Speciation and Enrichment of Cadmium and Lead from Water Samples using Fe$_3$O$_4$/rGO Sorbent in Dispersive Magnetic Micro-Solid Phase Extraction with Inductively Coupled Plasma-Optical Emission Spectroscopy

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This work reports the development of dispersive magnetic solid-phase extraction (DMSPE) with high resolution ICP-OES for the pre-concentration of cadmium and lead in water samples. The method uses magnetic reduced graphene oxide (Fe$_3$O$_4$/rGO) as adsorbent. The influences of sample pH, extraction time, desorption solvent and desorption time were evaluated and optimized. In the optimized conditions, linear calibration curves for Cd^{2+} and Pb^{2+} were obtained in the range of 10-2000 μg L^{-1} with correlation coefficients of 0.9996 and 0.9995, respectively. Low detection limits of Cd^{2+} and Pb^{2+} were found to be 9.03 μg L^{-1} and 12.4 μg L^{-1}, respectively. Good relative recovery values, in the range of 91-95% and excellent repeatability of 6.4-9.9%, ($n = 3$) were obtained. The results revealed that Fe$_3$O$_4$/rGO can be a suitable nanocomposite sorbent in the speciation and pre-concentration of Cd^{2+} and Pb^{2+} for tap water and drinking water samples. The method is rapid, selective, reliable and environmentally friendly for the determination of Cd^{2+} and Pb^{2+} in water samples.

Keywords: Dispersive magnetic solid phase, Fe$_3$O$_4$/rGO, Cadmium(II), Lead(II), ICP-OES.

INTRODUCTION

Cadmium and lead are the most of toxic pollutants that can have cumulative effect on humans, animals and plants [1]. They can easily enter the human body through various sources such as water, air and food [2]. Cadmium is not biodegradable and can remain in the organism for many years, once absorbed and lead to various acute chronic effects on humans. Cadmium is introduced into nature from waste batteries, paints, release from metal refineries and through other mechanical processes [3]. It can also be found in water sources or wastewater from the corrosion of galvanized pipes and industrial wastes [4].

Lead is a heavy metal, which is usually found in water sources or wastewater and particularly harmful and at high levels, it is considered carcinogenic. Lead poisoning can cause kidney damage, anemia and toxicity to the central nervous and gastrointestinal system [5].

Since cadmium and lead are found in water even at very low concentrations (< 1 g L^{-1}), highly reliable and sensitive anal-ytical tracing techniques are required [6]. Various analytical techniques have been explored for the pre-concentration and to trace heavy metals in aqueous solution which include atomic absorption spectroscopy, isotopic dilution mass spectrometry, inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [7]. Among these techniques, ICP-MS has been commonly used in tracing metals due to its sensitivity, selectivity, wide dynamic range and high capabilities for multi-element analysis. However, its high cost often limits the extensive application of ICP-MS [8].

Hence, ICP-OES has been widely applied in the determination of metals due to its inherent capability of low detection limit, high precision, accuracy and rapid simultaneous multi-element determination over a wide range of concentration. Generally, ICP-OES is the preferred method of many laboratories due to the affordable price [9]. On the other hand, it is difficult to detect trace metals in water samples directly using ICP-OES due to the fact that target analytes in water samples

often exist at a low level, while the complex matrices such as organic compounds and inorganic salts in water samples will cause significant interference with the determination signals. To solve this problem, a pre-concentration procedure is usually required prior to instrumental measurement [10].

Therefore, some efficient pre-concentration steps such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) [11], have been developed and employed prior to accurately determining trace metals. Recently, DMSPE method based on magnetic extraction has been reported as an alternative innovation of SPE to overcome the drawback of traditional methods such as LLE and SPE which are time consuming, require multi-steps procedures and consume large amounts of solvent [12]. It involves the addition of magnetic adsorbent to the sample solution. The targeted analyte is adsorbed and then separated from the sample solution by the application of an external magnetic field. DMSPE is a method which is becoming more promising because it has greater efficiency of absorption due to the release and absorption of analytes by tiny magnetic sorbents [13]. Other work has shown reliable determination of heavy metals in dairy products and water samples with good recoveries, by using magnetic graphene and AAS as detection method [14]. This article reports the development of a simple yet rapid, inexpensive and feasible DMSPE-ICP-OES with a new generation magnetic sorbent, Fe_3O_4/rGO for speciation enrichment of cadmium and lead in water samples. The method was validated and the obtained results were compared with the previous reports using other methods, in terms of LODs, precision and accuracy.

