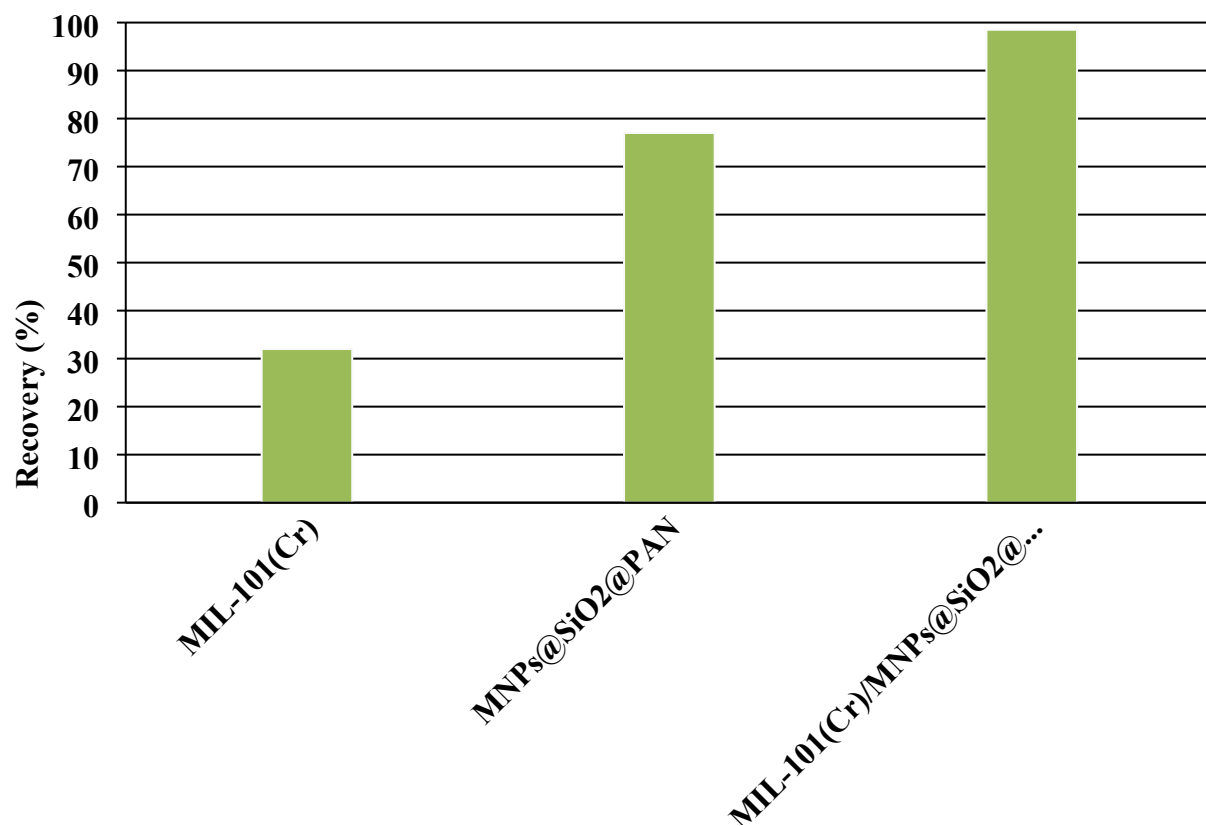


Fig. 2S: Response surface plots of the sorption step.

