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Original Research Article

Removal of toxic Tl(I) and Tl(III) ions from water sample a magnetite nanoparticle composite modified with aminodibenzo-18-crown-6 functionalized MIL-101(Cr)

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ABSTRACT

Herein, magnetic metal-organic framework nanocomposite consisting of aminodibenzo-18-crown-6 magnetite nanoparticles and MIL-101(Cr) was synthesized. The nanoadsorbent was characterized with FT-IR, VSM, SEM and XRD. The nanoadsorbent was suitable for extractive preconcentration of Tl(I) and Tl(III) ions. The total amount of thallium was then determined by reducing Tl(III) to Tl(I) by hydroxylamine hydrochloride and also extracting it. Experimental design was employed for optimizing the effective variables. Under the optimal conditions, limit of detection and relative standard deviation (%) of the developed method was as low as 1.5 ng L⁻¹, the quantification limit is 5.0 ng L⁻¹, the linear range extends from 5 to 400 ng L⁻¹, and is <12% (for n = 5 at levels of 5, 50 and 250 ng L⁻¹), respectively. Maximum sorption capacity of the sorbent for Tl(I) and Tl(III) ions was 197 mg g⁻¹. This method was utilized for analysis of a certified reference material (NIST SRM1643d water sample and to various real water samples.

Keywords: magnetite nanoparticles, limit of detection, quantification limit, preconcentration, Experimental design

Introduction

The utilization a magnetic metal-organic framework nanocomposite consisting of aminodibenzo-18-crown-6 magnetite nanoparticles and MIL-101(Cr). [1,2] and It was employed to the speciation analysis of Tl(I) and Tl(III) ions. [3–5] has devoted great attention. These materials have been widelyutilized as adsorbents in solid phase extraction (SPE) due to high surface area and adsorption capacity [1,2,6]. Nevertheless, are utilized as the SPE adsorbents some limitations can be occurred including their poor dispersibility in water media, their difficult collection from extraction media, long sample loading time and high back pressure in the case of using a packed cartridge[4]. The total amount of thallium was then determined by reducing Tl(III) to Tl(I) by hydroxylamine hydrochloride and also extracting it[2]. Fe₃O₄ nanoparticles can be modified with specific functional materials such as metal-organic frameworks (MOFs) [9], MOFs are a fascinating group of hybrid porous crystalline materials with large structural diversity and also unique properties [12, 13]. Among various MOFs, MIL-101 has been widely employed due to its very high chemical and physical stability in solution, high metal content, and excellent surface area [14]. Thallium is being released into the environment from industrial and mineral sources [17, 18] and it can penetrate the human body via inhalation or contaminated food and drinking water [18]. this study we have utilized a functionalized magnetic MIL-101(Cr) as a novel nanosorbent for the preconcentration and separation of thallium from different water samples. Modification of magnetite MIL-101 with Fe₃O₄@aminodibenzo-18-crown-6 nanoparticles led to its selectivity toward Tl(I) ions and also facilitated magnetic separation of the sorbent from extraction media.

Experimental

Materials

All reagents including

FeCl₃, (NH₄)₂Fe(SO₄)₂·6H₂O, Cr(NO₃)₃·9H₂O (≥98%), HCl, HNO₃, NaOH, H₂SO₄, (3-chloropropyl)triethoxysilane (CPTES, ≥98%), terephthalic acid (28% w/w), tetraethyl orthosilicate (TEOS, ≥99%), triethylamine (TEA, ≥98%), hydroxylamine hydrochloride (≥99%), 4'-aminodibenzo-18-crown-6 (ADB18C6, ≥98%), acetone, methanol (≥99%) and ethanol (97%) were of analytical grade and purchased from Merck (Darmstadt, Germany, or Fluka (Seelze, Germany). Standard solutions of 1000 mg L⁻¹ of Tl(I) and Tl(III) were purchased from Merck. All working solutions were prepared using deionized water. Standard solutions of potentially interfering ions were prepared in 2% (v/v) HNO₃ solution. The working solutions

were prepared by diluting an appropriate amount of the stock solution with deionized water. All of these solutions were stored at ambient temperature prior to use.