EXPERIMENTAL

Graphite flakes (99% purity) were procured from Qingdao Lihaofeng Graphite Co. Ltd. (China). Ferric chloride hexahydrate and ferrous sulphate heptahydrate were purchased from Sinopharm Chemical Reagent Co. Ltd. Standard cadmium and lead were obtained from Aladdin Chemistry Co. Ltd.

Preparation of standard and sample solutions: The 1000 mg L^{-1} of stock solution of cadmium and lead were diluted using deionized water to 10.0 mg L^{-1} in a 100 mL plastic volumetric flask. A series of working solution of cadmium and lead ranging from 0.1 mg L^{-1} until 2.0 mg L^{-1} were then prepared for analysis and optimization. The samples used in this study were tap water and drinking water. Tap water was collected from the laboratory at the Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), Shah Alam, Malaysia. Drinking water was purchased from the local shop in Shah Alam, Malaysia. The samples were filtered with 0.45 µm Nylon filter and kept in polyethylene bottles at 4 ºC prior to analysis.

The ICP-OES settings for the analysis of cadmium and lead were 3 nm slit, voltage of 617 V, RF power of 1350 W, pump rate of 100 mL s^{-1} and nebulizer flow of 30 psi. The emission wavelength of cadmium and lead were pre-set by the instrument.

Preparation of Fe_3O_4/rGO nanoparticles: Magnetic reduced graphene oxide (Fe_3O_4/rGO) nanocomposite was synthesized by electrostatic deposition of Fe_3O_4 nanoparticles onto the surface of GO nanosheets *via* one-pot reaction. The synthetic

method involved a single-step mechanism which manifested in ultrapure water at room temperature. This method was adopted from previous reports with slight modifications [15]. First, 25 mg of GO nanosheets was dissolved in 20 mL of ultrapure water by ultrasonication for 1 h. The pH of the solution was adjusted to 11 by slowly adding drops of 25% ammonia solution. Under continuous agitation, 125 mg of $FeCl_2$·$4H_2O$ was added slowly into the mixture. Black suspensions of rGO/Fe_3O_4 formed immediately. The mixture was left agitated for 3 h to allow complete bonding between Fe_3O_4 and rGO nanosheets. The black Fe_3O_4/rGO suspensions were separated using centrifuge at 4000 rpm and washed thrice with ultrapure water. The nanocomposite residue was dried overnight in a hot air oven with the temperature maintained at 60 ºC.

Dispersive magnetic solid phase (DMSPE-Fe_3O_4/rGO) extraction procedure: Fe_3O_4/rGO magnetic nanoparticles (40 mg) was added into 10 mL filtered sample, which contained the analytes which had been adjusted to pH 4. To increase the adsorption of lead and (Fe_3O_4/rGO) the solution was stirred for 15 min using an ultrasonicator for extraction process. After the supernatant decanted at the bottom, an external magnetic flied was used to extract the analytes, with the magnet placed under the bottom of flask. Hydrochloric acid (1%) was then added into the vial containing the sorbent. The solution was ultrasonicated for 5 min to allow for the desorption process. After 5 min, the eluent was separated using an external magnetic field prior to determination of the amount of target analytes in the eluent using ICP-OES.

Method validation: The developed DMSPE-ICP-OES method using Fe_3O_4/rGO as sorbent was validated with respect to several validation parameters such as linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy. This is to ensure that the analysis result is reliable for the intended purpose. The linearity of the method was determined by plotting a calibration curve at five different standard concentrations. The limit of detection (LOD) and limit of quantification (LOQ) were determined using linear regression where LOD = 3.3 σ S^{-1} and LOQ = 10 σ S^{-1}, in which σ is the standard deviation of the lowest concentration and S is the slope of the calibration curve LOD = 3.3 σ S^{-1}. The precision (RSD) of the method were determined by a triplicate reading (*n* = 3) and to ensure accuracy, the values were obtained in term of relative recoveries where the sample was spiked with a low concentration of standard solution.

