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Original Research Article

Fabrication and Characterization of a Novel Magnetic MIL-101(Cr) Nanocomposite for Selective Selenite Removal

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ABSTRACT

Herein, a novel magnetic composite consisting metal-organic framework was fabricated and applied as a sorbent for selenite ions removal (Se (IV)) from water samples. The sorbent made from a metal-organic framework (MIL-101(Cr)) as a selective receptor and modified magnetite nanoparticles@amino dithiocarbamate (MNPs@ADTC) as the magnetic core. Se (IV) ions were selectively absorbed into MIL-101(Cr)/MNPs@ADTC at lower pH (1.85), while Se (VI) ions remained in the initial solution. Optimization of the parameters that affect the removal efficiency was carried out by experimental design method. Three parameters such as adsorption time, MIL-101(Cr)/MNPs@ADTC dosage, and sample pH were considered as affecting factors and the optimum value for these factors was as following: pH, 1.85; adsorption time, 14.0 min; and (c) MIL-101(Cr)/MNPs@ADTC dosage, 16.0 mg. Afterwards, the equilibrium sorption data were studied using Langmuir and Freundlich models. The mechanism for adsorption of Se (VI) ions onto MIL-101(Cr)/MNPs@ADTC was found to follow Langmuir models. Accordingly, maximum adsorption capacity and Langmuir constant were 222 mg g⁻¹ and 0.41 L mg⁻¹, respectively. Finally, adsorption kinetic was evaluated by use pseudo first/second order models and the obtained data revealing a pseudo second order model based on the correlation coefficient.

Keywords: Selective removal; Selenate; Magnetite composite; MIL-101(Cr); Langmuir model.

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Introduction

Magnetic nanoparticles (NPs) have attracted considerable attention recently for the removal of various classes of compounds. The modification of magnetic nanoparticles with different functional groups is a rational strategy to the selective removal of the target compound from the medium [1-3]. Fe₃O₄ NPs, as the most used magnetic nanoparticles, are usually functionalized to get better their selectivity and high uptake capability toward the target compound [4]. Functionalization of Fe₃O₄ NPs can be reached through different functional materials for example; conducting polymers, molecularly imprinted polymers, grapheme oxide, inorganic materials and metal-organic frameworks (MOFs) [5-8]. In particular, MOFs, as the highly porous materials, are appeared as a new type of microporous materials (pore sizes < 2 nm). Among various MOFs, MIL-101 has demonstrated great potential for many applications especially in the analytical field because of its high surface area, very high chemical and physical stability in aqueous solution, and high metal content [9, 10]. The predominant chemical states of selenium as inorganic forms including of Se(IV) and Se(VI) or as organic species for example diethyl selenide, dimethyl diselenide and dimethyl selenide, determines the toxicity and bio-availability [11]. Generally, inorganic selenium forms are more hazardous than its organic species. Thus, highly efficient removal methodologies are required [12].

Herein, a new composite consisting of magnetic NPs and MOFs was fabricated and employed as selective sorbent for selenate removal (Se (IV)) from aqueous sample. The composite made from MIL-101(Cr) as a MOF and magnetite nanoparticles@amino dithiocarbamate (MNPs@ADTC) as the modified magnetic core. Solution pH, amount of MIL-101(Cr)/MNPs@ADTC and adsorption time were considered as affecting parameters and optimized in details. Also, the adsorption behavior of sorbent was assessed using Freundlich and Langmuir isotherms. In addition, adsorption kinetic was explored by use using pseudo first and pseudo second order models. Ultimately, the sorbent combined with ETAAS was employed for the removal and determination of selenium in water and agricultural samples.

Experimental

Reagents and chemicals

Prior to use, all glassware were first washed with HNO₃ and further rinsed with purified water. FeCl₃, Cr(NO₃)₂ .9H₂O, CS₂, (NH₄)₂Fe(SO₄)₂.6H₂O, HNO₃, NaOH, (3-chloropropyl)-triethoxysilane (3-CPTES), terephthalic acid (BDC), tetraethyl orthosilicate, terephthalic acid and tris(2-aminoethyl)amine were obtained from Fluka (Seelze, Germany) and Merck (Darmstadt, Germany). Organic solvent used for synthesis and modification were of analytical grade and used without purification.