Instrumentation

Determination of thallium species was conducted by an AA220 Varian Spectra instrument equipped with a graphite furnace atomizer (GTA-110) and an ASC-6100 auto sampler (Varian Company, USA,) with a deuterium background corrector. A thallium hollow cathode lamp with wavelength of 276.8 nm, slit width of 0.7 nm and a lamp current of 10.0 mA was used. A pyrolytic graphite coated graphite tube was used too. In all tests, the injection volume was 20 μL . A solution consisted of 300 mg L^{-1} $\text{Mg}(\text{NO}_3)_2$ and 1200 mg L^{-1} $\text{Pd}(\text{NO}_3)_2$ was used as chemical modifier. The operation conditions of ETAAS are tabulated in Table 3(Electronic Supplementary Information). High purity argon (99.995%) was utilized as protective and purges gas. The pH of the solutions were measured at 25 ± 1 $^{\circ}\text{C}$ with a digital Metrohm 827 pH meter (Herisau, Switzerland) equipped with a combined glass-calomel electrode. (Karlsruhe, Germany). X-ray diffraction (XRD) pattern was obtained with a Philips-PW12C diffractometer (Amsterdam, the Netherlands) using $\text{Cu K}\alpha$ radiation. A Bruker IFS-66 FT-IR Spectrophotometer was employed for FT-IR spectra recording. Scanning electron microscopy (SEM) was conducted using an SEM (KYKY-3200, Zhongguancun Beijing, China) instrument. Magnetic properties of nanocomposites were measured by a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature in a magnetic field strength of 1 Tesla.

Synthesis of the nanocomposite

Synthesis of the magnetic nanocomposite

Synthesis of aminodibenzo-18-crown-6 functionalized Fe_3O_4 nanoparticles The synthesis of functionalized Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{ADB18C6}$ NPs) was performed based on our previous works with some modifications and the related data are included in Electronic Supplementary Materials [26]. The synthesis $\text{Fe}_3\text{O}_4@\text{ADB18C6}$ NPs was confirmed by FT-IR spectroscopy, VSM and SEM techniques. A schematic representation of this synthesis is exhibited in Fig. 1a. Synthesis of the MIL-101(Cr)/ $\text{Fe}_3\text{O}_4@\text{ADB18C6}$ NPs composite Briefly, 2.0 mmol H_2BDC was dissolved in 50 mL of deionized water and sonicated for 10 min (mixture A). Then, 0.5 g $\text{Fe}_3\text{O}_4@\text{ADB18C6}$ NPs was suspended in a solution containing 50 mL deionized water and 2.0 mmol $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (mixture B). In the next step, two

mixtures (A and B) were transferred into an autoclave and it was heated at 220 °C for 16 h [19]. Finally, MIL-101(Cr)/ Fe₃O₄@ADB18C6 NPs composite was recovered from the supernatant solution by magnetic decantation and washed with water (4 × 30 mL) and ethanol (4 × 25 mL), respectively and dried at room temperature. The nanocomposite was characterized by FT-IR spectroscopy, VSM, high-angle XRD, and SEM.

