Mo(II) recovery from real water samples by adsorption onto superparamagnetic adsorbent as Fe@Mg-Al LDH ions in water samples

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ABSTRACT: A novel, simple, sensitive and effective method has been developed for removal of Mo(II) on the superparamagnetic adsorbent as Fe@Mg-Al LDH adsorbent. Spectrometry was used to track the effects of Fe@Mg-Al LDH dose, pH extraction, and contact duration on Mo(II) removal from sample water. This research also looked at adsorption isotherm models for the sorption of Mo(II). The magnetic Fe@Mg-Al LDH adsorbent Mo(II) adsorption capability was 29.74 mg/g respectively. The Freundlich isotherm model fits the removal of Mo(II) utilizing magnetic Fe@Mg-Al LDH adsorbent. This approach has an outstanding linear range of 0.5-26 mg/L for Mo^{2+} ions. The limits of detection (LODs) for Mo^{2+} ions adsorption by magnetic Fe@Mg-Al LDH adsorbent were reached by utilizing a signal-to-noise ratio of 3 (LOD= 2.35 μg/L). These findings show that magnetic Fe@Mg-Al LDH adsorbent is an effective adsorbent for extracting Mo(II) from different sample waters.

Keywords: *FAAS, Mo(II), Preconcentration, SPE, Superparamagnetic adsorbent as Fe@Mg-Al LDH*

INTRODUCTION

Following the growing population and industrialization of human life, extensive environmental problems have been created in relation to carcinogenic compounds due to the presence of heavy metals. Therefore, many studies have been conducted to remove compounds from water, air, and soil. 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 [1, 2]. 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 $[M^{II}_{1-x} M^{III}_{x} (OH)_2](A)^{x+}_{x/m} \cdot nH_2O$. Generally, M^{2+} is a divalent cation such as Ni^{2+}, Fe^{2+}, Co^{2+}, Mg^{2+}, etc., and M^{3+} is

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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 A^m can vary over a wide range [3, 4]. 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 [5-8].

The direct determination of Molybdenum ions in water samples by flame atomic absorption spectrometry (FAAS) is very difficult due to the low concentration of Molybdenum ions and also interfering because of influences of the components of the matrix. Therefore, separation and preconcentration steps are often required to achieve accurate, sensitive and reliable results by FAAS. Several techniques including precipitation/co-precipitation [6], liquid-liquid extraction [7] cloud point extraction [8] and solid-phase extraction [9] (SPE) have been developed for the separation and preconcentration of trace Molybdenum Among all methods, solid-phase extraction is the most common technique used for preconcentration of an analyte in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [9, 10]. In recent years a new kind of SPE, magnetic solid-phase extraction (MSPE), has attracted so much attention. The MSPE is based on magnetic materials as sorbent, which can be isolated from the matrix quickly by using a magnet. Compared with other isolation methods, MSPE can improve the extraction efficiency and simplify the process of preprocessing. In recent year, the application of nanomaterials such as activated carbon [11, 12], Different methods, and co-extractant ligands has attracted considerable atten-

tion [13-16]. However, the use of classical extraction methods for this purpose is usually for the Extraction and separation of Mo ions have been suggested including liquid chromatography [17] supercritical fluid extraction [18, 19], flotation [24], aggregate film formation [25], liquid membrane [26], column adsorption of pyrocatechol violet-Mo complexes on activated carbon [27], ion pairing [28, 29], preconcentration with yeast [30], and solid phase extraction using C_{18} cartridges and disks [31-33]. Solid phase extraction (SPE) or liquid-solid extraction is poplar and growing techniques that are used to sample preparation for analysis. However, the disks modified ligand is a selective approach to separation and preconcentration of heavy metals in water samples [34-42]. In a recent series of papers, [43-45] the determinate relies on the esterase activity of a DNA-linked Mo complex. For optimization of the system and exploration of structure- activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Mo^{2+} in low concentration. The chelated ions were desorbed and determined by GF-AAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, superparamagnetic adsorbent based on LDH.