Instrumentation

The determination of selenate was conducted on Varian Spectra model AA 220 with a graphite furnace atomizer (GTA-110) (Varian Company, USA). A selenium hollow-cathode lamp (as a radiation source) at a wavelength of 196.0 nm that was operated at 12 mA with a spectral bandwidth of 2.0 nm. Other operating parameters were adjusted as proposed by the manufacturer. The pH of solutions was adjusted with a digital Metrohm 827 pH meter (Herisau, Switzerland) equipped with a combined glass-calomel electrode. Magnetization curves of the fabricated composite were recorded using a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) in a magnetic field strength of 1 Tesla. X-ray diffraction (XRD) pattern was accomplished by a Philips-PW 12C diffractometer (Amsterdam, the Netherlands) with use Cu K_{α} radiation. The elemental composition was determined using the on a Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK). Scanning electron microscopy (SEM) images was obtained using an SEM (KYKY-3200, Zhongguancun Beijing, China) microscope. All the experiments were performed at room temperature.

Synthesis of modified magnetite nanoparticles@amino dithiocarbamate

The synthesis of magnetite NPs were performed by chemical oxidation according to the previously published literatures [13, 14]. In the next step, the Fe₃O₄@SiO₂ NPs nanocomposite was prepared by chemical reaction according to the following procedure. Briefly, 1.0 g of synthesized Fe₃O₄ NPs was dispersed in a mixture solution of 4 mL of 28% NH₄OH, 250 mL distilled water and 75 mL alcohol. Then, the reaction was contained by slow addition of 3.0 mL TEOS under vigorous stirring [13]. The reaction was accomplished for 10 h stirring at 40°C. The Fe₃O₄@SiO₂ NPs were collected by an external strong magnetic field (1.4 T), washed twice times with purified water and ethanol and then dried at ambient temperature [14]. Then, 1.0 g of prepared Fe₃O₄@SiO₂ NPs was suspended in 100 mL purified toluene, and mixed well for 1 hour. 1.0 mL 3-CPTES was then

dissolved in the dispersed solution and it was refluxed for 15 h. The black precipitate was removed from the medium reaction by a permanent magnet and washed two times with ethanol and acetone. The isolated Fe₃O₄@SiO₂@CPTES magnetic NPs were then dried at 50 °C in vacuum. Then, the Fe₃O₄@SiO₂@CPTES particles were coated with tris (2-aminoethyl) amine (TAEA) to afford Fe₃O₄@SiO₂@TAEA NPs. Typically; Fe₃O₄@SiO₂@CPTES (1.0 g) was suspended in 100 mL of triethylamine and toluene mixture (1:1 v/v) by ultra-sonication. After that, 2.0 mL of tris(2-aminoethyl) amine was added slowly to the above suspension and refluxed for 24 h. Subsequently, the particles (Fe₃O₄@SiO₂@TAEA) were rinsed two times with ethanol and dried at room temperature. Finally, 2 mL NaOH (1.0 mol L⁻¹) and 5.0 mL CS₂ was added into a dispersion of 1.0 g Fe₃O₄@SiO₂@TAEA in 100 mL 2-propanol, which had been treated ultrasonically. The resulting solution was stirred at room temperature for 6 h and dried at 50 °C in vacuum.

Synthesis of nanocomposite

The synthesis route of nanocomposite was illustrated in figure 1b. Typically, Fe₃O₄@AAADTC NPs (0.5 g) was dispersed in a solution of chromium (III) nitrate.9H₂O (2 mmol) in 50 mL deionized water (Solution A). 2 mmol BDC was added in 50 mL of distilled water and mixed well by vigorous stirring for 20 min (Solution B). After that, solution A and B were placed into an autoclave and followed by heating at $180\,^{\circ}$ C for 25 h. Consequently, the black particles were isolated from the supernatant solution by magnetic decantation and were rinsed subsequently three times with ethanol and purified water, respectively, and dried at 50 °C in vacuum.

Extraction procedure

The procedure for the magnetic solid phase extraction (MSPE) of selenite ions was according to the following steps: a series of 50 mL of 0.5 µg L⁻¹ aqueous solution of Se (IV), adjusted to pH 1.85 using hydrochloric acid solution (0.1 M), was placed in suitable test tubes. In order to removal Se (IV) ions, 16.0 mg of the nanocomposite was added to the test tubes and stirred mechanically for 14 min to facilitate adsorption of Se (IV) ions onto the nanocomposite. Then the nanocomposite was isolated from the solution by using the external strong magnet. Finally, an aliquot of solution was introduced into ETAAS instrument to determine the adsorbed amount of Se (IV) ions onto the nanocomposite.

