Fabrication of Solid phase extraction Hg(II) ions in water samples by layered double hydroxide Fe@Mg-Al

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ABSTRACT: Layered double hydroxide (LDH) has recently attracted the attention of chemists in the use of these materials as organic and inorganic composites. LDHs have relatively weak intra-layer bonds and so have a high ability to capture organic and inorganic ions. In this study, the superparamagnetic adsorbent as Fe@Mg-Al LDH was synthesized by different methods with two-step for the removal of heavy metal ions from water samples. An easy, practical, economical, and replicable method was introduced to remove water contaminants, including heavy ions from aquatic environments. For better separation, the ethylenediaminetetraacetic acid ligand was used, forming a complex with Hg^{2+} ions to create suitable conditions for the removal of these ions. This was treated with ethylenediaminetetraacetic acid ligand in another solvent-free procedure for the formation of a Fe@Mg-Al LDH. Cold vapor atomic absorption spectrometry (CVAAS) was utilized for determination of Hg2+. The effects of solution pH solution, elution conditions on pre-concentration of trace Hg^{2+} were studied and the effect of interfering ions was also investigated. Preconcentration factor was 100 .The method was successfully applied to the recovery of Hg^{2+} in different type of water samples. Hg^{2+} ions was studied by floating in aqueous environments with this superparamagnetic adsorbent due to effective factors such as pH, the amount of superparamagnetic adsorbent, contact time, sample temperature, volume, and ligand concentration.

Keywords: *CVAAS, Fe@Mg-Al LDH, Layered double hydroxide (LDH), Preconcentration, SPE.*

INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic make these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples [1, 2], also in medical imaging uses such as magnetic resonance imaging (MRI) [3, 4], in isolating substances and materials in anions– cations pre-concentration [5]. In recent years, SPE method have been well used for determination of Hg (II) ions in numerous environmental samples [6, 7] because of its simplicity, rapidity, minimal cost, low consumption of reagents and its ability to combine with different de-

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tection techniques either in on-line or off-line mode [8]. The layered double hydroxide (LDH) is one of the most popular adsorbents that has received a lot of attention today due to its ease of preparation, affordability, environmental friendliness, and non-toxicity [9]. Layered double hydroxide (LDH) has recently attracted the attention of chemists in the use of these materials as organic and inorganic composites. LDHs have relatively weak intra-layer bonds and so have a high ability to capture organic and inorganic ions. LDHs have numerous applications, for example, catalysts in chemical reactions, photocatalysts, anion exchangers, sensors, plastic additives, removal of heavy metals from the soil, and wastewater heavy-metal precipitating agents. The general formula for LDHs is shown as $[MII_{1-x} MIII_x (OH)_2](A)^{x+}_{x/m} \cdot nH_2O$. Generally, M^{2+} is a divalent cation such as Ni^{2+}, Fe^{2+}, Co^{2+}, Mg^{2+}, etc., and M^{3+} is a trivalent cation such as Fe^{3+}, Al^{3+}, Cr^{3+}, and so on. The value of x for most LDHs is usually set at about 0.20 to 0.33, which is proportional to the mole fraction $M^{3+}/(M^{2+}+M^{3+})$. A represents an interlayer anion with a capacity of m such as NO_3^-, CO_3^{2-}, Cl^- and SO_4^{2-}. The values of M^{2+}, M^{3+}, x, and Am can vary over a wide range [10]. Wataru et al. used YVO_4: Eu^{3+} nanoparticles that have a negative surface charge because citrate anions are adsorbed on their surface. The negative charge of YVO_4: Eu^{3+} nanoparticles and the positive charge of LDH nanoplates are placed on the layers of quartz glass with the layer-by-layer (LbL) method to create multilayer films that are held together by electrostatic forces. The researchers found a relationship between the number of deposition cycles and the intensity of photoluminescence of multilayer films [10].

