Electronic Supplementary Material

A new magnetic tailor made polymer for separation and trace determination of cadmium ions by flame atomic absorption spectrophotometry

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2.1. Apparatus

Atomic absorption spectrometer (AAS) model AA-680 Shimadzu (Kyoto, Japan) in an air-acetylene flame was used for monitoring of cadmium amounts according to the provided user's manual by the manufacturer. The wavelength of 228.8 nm from a cadmium hollow cathode lamp was used as the radiation source. The operated current and spectral band pass for the measurements was 5 mA and 0.5 nm, respectively. All measurements were carried out in an air/acetylene flame. The pH adjustment of solutions was done by a digital pH meter equipped with a combined glass calomel electrodmodel (Metrohm 827 Ion analyzer (Herisau, Switzerland)) in the room temperature. The heating and stirring of the solutions was carred out by Heidolph heater stirrer model MR 3001 (Germany). The obtained infrared spectra of materials in the range of 4000–200 cm^{-1} prepared in KBr were recorded using Bruker IFS66/S FT-IR spectrometer. A Philips-PW 17C diffractometer with Cu K_{α} radiation was applied for evaluation of high angle X-ray diffraction patterns of prepared materials. To investigate the morphology of synthesized tailor made polymer, scanning electron microscopy (SEM (KYKY, EM3200)) was used by gently distributing the powder sample on the stainless steel stubs. A BAHR-Thermoanalyse GmbH (Germany) with heating and cooling rates of 10 °C min^{-1} was used for evaluation of thermal properties of synthesized sorbents. The samples were weighed as a thin film and carefully packed into a clean aluminum pan (11.5-12.5 mg), and sealed by crimping an aluminum lid on the pan (Shimadzu universal crimper). An Al_2O_3 empty pan sealed with a cover pan was used as a reference sample. A scanning range of 10 to 800 °C was used for samples at 10 °C min^{-1} in nitrogen gas. Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK) was used for elemental analysis of the sorbent.

2.6.1. Shrimp, crab and fish samples

All used samples including: shrimps, crabs and fishes were purchased from four local hypermarkets located in four different places of Tehran, Iran. After gathering, the obtained food samples (crab, fish and shrimp) from each hypermarket were accidentally picked, mixed, and kept in an ice sack and transferred to the lab and maintained at − 20 °C prior to analysis. The sampling was conducted in September 2013. A portion of shrimps and fishes muscle tissues were removed and lyophilized in order to obtain a specific weight, and were finely crashed. To digest of the samples for metal analysis, 5 mL of concentrated nitric acid was poured to 0.5 g of the grounded samples at 135 °C for 4 h, after that, 1 mL of hydrogen peroxide (30%) and 1 ml of concentrated perchloric acid were added to the solution. The temperature was kept at 150 °C until the solution was clear. Afterward, the obtained solution was filtered and the resulted clear solution was diluted to 100 mL and the pH was regulated to 8.0 by NaOH or HNO_3 for subsequent analysis. Cadmium ions level in the final solution was monitored after extraction by the applied solid phase extraction.

2.6.2. Agricultural products

Farm yield, including persimmon, apple, tomato, mushroom and potato were gathered from farm grounds in South of Tehran, Iran. All gathered products were kept in paper bags with regards to their kind and transferred to the lab for preparation and treatment. The samples were washed with distilled water. Next, 0.5 g of each sample was crashed, homogenized and dried at 80 °C and triturated in porcelain mortar. After fractionation of samples by sieving, sizes less than 20 μm were dissolved in 10 mL of 3 mol L^{-1} HNO_3 and the temperature of the solution was kept at 150 °C until the solution was clear and the obtained solution after filtration diluted with distilled water to a volume of 100 mL. After that, the pH was regulated to 8.0 for additional analysis. The

cadmium ions levels in the final solution were monitored after extraction by the proposed solid phase extraction.

3.2.2. Evaluation of the sorbent amounts

In comparison to traditional sorbents with micro-sized, nanoparticles have several advantages such as high sorption capacity, fast and high extraction efficiency that related to the higher surface area-to-volume ratio and a short diffusion route. According to the mentioned explanations, a low amount of the nanoparticles can be used for satisfactory extraction of targets from samples solutions. The extraction time for magnetic sorbents is short according to the magnetically separation of the materials with an external magnetic field. For this aim several amount of magnetic tailor made polymer was used in the range of 5-20 mg. It should be noted that other parameters for retention of target ions was kept constant at optimum conditions as follow: the pH of solution: 8 and sorption time of 5 min. The adsorption efficiency of cadmium ions in 5, 10, 15 and 20 mg of the sorbent was 72%, >99%, >99% and >99%, respectively. Therefore, low amount (10 mg) of the synthesized nanosrbent is adequate for extraction of cadmium ions and this observation is related to the high surface area of nanosorbents. No significant increasing observed for extraction efficiency of target ions at higher amounts of the applied sorbent. Hence, for further experiments, 10 mg of the sorbent was used.