Equilibrium and kinetic study

Static equilibrium binding and kinetic analysis was explored in order to investigate the binding performance of the MIL-101(Cr)/Fe₃O₄@AADTC nanocomposite. The Se (IV) solutions at different concentrations with 16 mg MIL-101(Cr)/Fe₃O₄@AADTC nanocomposite were put into a test tube. The pH of solution was adjusted to 1.85 and the mixture was shaken 14.0 min to facilitate the adsorption of Se (IV) ions onto the MIL-101(Cr)/Fe₃O₄@AADTC nanocomposite. After magnetic separation, the adsorbed amounts of Se (IV) ions by the MIL-101(Cr)/Fe₃O₄@AADTC nanocomposite were calculated by subtracting the residual Se (IV) ions from initial ions by ETAAS analysis.

Results and discussion

Characterization of the sorbent

FT-IR, CHNS analysis, SEM, VSM and XRD were applied to investigate the chemical bonds, elemental analysis size, magnetic properties and morphology of the prepared nanocomposite. FT-IR spectrum was obtained for the prepared MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite to certain the synthesis of nanocomposite. The characteristic absorption bands at 2930 cm⁻¹, 1458 cm⁻¹, 3372 cm⁻¹, 821 cm⁻¹, 573 cm⁻¹ and 1014 cm⁻¹ which attributed to the C-H aliphatic, C=C, N-H, C=S, Fe-O, Si-O-Si stretching vibrations, respectively, ensuring the preparation of MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite (Figure 1).

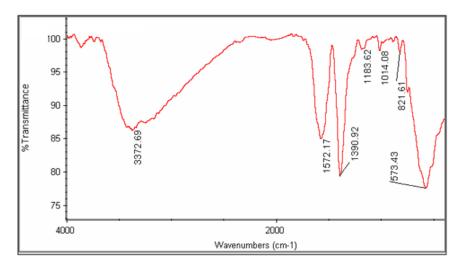


Figure 1: FT-IR spectrum of MIL-101(Cr)/MNPs@ADTC nanocomposite.

In order to elemental composition of MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite, the CHNS analysis was done. The obtained results shows the existence of C (30.1%), H (1.8%), N (3.2%) and S (4.0%) in the structure of the MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite which confirm that MIL-101(Cr) nanocomposite was efficiently modified with Fe₃O₄@ADTC NPs.

The surface morphology of modified MNPs and MIL-101(Cr)/Fe₃O₄@ADTC was examined by SEM images. As depicted in Figure 2a, Fe₃O₄@ADTC NPs are spherical shape with the average size of 45 nm. Figure 2b shows that the surface of MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite is not smooth due to its functionalization with Fe₃O₄@ADTC NPs.

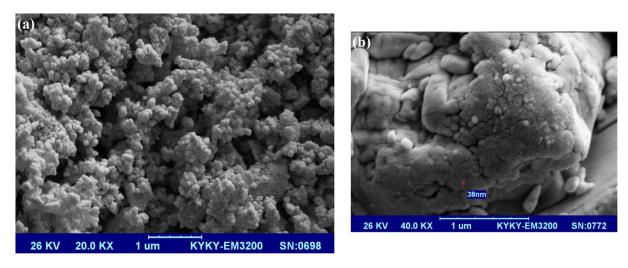


Figure 2: SEM images of (a) MNPs@ADTC and (b) MIL-101(Cr)/MNPs@ADTC nanocomposite.

It should be noted that the magnetic adsorbent must have sufficient magnetic strength to facilitate fast separation under an external magnetic field. VSM analysis was applied to explore the magnetic properties of Fe₃O₄ nanoparticles, Fe₃O₄@ADTC NPs and MIL-101(Cr)/Fe₃O₄@ADTC. The saturation magnetization intensity of Fe₃O₄ NPs, Fe₃O₄@ADTC NPs and MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite were 64, 48 and 30 emu g⁻¹, respectively, as illustrated in Figure 3. Those amounts are sufficient to achieve a magnetic isolation with a conventional magnet in MSPE [14].