RESULTS AND DISCUSSION

Characterization of nanocomposite: The characteristic IR adsorption peaks of functional groups observed from FT-IR spectra of Fe_3O_4/rGO are shown in Table-1. The band at 587 cm^{-1} in magnetic nanoparticles is resonance to the Fe-O bond stretching vibration characteristic of Fe_3O_4. The spectra exhibit broad peaks of high intensities that appeared in the high frequency regions between 3396 and 3421 cm^{-1} which can be attributed to the O-H stretching and bending of the free or adsorbed water molecules in the investigated materials. The characteristic peaks appeared in the Fe_3O_4/rGO nanocomposite spectrum at 1619, 1201 and 1051 cm^{-1} denote the C=C stretching

TABLE-1
CHARACTERISTIC IR ADSORPTION BANDS OF
FUNCTIONAL GROUPS IN Fe$_3$O$_4$/rGO NANOCOMPOSITE

Wavenumber (cm^{-1})	Functional groups
587	Fe-O bond stretching vibration
1051	C-O stretching of the epoxy group in GO nanosheets
1201	C-O-H bending of the phenolic group
1619	C=C stretching of the aromatic ring
3396	O-H stretching and bending of the free or adsorbed water

of the aromatic ring, the C-O-H bending of phenolic group and C-O stretching of epoxy group.

FESEM studies: The field emission electron microscopy (FESEM) image of Fe$_3$O$_4$ nanoparticles obtained using a Zeiss Supra 40VP microscope, indicates the complete formation of Fe$_3$O$_4$/rGO nanocomposite (Fig. 1). It can be clearly seen that Fe$_3$O$_4$ dispersed over the wrinkled surface of rGO nanosheets that has become more corrugated due to the escaped oxygen-containing functional groups from its surface [16].
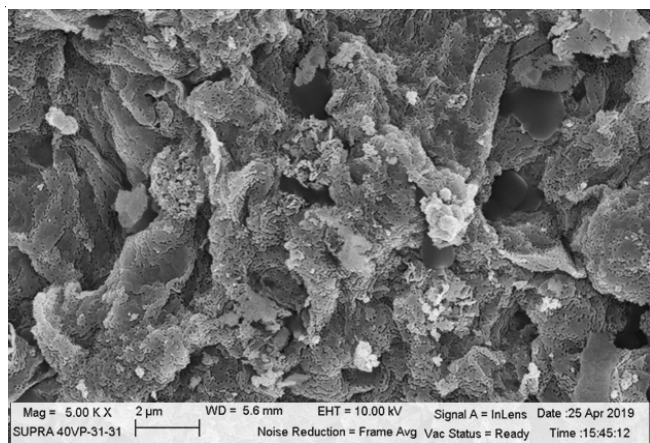

Fig. 1.   FESEM image of Fe$_3$O$_4$ nanoparticles at magnification of 5000x with acceleration voltage of 10.0 kV

VSM analysis was carried out at room temperature to provide information on the magnetic properties of the synthesized Fe$_3$O$_4$/rGO nanocomposite by measuring its magnetic moment under sinusoidal vibration perpendicular to a uniform magnetic field. Fig. 2 shows the magnetization hysteresis loops obtained from the analysis, which demonstrates a superparamagnetic behaviour pattern. The nanocomposite exhibits a high saturation magnetization (MS) at the value of 64.835 emu g^{-1} as well as a low magnetic coercivity (HC) and remanence (MR), indicated that it can be easily demagnetized by the removal of the external magnetic field. This superparamagnetic behaviour is attributed to the nanoscale (< 100 nm) Fe$_3$O$_4$ particles that were incorporated into this nanocomposite [17]. Hence, this finding indicates that the synthesized Fe$_3$O$_4$/rGO nanocomposite can be effectively used as an magnetic solid-phase extraction (MSPE) adsorbent which provides easy separation from the bulk sample solution by applying an external magnetic field.