In the present work, superparamagnetic adsorbent based on LDH was employed for production of solid phase. The synthesized and characterized new sorbent superparamagnetic adsorbent based on LDH was utilized for preconcentration of Mo(II) from water samples. Determination of Mo(II) concentration was achieved by GF-AAS after preconcentration procedure.

MATERIALS AND METHODS

Reagents and Chemicals

The analytical grade D.W. (deionized water) was obtained by reverse osmosis system. All containers and glassware were kept overnight in 10% nitric acid and rinsed three times with water before use. 1,000 mgL^{-1} stock Mo standard solution was prepared from $Mo(NO_3)_2.4H_2O$ (Merck) and diluted as required to the μgL^{-1} levels. BDH Limited, Poole, England. Dioc-

tyl phthalate, DOP, (purity>99.55%), sodium hydroxide (NaOH) and 1-ethyl-3-(3-dimethylaminoprophy) carbon diimidehydrochloride, chitosan and graphene oxide was purchased from BDH, UK. Mo nitrate, $Mo(NO_3)_2$, cadmium nitrate, $Mo(NO_3)_2$ was purchased from Merck. In interference study, cations were added as nitrates and the anions were added as sodium salts. Feasibility of the suggested method was tested with Lake Ontario water certified reference material (TMDA-53.3, lot 0310).

Apparatus

A Philips X Pert-Pro diffracrometer (Mo Kα λ=1.54060 Å, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FT-IR-ATR spectrometer were used to confirm the synthesized superparamagnetic adsorbent based on LDH. Determination of Mo(II) in solutions were carried out by Perkin Elmer Analyst 200 GF-AAS equipped with deuterium background correction. All measurements were performed in an air/acetylene flame. GFL 3005 orbital shaker having speed and time control was used for preparation of the sorbent. During the solid phase extraction experiments, VelpScientificaSP311 peristaltic pump with Tygon tubes was used. A Thermo Orion 5 Star model pH meter, Heidolph MR 3001 K model magnetic stirrer, Sartorius TE214S electronic balance, Eppendorf Research micro pipettes were used for the present work. Funnel tipped glass tube (10×100 mm) equipped with stopcock was used as a column for the enrichment experiments.

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).

Preparation of Solid Phase

Adsorption characteristics of Mo(II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of superparamagnetic adsorbent based on
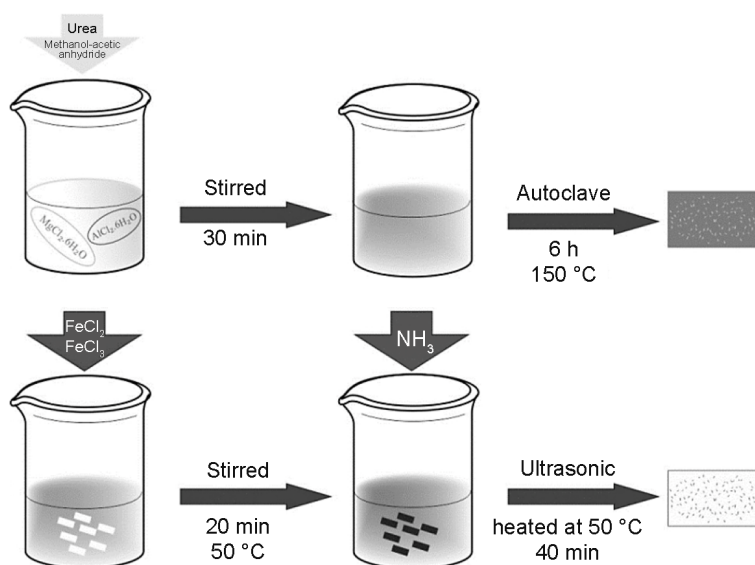