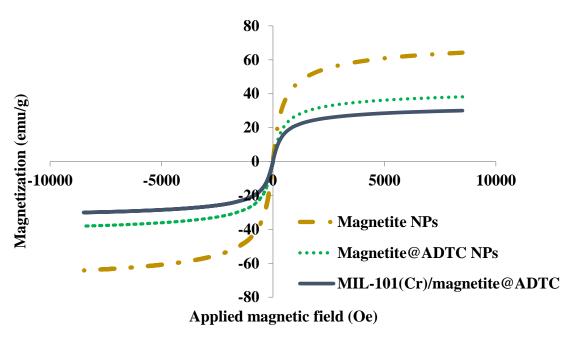
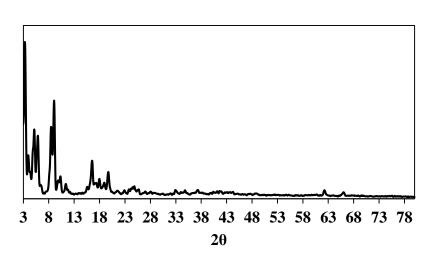


Figure 2: VSM curves of the nanosorbents.

Figure 4 illustrates the XRD patterns of MIL-101(Cr) and MIL-101(Cr)/Fe₃O₄@ADTC nanocomposite. As depicted in this figure, the diffraction intensities of the MIL-101 framework were decreased which can be originated of grafting of Fe₃O₄@ADTC NPs on the MOF surface. In addition, the characteristic peaks of Fe₃O₄@ADTC NPs and MIL-101(Cr) were observed in the XRD pattern of magnetic MIL-101(Cr), implying that the nanocomposite was consisted of magnetic nanoparticle and the MOF.

(a)



(b)

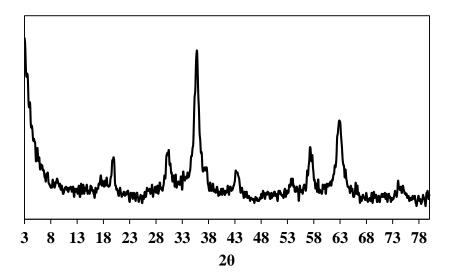


Figure 4: The XRD patterns of (a) MIL-101(Cr) and (b) MIL-101(Cr)/MNPs@ADTC nanocomposite.

Optimization of the uptake parameters

The experimental design methodology enables the analyst to specify the best optimum points with minimum numbers of test, experimental cost and time. Thereby, the predominant factors affecting the removal efficiency of the proposed procedure were investigated and optimized by means of Box-Behnken design (BBD). The experiments were performed randomly in order to minimize the effect of uncontrolled parameters. The exact optimum value of variable can be attained with the using of response surface methodology (RSM) illustrating graphically relationships between affecting factors and experimental responses [15-17]. Also, the interactions of variables and the curvature among experimental variables were evaluated.

In this regards, the most affecting parameter on the removal Se (IV) ions including; solution pH, sorbent dosage and uptake time were selected and optimized in details. The number of trials (N) is obeying the following expression:

$$N=2K(K-1)+C_0$$

where K is the number of variables to be optimized and C_o is the number of central points [18]. To this aim, three parameters including; the pH of sample solution, sorbent dosage and uptake time

were selected, therefore, K is 3. Moreover, a value of five for C_o was set to obtain a good estimate of pure error sum of squares. Hence, in total seventeen trails should be performed. Table 1 shows the levels of each factor in BBD model.

Table 1: Experimental variables and levels of the Box Behnken design (BBD).

	Level		
	Lower	Central	Upper
A: pH	1.0	1.5	2.0
B: Sorption time (min)	4.0	9.0	14.0
C: Sorbent amount (mg)	10.0	15.0	20.0

F-value for the model obtained 258.52 (p-value < 0.0001) and indicated that the fitted model is significant. There is only a 0.01 % chance that a model with this F-value could happen because of noise signal. As can be seen in Table 2, the p-value of the lack of fit (LOF) in the ANOVA analysis achieved equal to 0.1004 that indicates the LOF is not significant relative to the pure error [19].

Table 2: The ANOVA table.