Mercury and mercury compounds are included in all lists of priority pollutants and different regulations and guidelines have been developed limiting their levels in water and sediments [11-18]. But it plays an important role in science and technology, and inevitably exists in the environment [18]. The detection of mercury has long held the attention of the analytical community and, as such, a large number of protocols have arisen [18]. On the other hand, the toxicity level of mercury is becoming lower and lower, the direct determination of mercury at sub-microgram per liter level is suffered from the matrix interferences. It is

evident that the use of separation and preconcentration procedures is still often necessary before the determination step, despite recent advances in analytical instrumentation [18]. Recently, CNTs have been shown to be excellent classes of sorbent materials for SPE [18]. Since the first application of CNTs in SPE by Cai et al that he use multi-walled carbon nanotubes (MW-CNTs) [18], In recent years many reports have been distributed focusing on progress of use CNTs-based SPE methods for a great variety of analytes, including phenolic compounds [19], insecticides [20], pharmaceuticals [21, 22], inorganic ions [23], organometallic compounds [24]. The one of the important advantage of CNTs for SPE adsorbents is their high surface spaces, which endue CNTs with high sorption capacities. Then, the selectivity of adsorbent (CNTs) can be controlled by covalently or non-covalently modification of the CNTs functional groups. Also, inherent properties of CNTs such as well chemical and thermal stability make them appropriate to be used as adsorbents for SPE column. Other carbon allotropes, for instance graphite and diamond, have also been established as adsorbents in SPE or SPME [25]. Graphene oxide is a novel two-dimensional nanomaterial or in fact can be mention graphene oxide is graphene but with more chemically reactive functionalities [26, 27] which can be more functionalized [28, 29]. Graphene oxide surface has a significant amount of the sp^2-hybridized carbon backbone structure remains intact [30], allowing the nano plate to retain a high degree of planarity, as proven in thin-film deposition and fabrication experiments [31, 32], and a consistently high surface to volume ratio [33]. The extraordinary properties of graphene and its derivate like graphene oxide make it a greater candidate as an adsorbent for SPE technique. Firstly, graphene has a large surface area (theoretical value 2630 m^2 g^{-1}) [34], suggesting a high sorption capacity. Exactly, both sides of the planar sheets of graphene are accessible for molecule adsorption, while for CNTs and fullerenes, steric hindrance may exist when molecules access their inner walls. Secondly, graphene can be simply modified with functional groups, particularly via graphene oxide which has many reactive groups [35]. Functionalization may more enhance the selectivity and sensitivity of SPE. Thirdly, CNTs usually contain trace amounts of metal-

lic impurities that originate their synthesis and using the metal catalysts. These impurities could have negative effects on the applications of CNTs [36]. Nevertheless, graphene and graphene oxide instead, can be synthesized from graphite without the using metal catalysts. In fact, graphene is a layer of graphite, which does not use of any metal catalysts in its synthesis and exfoliation process. Accordingly, the pure material would be obtained [38]. Separation technique, in general, deal with the separation of components of mixtures to enhance the purity of substances while in preconcentration technique, one of the analytes or species have been selectively retained on a solid phase and then eluted with an appropriate eluent, and detected and quantified by an appropriate detection technique [36]. Actually, the SPE technique using graphene and derivate of graphene such as functionalization graphene oxide as a novel and great adsorbent [39]. Chemical modification of graphene oxide has been a promising way to achieve mass production of chemically modified graphene (CMG) platelets. Graphene oxide contains a range of reactive oxygen functional groups, which renders it a good candidate to use in the above-mentioned applications.

In the present work, Fe@Mg-Al LDH was employed for production of solid phase. The synthesized and characterized new sorbent Fe@Mg-Al LDH was utilized for preconcentration of Hg (II) from water samples. Determination of Hg(II) concentration was achieved by CVAAS after preconcentration procedure.

EXPERIMENTAL

Apparatus
The concentration of the metal ion solutions was determined by using the Varian model spectra cold vapour AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420.

Materials and reagents
All the necessary materials and reagents were of analytical grade and were purchased Merck, Aldrich and Sigma Company. All the dilutions were prepared by ultrapure deionized water. BDH Limited, Poole, England. Dioctyl phthalate, DOP, (purity> 99.55%), sodium hydroxide (NaOH) and diethylenetriamine (DTA) was purchased from BDH, UK.

Synthesis method of Fe@Mg-Al LDH
To fabricate the superparamagnetic nano-adsorbent, which is done in two phases, initially, 48.7 g of $MgCl_2.6H_2O$, 2.96 g of $AlCl_2.6H_2O$, 5.09 g of urea, and 12 mL of methanol-acetic anhydride were stirred on a magnetic stirrer for 30 min. When the solution became clear, it was placed in an autoclave for 6 h at 150 °C. The solid phase was then separated from the liquid using a centrifuge and washed with water and ethanol. The white product was then dried at 120 °C for 12 h. In the next step, 0.12 g of the white product obtained from the previous step was added to 0.08 g of $FeCl_2$, 0.216 g of $FeCl_3$, and 20 mL of deionized water. Afterward, the container containing the sample was placed on a magnetic stirrer at 50 °C for 20 min. After cooling the solution of a black sample, it was homogenized by an ultrasonic device, and then 1 mL of ammonia solution was added at the same time, and it was placed on a heater at 50 °C after 40 min. Finally, the black product was washed with distilled water, and was separated from the liquid by a magnet, and dried at room temperature (Fig. 1) [37].