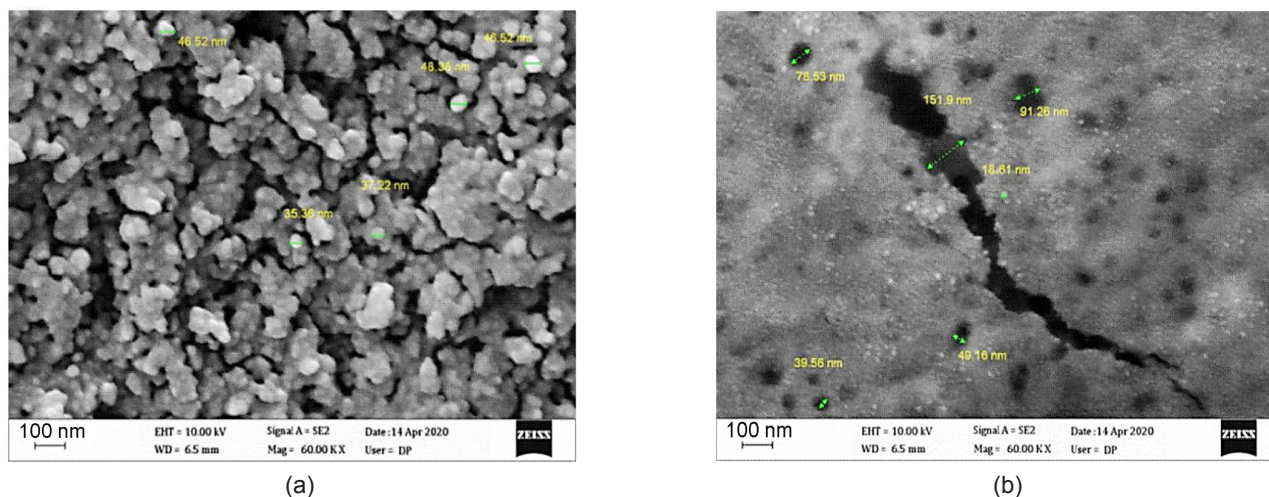**Fig. 1.** The synthesis scheme of Fe@Mg-Al LDH

Fig. 2. FESEM image of Mg-Al LDH (a) and Fe@Mg-Al LDH (b) nanoparticles

LDH. Sorbent for extraction of Mo(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, desorption of eluent, ion concentration and interfering ions and calibration curve.

General procedure

50 ngml^{-1} Mo(II) content was prepared as a 100 ml solution. This solution was added to the superparamagnetic adsorbent based on LDH sorbent. Absorption of the superparamagnetic adsorbent based on LDH sorbent by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25 min in order to allow easier Mo(II) ions [32]. At the end of this stage, the superparamagnetic adsorbent based on LDH sorbent which had been formed on the bottom layer of the beaker was removed through applying an external field with 2.0T magnetic powers and was im-

mediately decanted outside the supernatant. Mo(II) ions determinate1 ml of 1 molL^{-1} ion of eluent was injected into GF-AAS.

RESULTS AND DISCUSSION

Surface morphology

Figs. (2a-b) shows the FESEM analysis of Mg-Al LDH and Fe@Mg-Al LDH. Fig. 2a was related to the first phase of LDH contains Mg-Al, where the particles were displayed with 35-46 nm of sizes. Fig. 2b was related to the final phase of LDH contains Fe@Mg-Al, where the signed points were shown with 39-151nm and the iron element is quite clear.

Figs. 3a-b, which are related to the EDS test, show the first phase of LDH contains Mg, Al, and O and the second phase of LDH contains Mg, Al, O, and Fe respectively. The saturation magnetization of Mg-Al
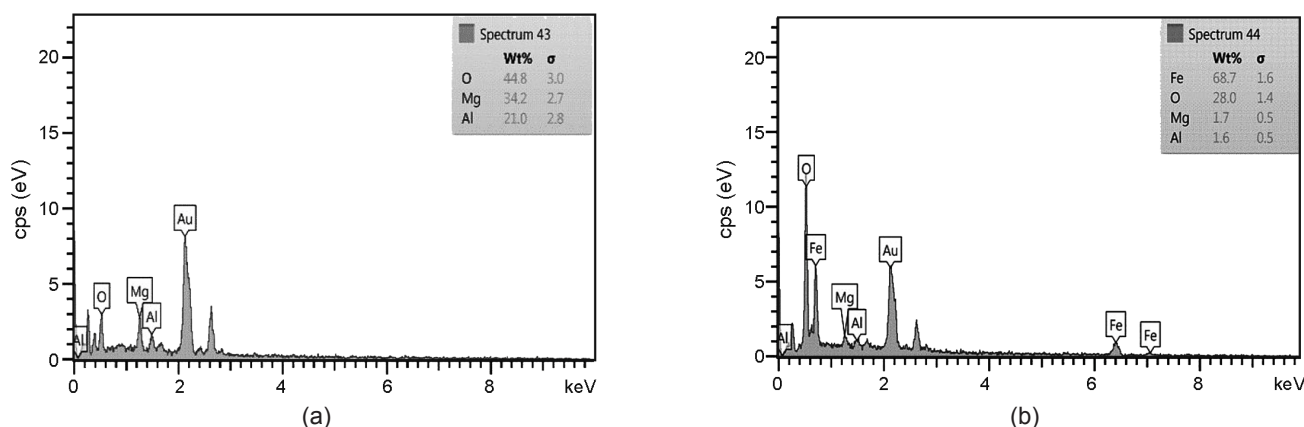