Optimization of DMSPE-Fe$_3$O$_4$/rGO parameters: Several parameters were optimized on DMSPE-Fe$_3$O$_4$/rGO in order to obtain the maximum extraction efficiency, namely sample pH,
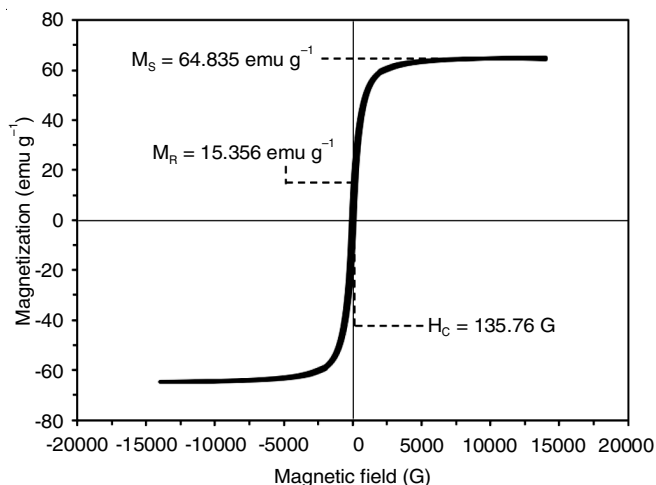

Fig. 2. VSM magnetization curves of rGO/Fe$_3$O$_4$ nanocomposite

extraction time, desorption time and desorption solvent. Standard mixture of 1 mg L^{-1} Cd and Pb in 10 mL of deionized water was used for the optimization process.

Effect of pH: The investigated pH values ranged from 2 to 13. Adjustments of pH were made using 0.1 M HNO$_3$ or 0.1 M NaOH solutions with pH meter. As shown in Fig. 3, the maximum extraction efficiency increases with increasing pH until it reached maximum which is pH 4. The acidity of the sample solution is very important for the adsoption of metal ions. At basic pH, the target analytes are in the form of precipitation so the target analytes does not adsorbed to the surface of sorbent [18]. Thus, pH 4 was selected as optimal pH for the extraction process.
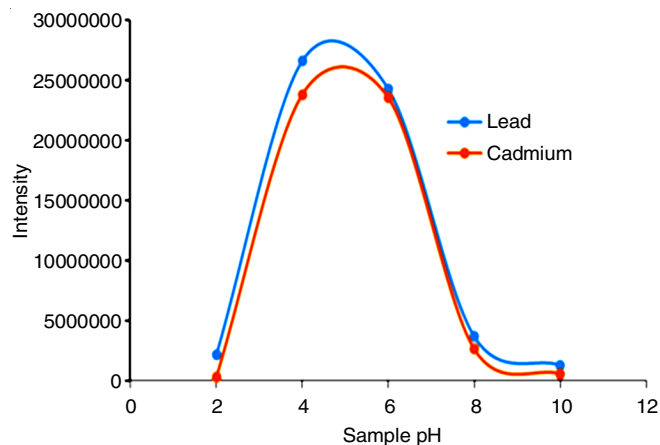

Fig. 3.   Effect of extraction time on the intensity of Cd and Pb of DMSPE-Fe$_3$O$_4$/rGO

Effect of extraction time: In order to determine the optimal time needed for cadmium and lead to be adsorbed on the sorbent, the effect of extraction time was studied for a duration of 5 to 25 min. The sample solution was ultrasonicated with different extraction time. As shown in Fig. 4, the adsorption intensities of Cd and Pb increased from 5 to 10 min. However, after approximately 15 min, the intensity slightly decreased for both Cd and Pb. Thus, 10 min was selected as the optimal extraction time for Cd ad Pb.
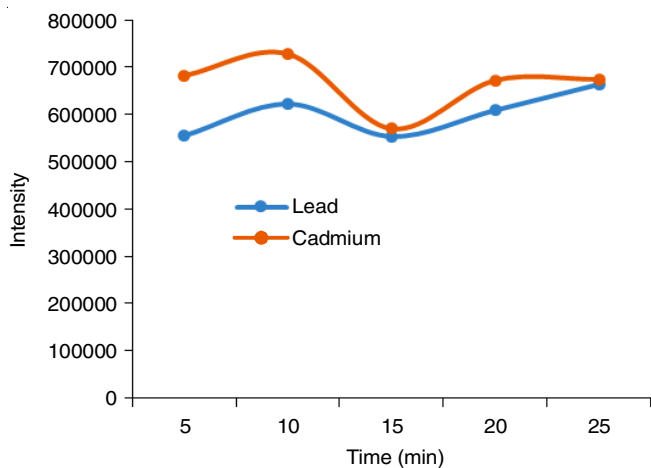
Fig. 4. Effect of extraction time on the intensity of Cd and Pb of DMSPE-Fe₃O₄/rGO