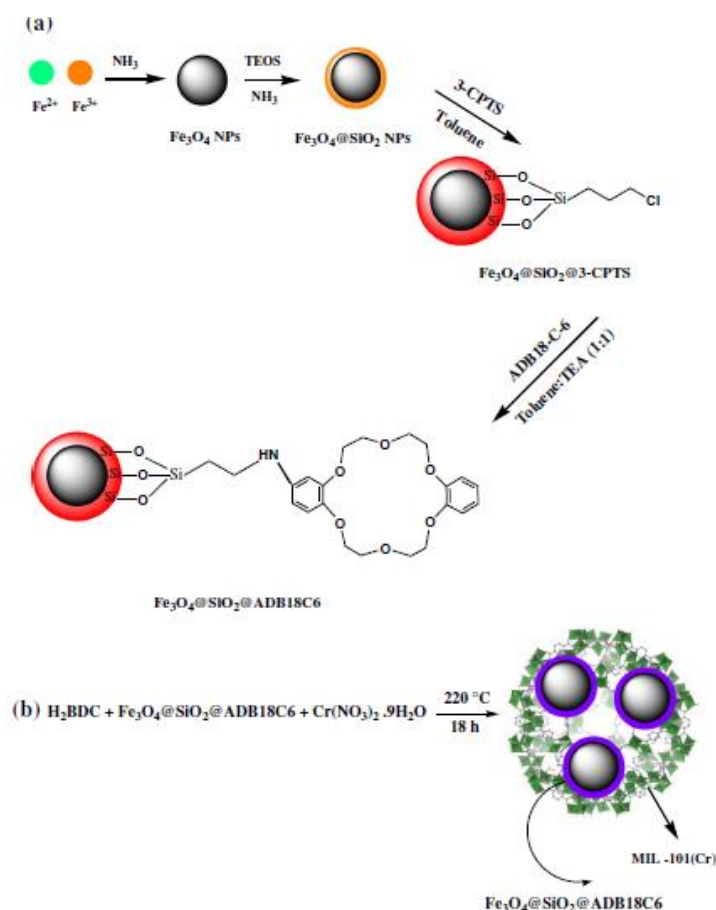


Figure 1, A schematic representation for synthesis of (a)Fe₃O₄@ADB18C6 NPs and (b)for the synthesis of MIL-101(Cr)/Fe₃O₄@ADB18C6Nanocomposite

Experimental design methodology

The effect of experimental variables, their interaction along with nonlinear interactions on the extraction performance was investigated using experimental design approach. A rational experimental design allows concurrent variation of all experimental variables, reduces the test time and number of trials which ends in the reduction of the overall required costs. Box-Behnken design (BBD) is perhaps the most widely used experimental design method employed for fitting a second-order response surface. BBD is a spherical, rotatable, or nearly

rotatable second-order design and consists of linear, quadratic and interaction terms [17]. The precise optimum value can be achieved with the aid of response surface methodologies illustrating a graphical relationship between variables and responses [18].

In this study the StatGraphics plus 5.1 package was used for the analysis of experimental design data and calculating the predicted responses.

Results and discussion

Characterization studies

The FT-IR spectrum of MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 was recorded using KBr pellet method, Figure 2. The absorption peaks appeared at C-H aliphatic (29,500 cm⁻¹), C=C (1610 cm⁻¹), N-H (3350 cm⁻¹), OC-O (1150 cm⁻¹), Fe-O (580 cm⁻¹) and Si-O-Si (1035 cm⁻¹) confirmed the presence of PAT on the surface of MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 and successful synthesis of the nanocomposite.

The XRD pattern of MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 is shown in Figure 3. In the pattern, seven characteristic diffraction peaks appeared at $(2\theta) = 91/1^\circ, 92/11^\circ, 99/7^\circ, 112/2^\circ, 99/1^\circ$ Bragg diffractions of face centered cubic structured Fe₃O₄ @ ADB18C6, were observed. The morphology and dimension of MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 was explored by SEM imaging. The SEM image of nanocomposite (Figure 4a) depicted that Fe₃O₄ NPs with an average size of 55 nm were coated on the surfaces of GO nanosheets. Moreover, it is revealed that Fe₃O₄ NPs have grown on the surface of GO and well distributed, so the aggregation problem of MNPs is almost solved by employing GO as a support and spacer. The magnetic properties of MIL-101 (Cr), and MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 were investigated by VSM method and the corresponding plots are illustrated in Figure 4b. As exhibited in Figure 2b, the saturation magnetization of MIL-101 (Cr), and MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 was 62,31 and 39 emu g⁻¹ respectively, which is desirable for magnetic separation with a common magnetic field. For superparamagnetic composite, when the external field is zero the magnetization became zero. The hysteresis plot of all the mentioned composites passed through the zero point of magnetization and illustrated a superparamagnetic property.