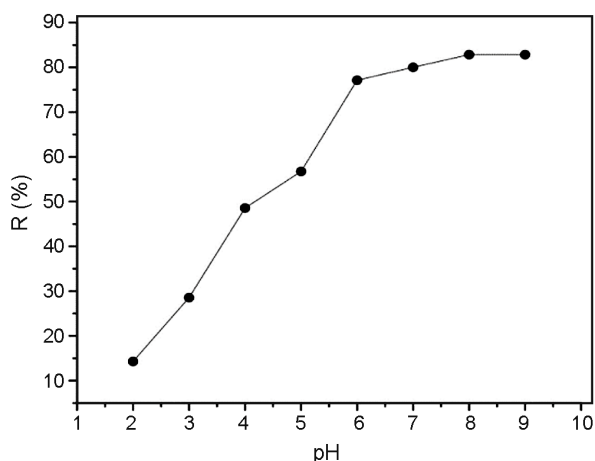**Fig. 3.** EDS of Mg-Al LDH (a) and Fe@Mg-Al LDH (b) nanoparticles

Fig. 4. Influence of sample pH and dissolving solvent of superparamagnetic adsorbent based on LDH on the percentage recovery of Mo(II).

and Fe@Mg-Al LDH are shown 6 and 18 emv/g respectively. This increase was due to the addition of iron nanoparticles to Mg-Al LDH.

Effect of pH
The pH of the sample solution plays important role in retention of metals on sorbent. The pH of the model solutions containing 5μg Mo(II) were adjusted to certain value using diluted HNO_3 and NaOH. As shown in Fig. 4, the recovery results were not dramatically affected by the change in pH under 8.0. According to this, pH=8 were chosen as centre value for the optimization protocol.

The effect of the amount of nao-adsorbent on the removal Mo(II) ions
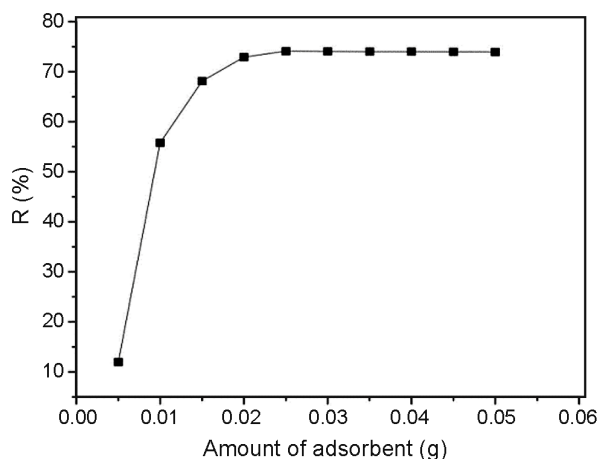To achieve the optimal amount of nano-adsorbent,