Effect of desorption solvents: The type of solvents use for desorption of analytes from the magnetite sorbent are vital for the desorption efficiency. In this study, 1% of nitric acid, hydrochloric acid, sulphuric acid and ammonia were used to identify the most efficient desorption solvent to desorp the target metals. Each desorption solvent (5 mL) was used to desorp the analyte *via* an ultrasonic bath for 5 min. From Fig. 5, 1% HCl showed the highest desorption recovery compared to other solvents. Hence, 1% HCl was chosen as the desorption solvent [19].
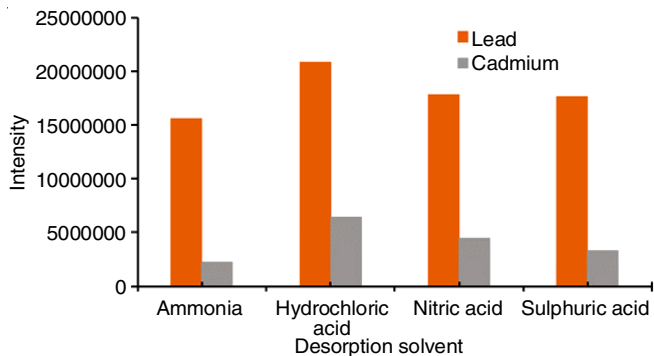

Fig. 5. Effect of desoption solvent on the intensity of Cd and Pb of DMSPE-Fe₃O₄/rGO

Effect of desorption time: The desorption time was optimized by increasing the ultrasonication time ranging from 1 to 9 min. According to Fig. 6, the desorption increased from 1 min until 5 min and decreased when ultrasonication exceeded 5 min. In this case, 5 min can be considered as sufficient time for the desorption of Cd ad Pb from the magnetite sorbent.

Method validation and analytical performances: The optimum conditions DMSPE-Fe₃O₄/rGO obtained are listed in Table-2. Using the optimized parameters, the method was validated with respect to the linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy. The obtained linearity, coefficient of determination (R^2), LOD and LOQ are shown in Table-3. The method showed good linearity (R^2) of 0.9996 (Cd) and 0.9995 (Pb) within the concentration range of 10-2000 µg L⁻¹. Based on calculation of LOD and
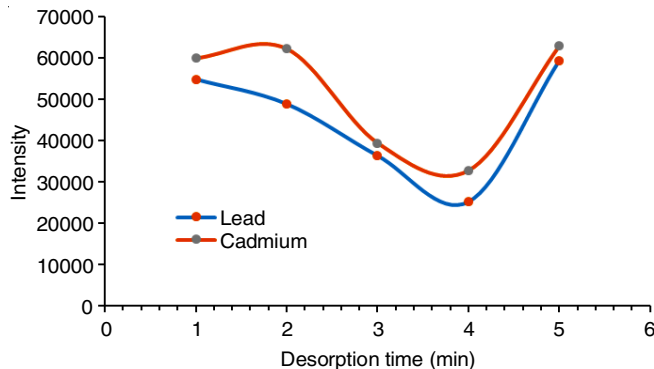

Fig. 6. Effect of desorption solvent on the intensity of Cd and Pb of DMSPE-Fe₃O₄/rGO

TABLE-2
OPTIMUM CONDITIONS OBTAINED FROM
STUDIES ON OPTIMIZATION PARAMETERS

Parameter	Optimum condition
pH of sample	4
Extraction time	15 min
Desorption solvent	Hydrochloric acid
Desorption time	5 min

TABLE-3
ANALYTICAL PERFORMANCE OF THE DEVELOPED METHOD

Target metals	Linearity (µg L⁻¹)	Correlation of coefficient (R^2)	LOD (µg L⁻¹)	LOQ (µg L⁻¹)	RSD (%)
Cd	10-2000	0.9996	9.03	27.37	9.93
Pb	10-2000	0.9995	12.4	37.69	6.38

LOQ of linear regression method, the values of LOD for both Cd and Pb were 9.03 and 12.4 µg L⁻¹, respectively. Meanwhile, the values LOQ obtained for both Cd^{2+} and Pb^{2+} were 27.37 and 37.69 µg L⁻¹, respectively. The relative standard deviation (RSD) for triplicate determination of 100 µg L⁻¹ standard solutions of Cd^{2+} and Pb^{2+} were 9.93% and 6.384%, respectively.