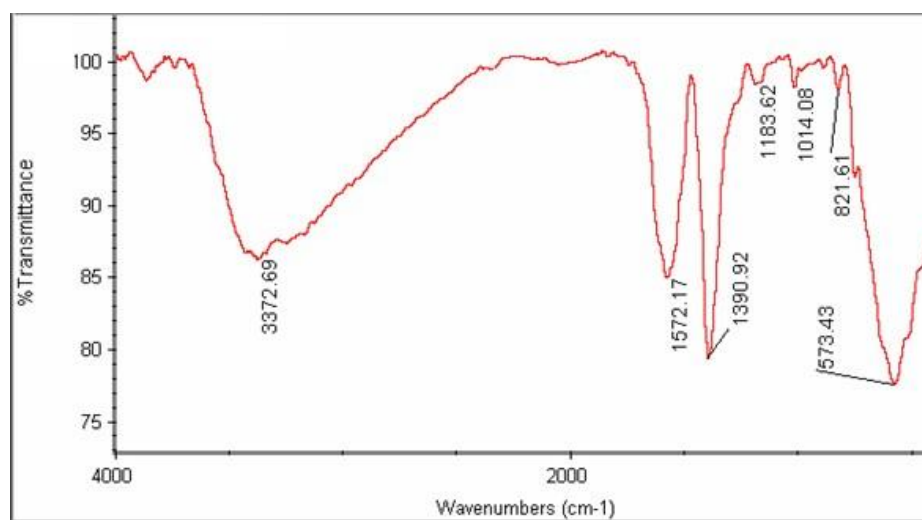


Figure 2, FT-IR spectrum of MIL-101 (Cr) / Fe₃O₄ @ ADB18C6

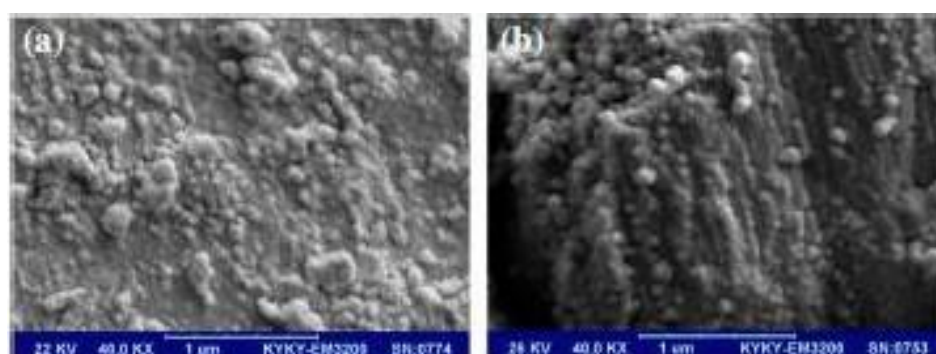


Figure 3, The SEM images of (a) Fe₃O₄@ADB18C6 and (b) MIL-101(Cr)/Fe₃O₄@ADB18C6 nanocomposite