	Sum of		Mean		p-value
Source	Squares	df	Square	F-Value	Prob > F
Model	4398.33	9	488.70	258.52	< 0.0001 Significant
A	1617.88	1	1617.88	855.86	< 0.0001
B-	350.45	1	350.45	185.39	< 0.0001
C-	42.69	1	42.69	22.58	0.0021
AB	2.28	1	2.28	1.21	0.3083
AC	0.12	1	0.12	0.065	0.8054
BC	7.56	1	7.56	4.00	0.0856
A^2	1464.13	1	1464.13	774.52	< 0.0001
\mathbf{B}^2	229.79	1	229.79	121.56	< 0.0001
\mathbb{C}^2	133.82	1	133.82	70.79	< 0.0001
Residual	13.23	7	1.89		
Lack of Fit	10.03	3	3.34	4.18	0.1004 Not-significant
Pure Error	3.20	4	0.80		-
Cor Total	4411.56	16			

The values for R-squared, adjusted R-squared and predicted R² were above 0.9. This result implies the data fitted adequately to suggested models. Arising from interpretation of results, the sample pH was the most significant positive parameter affecting on the removal of Se (IV) ions. This indicates that the pH of solution affecting the formation of complexes and the subsequent removal

of ions. Figure 5 depicts the response surface plots for the analysis of simultaneous effects for the uptake.

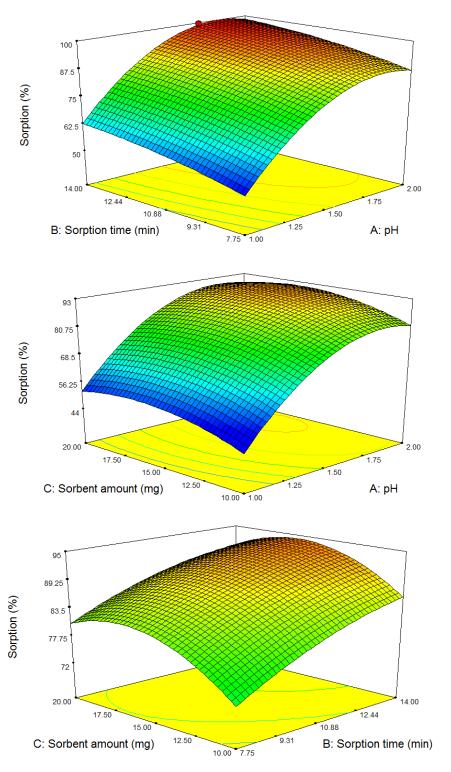


Figure 5: Response surface plots of the optimization.

Based on the optimization study, the best experimental conditions for the most removal of Se (IV) ions were as pH, 1.85; nanocomposite dosage, 16 mg, uptake time, 14.0 min.

Equilibrium and kinetic study

The adsorption assay was accomplished to study the adsorption capacity of MIL-101(Cr)/MNPs@ADTC toward Se (VI) ions. For this aim, linear form of Langmuir and Freundlich isotherms were employed. At first, the adsorbed amounts of Se (VI) ions at different initial concentrations were determined by the following equation:

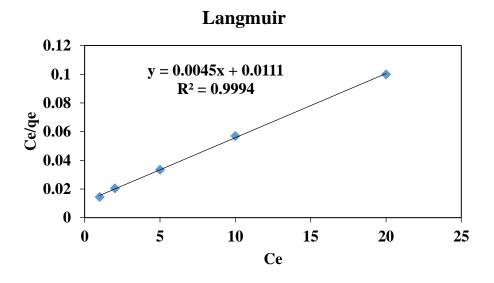
$$q_e = \frac{V}{W}(C_0 - C_e) \tag{4}$$

Where q_e is the adsorbed amount of Se (VI) (mg g⁻¹), V represents the total volume of mixture (L), W is MIL-101(Cr)/MNPs@ADTC mass (g), C_e and C_0 are the final and initial concentrations of Se (VI) (mg L⁻¹) in the sample, respectively. Equation (5) and (6) represent the linearized form of Langmuir and Freundlich isotherms, respectively [20-23]:

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{k_L q_{\text{max}}} \frac{1}{C_e}$$
 (5)

$$Log \ q_e = Log \ K_F + \frac{1}{n} Log \ C_e \tag{6}$$

 Q_{max} is the maximum adsorbed amount of Se (VI) per grams of MIL-101(Cr)/MNPs@ADTC and k_L is the Langmuir constant. In equation (6), q_e is the adsorbed amount of Se(VI) (mg) on MIL-101(Cr)/MNPs@ADTC (g), C_e is the equilibrium concentration of Se(VI), and K_F and 1/n are empirical constant values that are related to the parameters affecting the adsorption process [20]. The results exhibited that the adsorption of Se(VI) ions on MIL-101(Cr)/MNPs@ADTC is fitted good to the Langmuir model rather than Freundlich model owing to the higher correlation coefficient ($R^2_{Langmuir} = 0.9994$, $R^2_{Freundlich} = 0.9858$) (Figure 6).



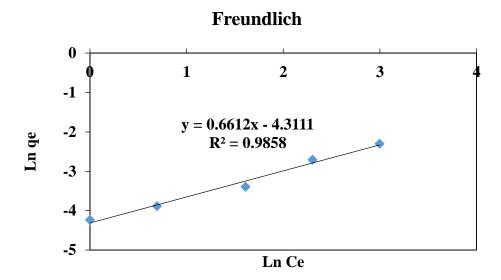
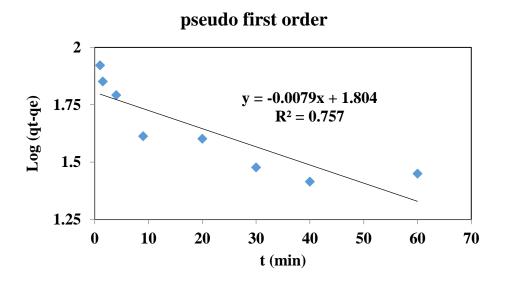


Figure 6: The linear plots of Langmuir and Freundlich models.

Accordingly, q_{max} (mg/g) and the Langmuir constant value calculated which were 222 and 0.405 L mg⁻¹, respectively. In order to explore the kinetic mechanism of the adsorption process in the adsorbent, the experimental data were fitted by two kinetic models. Accordingly, Lagergren pseudo first-order and pseudo second-order models were employed (Figure 7). The dynamic assay was accomplished (1-60 min, 25 mg L⁻¹) to explore the kinetic mechanism. The kinetic data were well fitted to pseudo-second order kinetic model owing to the higher correlation coefficient ($R^2_{first-order} = 0.7570$, $R^2_{second-order} = 0.9992$). Accordingly, the rate constant of adsorption (k_{ads}) was

determined that was 99.0 g mg⁻¹. min⁻¹ and indicates a second-order kinetic model [22]. It is clear that the pseudo second order kinetic model achieved a good correlation adsorption of Se (VI) ions onto nanocomposite compared with pseudo first-order models.



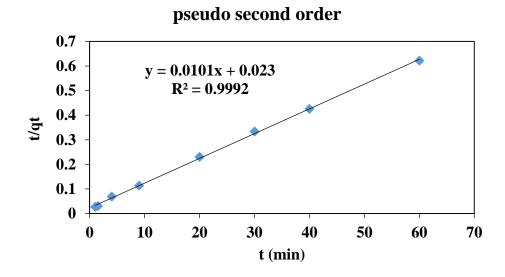


Figure 7: The linear plots of pseudo-first and pseudo-second order kinetic models.

Conclusion

In conclusion, a novel sorbent comprising of MNPs@amino dithiocarbamate nanoparticles and MIL-101(Cr), was prepared by simple and facile route and employed as a MSPE sorbent for selenate removal. The presence amino dithiocarbamate functional groups and magnetic

nanoparticles on the surface of sorbent cause the selective and fast removal of Se (IV) ions from matrix solution. The magnetic features of the nanoadsorbent facilitates the separation of solid material from extraction medium and accelerates the removal process [24]. The functionalization processes were characterized by FT-IR, SEM, VSM and XRD. The noticeable water and low pH stability of the nanocomposite, makes it more convenient sorbent for adsorption purposes. The synthesized nanocomposite could be the ideal candidate of sorbent for conventional determination of Se (IV) ions due to its high sorption capacity, short adsorption time and magnetic property. Compared with other SPE sorbents, the developed MIL-101(Cr)/MNPs@ADTC sorbent presented comparable or better the analytical characteristics than the previously reported method.

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