Application of DMSPE-Fe₃O₄/rGO of drinking and tap water samples: The proposed method was employed for the tracing of cadmium and lead in drinking and tap water samples. Relative recovery studies were conducted by spiking waters samples to give a final concentration 1000 µg L⁻¹. The results are presented in Table-4. The results indicate good relative recoveries in the range of 91% to 95%. For tap water samples, Cd^{2+} showed relative recovery of 95% with RSD of 1.5%, while Pb^{2+} showed 93% recovery and slightly higher RSD of 2.0%. For the analysis of analytes in drinking water samples, the recovery for Cd^{2+} was found to be 92% and for Pb^{2+} the recovery was 91%. Both Cd^{2+} and Pb^{2+} displayed almost similar RSD% (1.2% for Cd^{2+}, 1.0% for Pb^{2+}). The results suggested

TABLE-4
ANALYTICAL RESULTS OF SPIKED REAL WATER SAMPLES

Sample	Analyte	Relative recovery (%): Spiking level (n = 3) 1000 µg L⁻¹	RSD (%)
Tap water	Cd	95	1.5
	Pb	93	2.0
Drinking water	Cd	92	1.2
	Pb	91	1.0

TABLE-5
A COMPARISON OF ANALYTICAL PERFORMANCE DATA OF
DMSPE/Fe_3O_4/rGO/ICP-OES WITH PREVIOUSLY REPORTED METHODS

Sample	Method	Solid phase	Detection method	Element	LOD (μg L^{-1})	RSD (%)	Recovery (%)	Ref.
Tap water	SPE	–	ICP-MS	Cd	1.7	2.8	97.8-98.4	[20]
				Pb	1.5	3.7		
Water samples	MDSPE	Magnetic graphene	AAS	Cd	0.16	3.3	95-100.5	[15]
				Pb	0.50	2.1	95-105.5	
Seawater, lake water, mine water and tap water	DMSPE	MWCNTs	GFAAS	Cd	0.001	0.001	87-102	[21]
				Pb	0.030	0.03	85-103	
Water samples	MDSPE	MGO	GFAAS	Cd	0.050	1.3	86-102	[22]
				Pb	0.008	3.5	75-117	
Water samples	MSPE	MPPs-SH	ICP-MS	Cd	0.00021	N/A	88.1-109	[23]
				Pb	0.00290		86.4-106	
Water samples	DMSPE	rGO/Fe_3O_4	ICP-OES	Cd	9.03	9.93	92-95	This work
				Pb	12.4	6.38	91-93	

GFAAS = Graphite furnace atomic absorption spectrometry, MPPs-SH = Thiol-grafted magnetic polymer.

that DMSPE-Fe_3O_4/rGO is an efficient method for extracting Cd^{2+} and Pb^{2+} in water samples.

Thus, the performance of developed DMSPE-Fe_3O_4/ICP-OES method was compared with other detection methods employed in tracing of Cd^{2+} and Pb^{2+} in water samples with respect to similar validation parameters (LOD, RSD % and recovery %). From the comparison data (Table-5), it is found that LOD are comparable to other methods. Although RSD % are higher than other established methods, the values are still within acceptable percentage. The recovery percentage are also high, as compared to reports from previous studies using other methods.

Conclusion

In the present study, a dispersive magnetic solid-phase extraction (DMSPE) was prepared using Fe_3O_4/rGO as sorbent to determine Cd^{2+} and Pb^{2+} in water samples prior ICP-OES. The synthesized magnetite rGO adsorbent provided excellent adsorption capacity for Cd^{2+} and Pb^{2+}. The presented DMSPE-Fe_3O_4/rGO method was optimized and validated. From the validation, optimization and performace data, it can be concluded that newly developed DMSPE/Fe_3O_4/rGO/ICP-OES method offers good sensitivity, precision and accuracy in the analysis of Cd^{2+} and Pb^{2+} in water samples. In additon, Fe_3O_4/rGO also provides a good adsorption as sorbent for the extraction of Cd^{2+} and Pb^{2+} in the water samples. The DMSPE/Fe_3O_4/rGO/ICP-OES offers advantages over conventional methods for the determination of Cd^{2+} and Pb^{2+} in water samples, as it is simple, sensitive, displays good selectivity, economical and environmentally friendly.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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