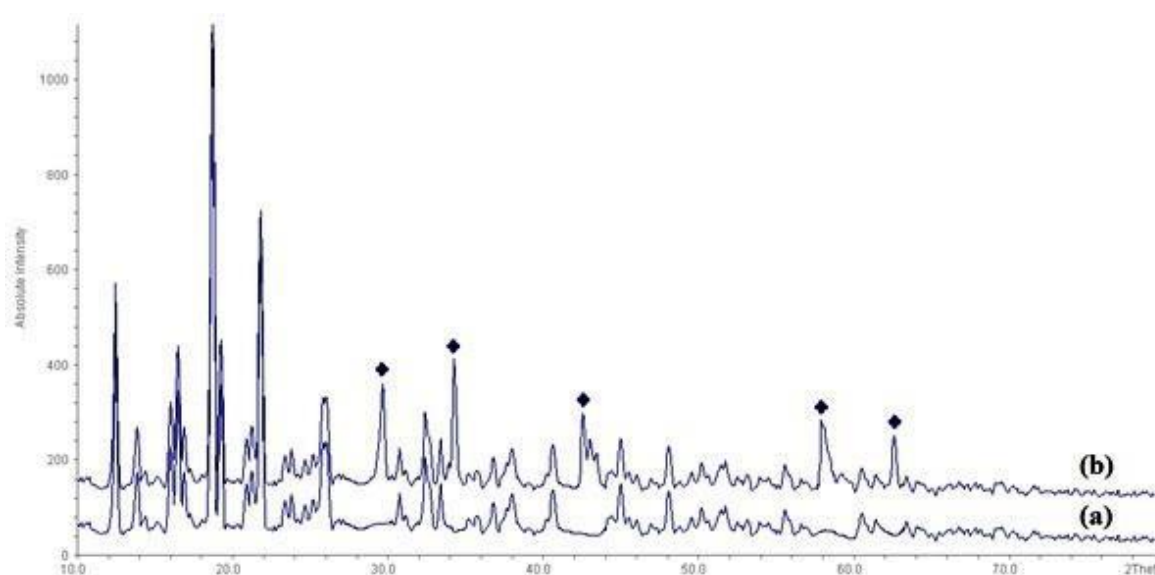


Figure 3, XRD pattern

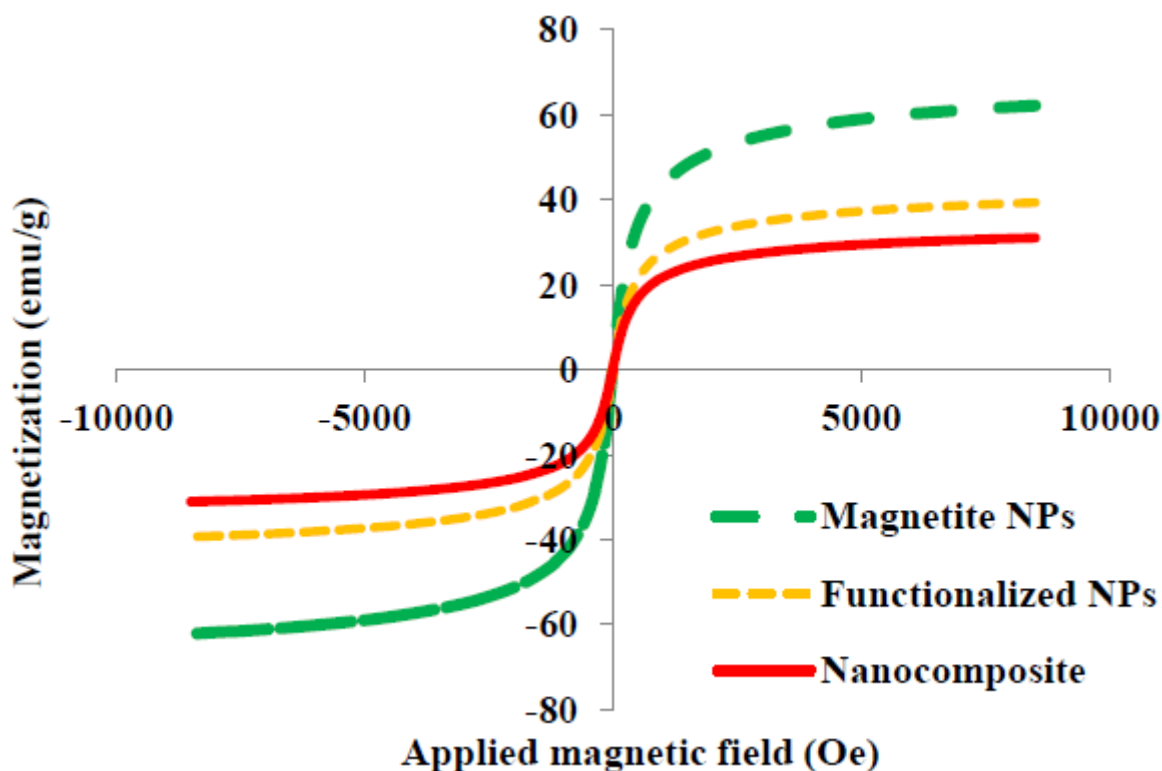


Figure 4, vibrating sample magnetometry plots of Fe₃O₄ NPs, Fe₃O₄@ADB18C6 NPs and MIL101(Cr)/Fe₃O₄@ADB18C6 nanocomposite

Optimization of uptake parameters

Box-Behnken design (BBD) was conducted to find the best conditions for uptake of Cr(VI) ions on the magnetic nanosorbent. pH of sample, sorption time and MIL-101 (Cr), and MIL-101 (Cr) / Fe₃O₄ @ ADB18C6 amount were selected and optimized in this step. The concentration of Tl(I) and Tl(III) (5.0 mg L⁻¹) was kept constant.