Preparation of Solid Phase
Sorption characteristics of Hg(II) ions by Fe@Mg-Al LDH by the batch equilibrium technique. The applicability of magnetic Fe@Mg-Al LDH sorbent for extrac-
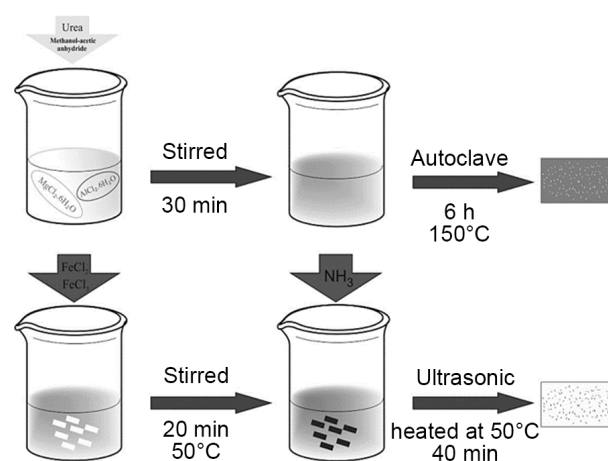

Fig. 1. The synthesis scheme of Fe@Mg-Al LDH.

tion of Hg(II) ions was studied by the batch equilibrium technique under several experimental controlling factors. These include the effect of pH, contact time, sorbent dosage, initial metal ion concentration and interfering ions.
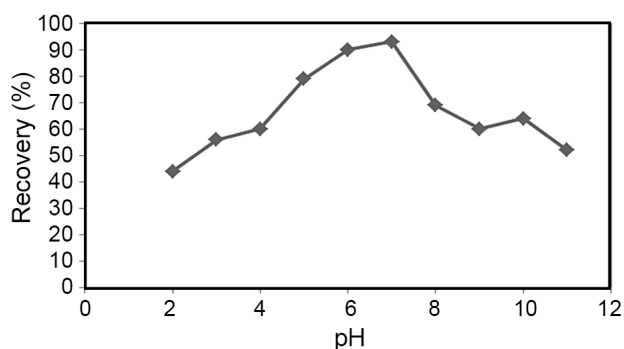
General procedure

100 ml solution with 50 ngml⁻¹ Hg content was prepared as a sample. This solution was added to the Fe@Mg-Al LDH sorbent and by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25 min in order to allow easier Hg ions absorption of the Fe@Mg-Al LDH sorbent [36]. At the end of this stage, the Fe@Mg-Al LDH sorbent which had been formed on the bottom layer of the beaker was removed through applying external field with 1.4T magnetic powers and was immediately decanted outside the supernatant. 1 ml of 1 mol.L⁻¹ ion of eluent was injected into CVAAS for measurement of Hg(II) ions concentrations.

RESULTS AND DISCUSSION

Optimization of SPE procedures
Effect of pH

The metal chelate stability constant and its chemical stability considerably influence the SPE recovery. The pH plays a very important role on metalchelate formation and following extraction. Therefore, pH was the first optimized parameter. pH of the analyte solutions was adjusted to desired values with diluted hydrochloric acid (0.1 mol L⁻¹) and/or ammonia solution

(0.1 mol L⁻¹) The variation in recovery of Hg(II) with pH is shown in Fig. 2. According to the results shown in Fig. 2 up to pH 6.5-7.0, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of Fe@Mg-Al LDH occurs and there is a weak tendency for retention between Hg(II) and Fe@Mg-Al LDH, whereas at higher values (pH>7), Hg (II) reacts with hydroxide ions to produce Hg(OH)2. Accordingly, pH 7.0 was selected for subsequent work and real sample analysis.

Stability studies

The stability of the newly synthesized Fe@Mg-Al LDH phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the Fe@Mg-Al LDH phase. The results of this study proved that the Fe@Mg-Al LDH is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. Finally, the Fe@Mg-Al LDH phases were also found to be stable over a range of 1 year during the course of this work.

Effect of shaking time studies

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and

Fig. 2. Influence of sample pH on the percentage recovery of Hg (II), conditions: 100 mg adsorbent, 50 ml of 5 mg/L of Hg (II) ions.