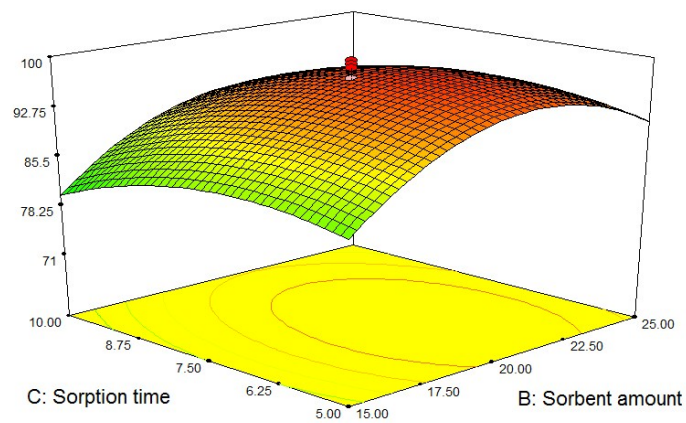
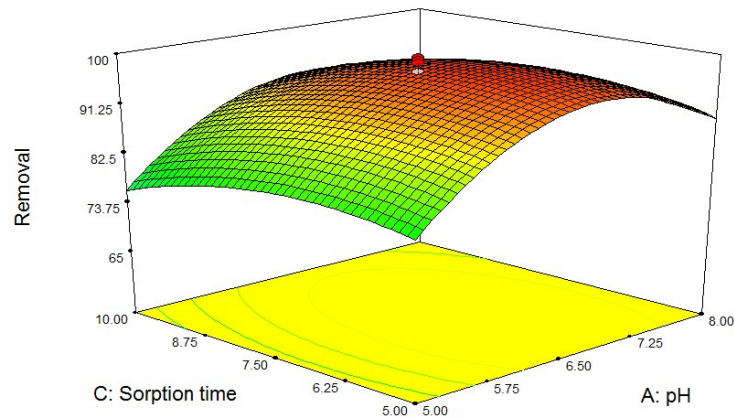
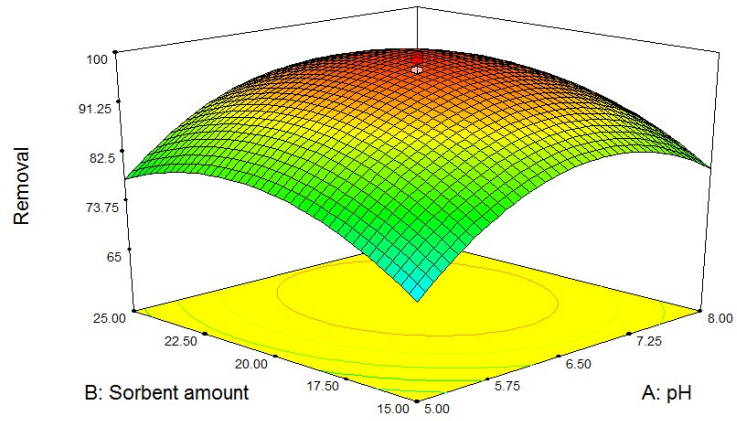


Fig. 3S: Response surface plots of the elution step.

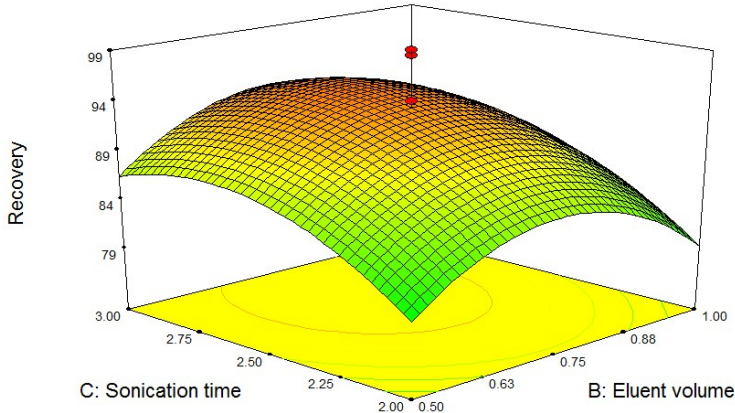
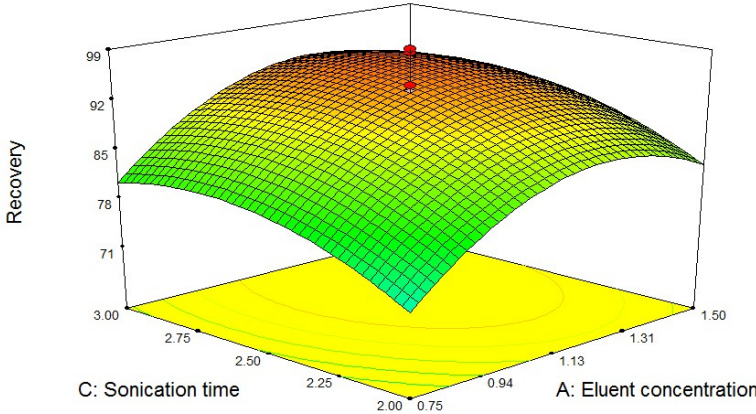
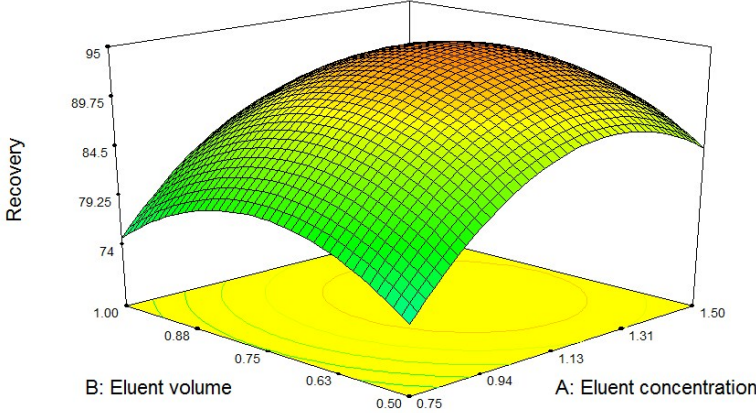


Fig. 4S: Durability study of MIL-101(Cr)/MNPs@SiO₂@PAN nanosorbent.