3.4. Evaluation of sample volume effect

The sample volume in the real samples analysis is an important factor that influence on the pre-concentration factor of target ions by the applied sample preparation method. Hence, the recovery of target ions by the introduced solid phase extraction method was examined. For this aim, several sample volumes in the range of 25-400 mL containing 1 μg of cadmium ions was extracted by 10 mg of the synthesized tailor made sorbent. After retention of known amount of

cadmium ions by the sorbent, the target ions were removed from the recognition sites of imprinted material. According to the obtained data that presented in Figure 5S (ESM), the increasing of sample volume until 250 mL do not have any significant effect on the recovery of cadmium ions by the applied method.
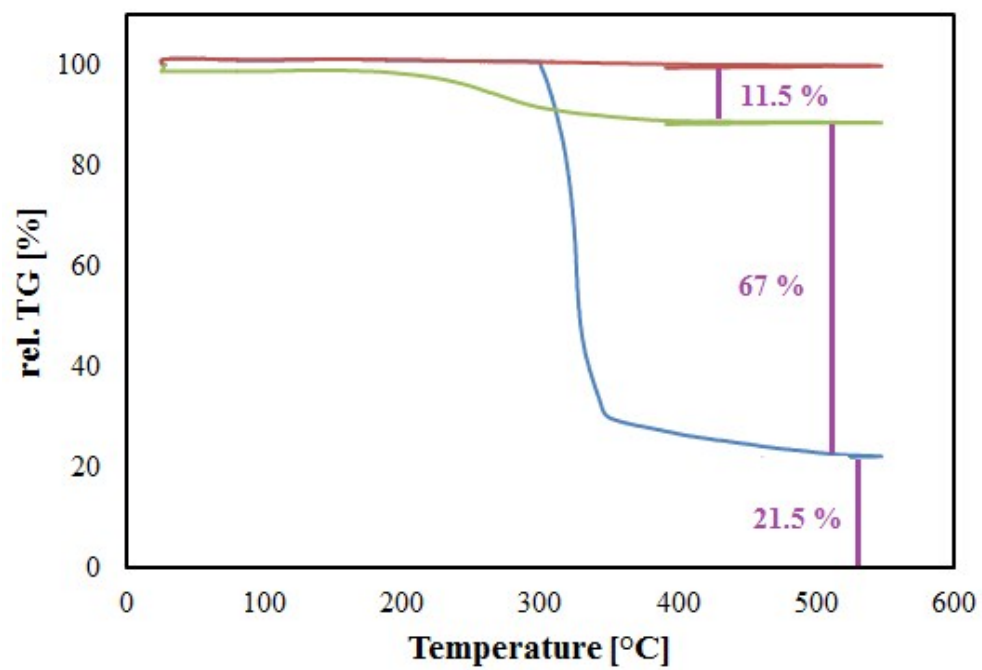
Figure 1S. XRD patterns of synthesized Fe_3O_4 and magnetic ion imprinted polymer.
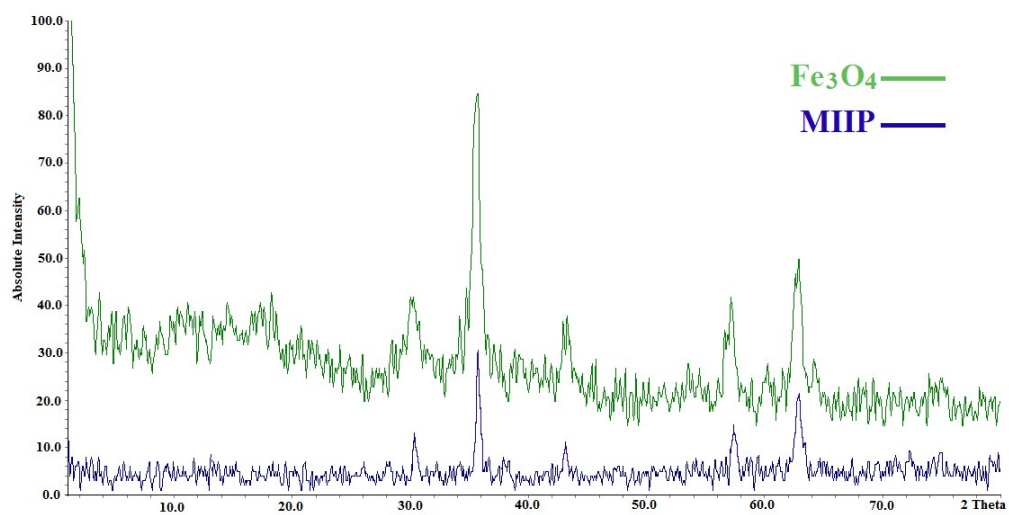
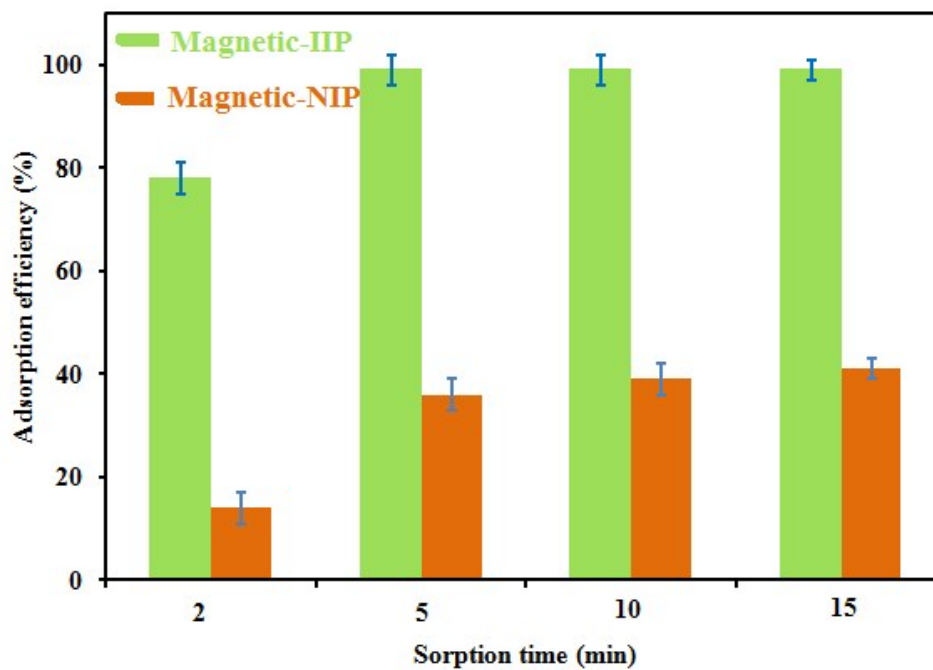**Figure 2S.** FT-IR spectra of Fe_3O_4 and leached magnetic ion imprinted polymer.
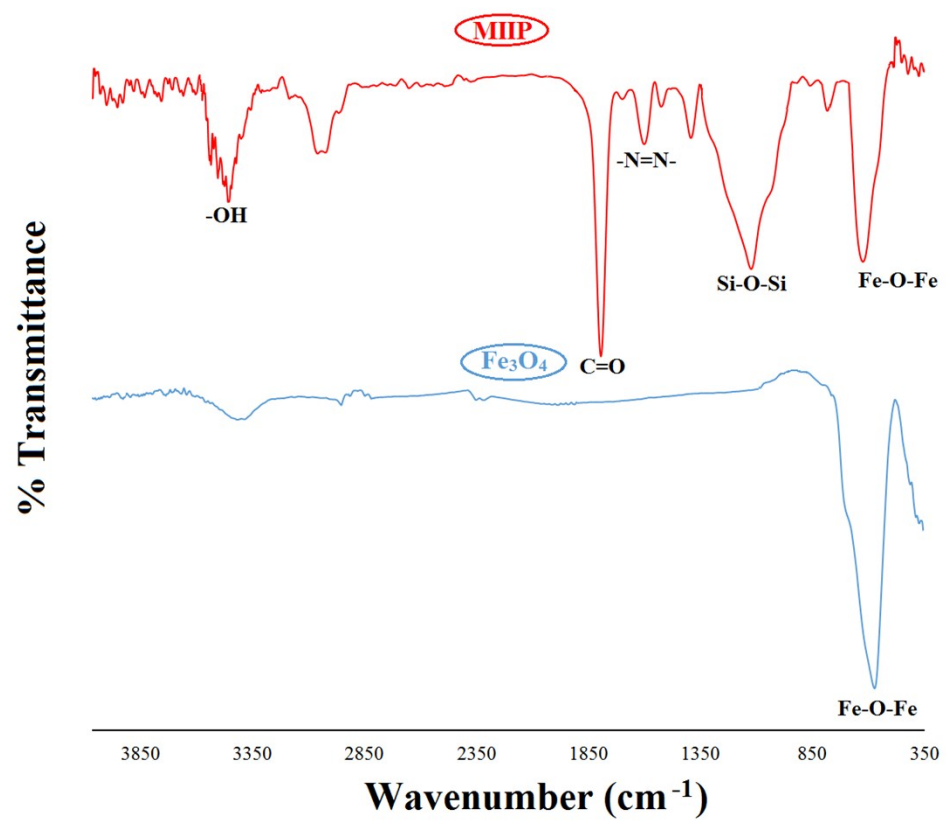
Figure 3S. Thermogravimetric analysis curves of synthesized sorbent after each step.
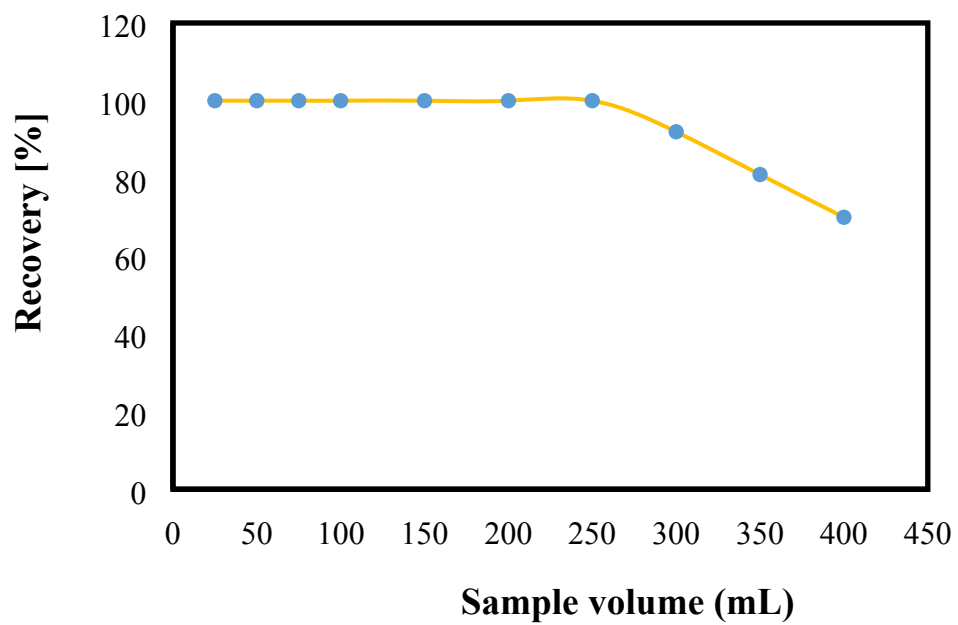
Figure 4S. The effect of sorption time on the MIIP and MNIP adsorption efficiency (%) of cadmium ions (The obtained results are the mean of three measurements).

Figure 5S. The effect of sample volume on the recovery of cadmium ions on the synthesized magnetic ion imprinted polymer nanoparticles.

Table 1S. Determination of cadmium ions in certified reference material (Validation of the proposed method).

Analyte	Certified value $(X \pm \frac{ts}{\sqrt{n}})$	Proposed procedure value $(X \pm \frac{ts}{\sqrt{n}})$	Recovery [%]
Cadmium	1.66 ±0.07	1.64 ±0.08 [a]	98.7

a) mg Kg^{-1}

$$\text{Recovery (\%)} = \left[\frac{Experimental\ value}{Certified\ value} \right] \times 100$$

Table 2S. (A) Comparison of the obtained data by the proposed method with higher sensitive instrument. (B) Optimum parameters for determination of cadmium by GFAAS (ammonium phosphate was used as the modifier agent).

A)

Sample	Cadmium concentration ($\mu g\ kg^{-1}$)	
	Proposed method	**GFAAS**
Fish	8.80	8.65
Shrimp	7.40	7.35

B)

Stage	Temprature (℃)		Time (s)	
	Start	End	Ramp	Hold
Drying	20	140	40	0
Pyrolysis	500	500	20	0
Atomization	1800	1800	0	5
Cleaning	1900	1900	0	4