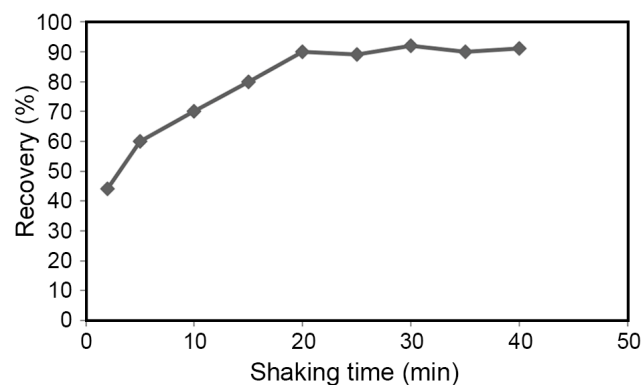**Fig. 3.** Effect of shaking time (min) on the percentage extraction of Hg(II) by the Fe@Mg-Al LDH phases.

evaluated as µmol g^{-1} and correlated to that determined at 20 min shaking time. Fig. 3 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between magnetic nano- Fe$_3$O$_4$ -DOP- DTA phase and Hg(II). One minute shaking time was found to be sufficient to establish 84% of the determined µmol g^{-1} value at 30 min whereas 10 min shaking time led to 90% extraction. The data and results presented in this section reveal the superiority of Fe@Mg-Al LDH phase as previously declared in the stability studies.

Distribution coefficient (K$_d$)

The distribution coefficient (K$_d$) data of the tested metal ions with the two newly Fe@Mg-Al LDH phase are summarized in Table 1. It is evident that Hg(II) is the strongest sorbed metal ion by magnetic Fe@Mg-Al LDH phase. The distribution coefficient values of Hg(II) by the loaded magnetic Fe@Mg-Al LDH phase were found to be much higher than those reported for ion exchange resins containing Fe@Mg-Al LDH derivatives [37]. In addition, the K$_d$ values for Hg(II) by Fe@Mg-Al LDH phase were found to come on the second place after Hg(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxyl donor groups present in Fe@Mg-Al LDH for binding with Hg(II) [38-49]. On the other hand, the various tested metal ions as shown in Table 1 were found to exhibit lower tendency to bind with Fe@Mg-Al LDH phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K$_d$ value for Hg(II) and the lower ones for the other metal ions, except Hg(II), provide an additional evidence for the suitability of these two

Table 1. Distribution coefficient (K$_d$) values of various metal ions.

Metal ions	K$_d$
Mn(II)	67
Fe(III)	56
Co(II)	58
Cd (II)	34
Cu(II)	422
Ni(II)	459
Cu(II)	567
Hg (II)	3400
Pb(II)	1200

newly Fe@Mg-Al LDH phase for selective extraction of Hg(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K$_d$ values by Fe@Mg-Al LDH phase is consistent with the reported data.

Preconcentration of Hg (II) from natural water for off-line CVAAS

This study was undertaken in order to evaluate the potential application of Fe@Mg-Al LDH phase for preconcentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 l) were spiked with 20 pg ml^{-1} of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl [49]. However, some of these reagents are usually characterized by adsorption on the surface of Fe@Mg-Al LDH which lead to severe change in the nature of packing material as well as non-reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Hg(II), by 10.0M HCl acid is found to be high without causing any notable change to the chemical nature of the organic Fe@Mg-Al LDH. Therefore, 10.0 ml of 10.0M HCl was used for the elution of the adsorbed Hg(II) from the column bed. The preconcentration factor targeted from this study is 100 as given. As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory pre-concentration factor which can be further increased to 100-fold. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed selective extraction, removal and preconcentration of Hg(II) by Fe@Mg-Al LDH phase.

Effect of foreign ions

Effects of foreign ions were also investigated on the measurements of Hg (II). Here a certain amount of

Table 2. Effect of foreign ions on the percent recovery of 5 ppm Hg in water samples.

Ions	Amount taken (mg)	%Recovery
Na^+	10	90 (2.6)[a]
K^+	10	94(2.7)
Ca^{2+}	10	92 (2.5)
Mg^{2+}	10	93 (2.8)
Fe^{3+}	8	92(2.9)
Cr^{3+}	8	92(2.8)
Co^{2+}	5	93(2.5)
Cl^-	5	93(2.6)
Br^-	2.5	92(2.7)
F^-	2.5	100 (2.6)
Mn^{2+}	2.5	89(2.5)
Zn^{2+}	2.5	92(2.4)

a) Values in parentheses are RSD based on three replicate analyses.

foreign ion was added to 50 ml of sample solution containing 100 ng of each Hg (II) with a pH of 6.5. The amounts of the foreign ions and the percentages of the recovery of Hg (II) are listed in Table 2. As it is seen, it is possible to determine lead without being affected by the mentioned ions.