The number of experiments (N) in BBD is defined by the following expression:

$$N = 2K(K - 1) + C_0 \quad \text{Eq. 2}$$

Optimization of the preconcentration procedure

Sorption step

The optimization of the affecting parameters was conducted using a Box-Behnken design (BBD). The following parameters were optimized in sorption step: (a) sample pH value; (b) sorption time; and (c) nanosorbent amount. Respective data and figures are given in the

Electronic Supporting Material, Table 1. The following experimental conditions were found to give best sorption efficiency: (a) sample pH, 6.7; (b) sorption time, 15.5 min; and (c) nanocomposite amount, of 20.0 mg.

Table 1. Experimental parameters and their levels in the Box Behnken design for uptake of Tl(I) and Tl(III) ions.

		Level		
		Lower	Central	Upper
Sorption step	A: pH	3.0	5.5	8.0
	B: Sorption time(min)	7.0	16.0	25.0
	C: Sorbent amount (mg)	10.0	25.0	40.0

Elution step

The following parameters were optimized in elution step (a) elution time (b); eluent type and its concentration; (b) and eluent volume. Respective information are given in the Electronic Supporting Material, Table 2. As a result, the following experimental conditions were found to give best results: (a) elution time, 11.0 min, (b) 1.0 mol L⁻¹ HCl as the eluent; and (c) eluent volume, 0.7 mL.

Table 2. Experimental parameters and their levels in the Box Behnken design for uptake of Tl(I) and Tl(III) ions.

		Level		
		Lower	Central	Upper
Elution step	A: Eluent time (min)	5.0	10.0	15.0
	B: Eluent concentration (mol/L)	0.2	0.85	1.5
	C: Elution volume (mL)	0.2	0.6	1.0

Conclusion

In this work, magnetic metal-organic framework nanocomposite MIL101(Cr)/Fe₃O₄@ADB18C6 was synthesized and employed as a viable sorbent for removal of Tl(I) and Tl(III). The developed removal method was simple, fast and reliable. The magnetic metal-organic framework nanocomposite with the polymer coating led to its chemical stability in hard acidic medium and enhanced its selectivity towards Tl(I) and Tl(III) ions.

This new sorbent exhibited the advantages of high sorption capacities (197 mg g^{-1}), and fast extraction dynamic (11.0 min) compared to previously reported methods, Table 3. Owing to high surface area of the nanocomposite, satisfactory results can be obtained using fewer amounts of the sorbent (10 mg).

Table3 .Comparison of the sorption capacity of the new nanosorbent with those of the other reported sorbents.

Method	Instrument	LOD ^a	LR ^b	PF ^c	Ref.
MIL-101(Cr)/Fe ₃ O ₄ @ADB18-C-6 nanocomposite Modified magnetic halloysite nanotubes Fe ₃ O ₄ - modified graphene oxide-DLPMed Online microcolumn with immobilized oxine Ion-imprinted polymer Multiwalled carbon nanotubes Single drop microextraction Ion-imprinted polymer Titanium dioxide nanoparticles Chromosorb 105 resin	ETAAS ETAAS ETAAS FAAS FAAS ETAAS ETAAS ETAAS ETAAS ETAAS	1.5	0.0015-0.4	857	This
		1.8	0.007-0.435	275	[20]
		12	0.015-4	6500	[21]
		2500	20-200	77	[22]
		1500	10-700	125	[23]
		9.0	-	20	[24]
		700	3-22	50	[25]
		20	1-600	100	[26]
		87	0.6-2.5	100	[27]
		34-50	0.034-0.8	150	[28]

^a ng L⁻¹

^b Linear range ($\mu\text{g L}^{-1}$)

^c Preconcentration factor

^d Dispersive liquid phase microextraction

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