Table 3. Analytical Figures of merits for Hg.

Parameters	
RSD% n=10	2.88%
LOD(μm/L)	1.05
LOQ(μm/L)	3.086
Enrichment factor	100
Calibration equation	Y = 0.05x - 0.0007
Correlation coefficient	0.998

Figures of merits in method

In calibration curve was linear dynamic rang 1.0 ng/ml to 7.0 mg/ml for Hg (II). As analytical Figures of merit, limit of detection (LOD), limit of quantification (LOQ) defined as $3S_B/m$ and $10S_B/m$, relative standard deviation (RSD) for the proposed preconcentration and speciation method have been determined and listed in Table 3.

Determination of Hg(II) in natural tap water samples

In addition, the effect of packing amount of silica gel phase is also evident in Table 4, where the near

Table 4. Determination of Hg in real water samples.

Sample	Taken amount (μg)	cold vapor atomic absorption spectrometry (CVAAS) (μg)	%Recovery
Tap water (Tehran, Iran)	0	3.20(2.6)[a]	-
	30	33.14(2.4)	92.5
Tap water (Varamin, Tehran, Iran)	0	N.D[b]	-
	30	32.10(3.0)	91.9
Mineral water (Damavand Company)	0	N.D[b]	-
	30	30.39(3.1)	92.5

(a) Values in parentheses are RSD based on four replicated analyses; (b) No adsorption, passes through column

Table 5. Comparison of the total results of the proposed method with ICP-AES [a].

Sample	Hg^{2+} (mg.mL^{-1}) SPE- CVAAS	Hg^{2+} (mg.mL^{-1}) ICP-AES	F-test [c]	T-test [d]
1	13.6±1.5[b]	13.6±1.99	3.1	0.5
2	15.6±1.3	15.7±1.9	1.8	0.8
3	9.9±0.8	10.1±0.8	2.7	0.9
4	3.6±0.7	3.5±0.9	2.0	0.6
5	1.8±1.9	1.7±1.9	2.1	0.7

[a] All real samples were diluted 50 times before analysis; [b] Mean ± standard deviations based on five individual replicate analyses; [c] Tabulated F-value for (4,4) degrees of freedom at p (0.95) is 6.39; [d] Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.

Table 6. Comparison of published results of several on-line or several methods for determination of Hg²⁺.

Technique	Sorbent	RSD(%)	Duration of SPE	Enhancement factors	LOD (μg /L)	Ref.
SPE & CVAAS	Dimethylglyoxim/sodiumdodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs)	1.9%	15	25	4.6	49
SPE & CVAAS	2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N′-(pyrrol-2-ylmethyliden) acetohydrazide (ICOTPA)	4.0%	25	30	0.27	50
SPE & CVAAS	as Fe@Mg-Al LDH	2.88%	20	100	1.05	Present method

completion of Hg(II) removal was accomplished by the use of 5 mg phase. The results of the preconcentration of Hg(II) from aqueous solutions are presented in Table 4 of Hg(II) from DDW and natural tap water samples. Real samples marked 1 to 5, were collected at the at the distances of 5, 100, 250, 350 and 500 metres of the total waste water of electroplating plants in the eastern parts of Varamin, respectively. The total results obtained by the recommended procedure and ICP-AES have compared in Table 5. As it is seen, the results obtained by the proposed method and ICP-AES are in agreement with each other. Moreover, as it is expected, the Hg(II) concentration decreases as the distance from the electroplating plants increases.

CONCLUSIONS

The proposed SPE method possesses advantages such as easiness, and considerable selectivity in comparison with the previously reported procedures for isolation and determination of Hg²⁺ contents (Table 6). In summary, a selective and sensitive method for the determination of trace levels of Hg(II) based on Fe@Mg-Al LDH as a sorbent for the determination of the analytes in water samples. In addition, the preparation of magnetic Fe@Mg-Al LDH is relatively simple and rapid. However, the magnetic Fe@Mg-Al LDH sorbent has some drawbacks include lower reusability and stability, which can be repeated only 10 cycles [51]. This may make it difficult to put into practical use and should be a subject of further investigations.

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