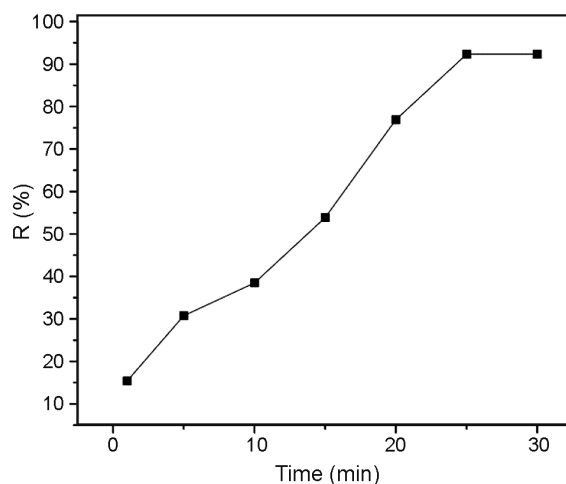**Fig. 5.** Efficiency rate by the amount of adsorbent

Fig. 6. Effect of time on the Mo(II) ions removal

The range of 0.005-0.05 g of nano-adsorbent were added to 25 mL of 0.1 mg/L Mo(II) solution and 1.5 mg/L of EDTA ligand, which was stabilized at pH=8 using a buffer. It was then placed on a magnetic stirrer for 30 min. The remaining ion concentration was then determined by GFAAS. The 0.025 g amount of nano-adsorbent was found for maximum adsorption of Mo(II) ions with Fe@Mg-Al LDH (Fig. 5).

The effect of time on the removal of Mo(II)
In this section, a buffer solution with pH=8 was used to stabilize a 0.1 mg/L of Mo(II) solution and 1.5 mg/L of EDTA ligand. Then 0.25 g of nano-adsorbent was added to the solution, and it was placed on a magnetic stirrer at different times for 1 to 30 min at 25 °C. The remaining Mo(II) ion concentration was then determined by GFAAS. Based on Figure 6 seen as time went on, efficiency increased and the curve had a steep slope up to 25 min. The time of 25 min was selected as the optimal time due to time savings and no significant difference between 25 and 30 min.

Temperature effect
The purpose of measuring the temperature is to investigate the Mo(II) ions extractions and thermodynamic parameters. In optimal conditions, the temperatures of 10, 15, 20, 25, 30, and 35 °C were studied for Mo(II) ions extractions with refrigerated incubator shaker apparatus. The remaining ion concentration was determined by GFAAS. As can be seen in Figure 7, the efficiency extraction increased with increasing temperature up to 30 °C. As the temperature rises, the ac-
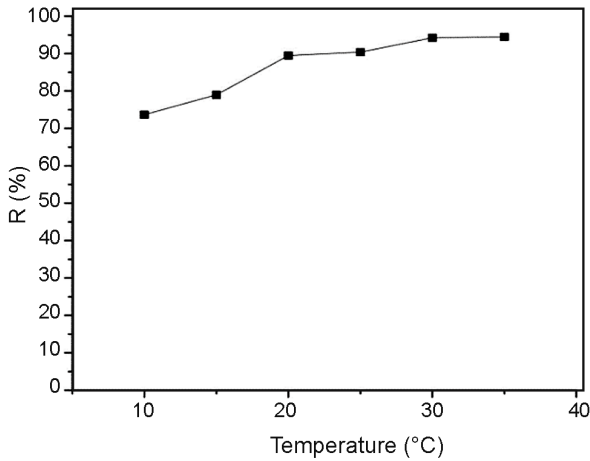
Fig. 7. Temperature effect on the removal of Mo(II) ions

tivity of the metal ions in the solution increase, and the chances of colliding with the empty sites of nano-adsorbent increase [28].

Freundlich-Langmuir-Temkin isotherms
Freundlich, Langmuir, and Temkin isotherms were used to achieve the adsorption model. The amount of adsorbed Mo(II) ions at equilibrium qe (mg/g) was calculated. Adsorption isotherms are equations for describing the equilibrium state of the adsorbed component between the solid and fluid phases. At this stage, experimental data on adsorption equilibrium with Freundlich, Langmuir, and Temkin isotherms were examined. Its equation line was following Equations 1, 2, and 3, respectively [30, 31].

$$\frac{C_e}{q_e} = \frac{1}{Q_0^b} + \frac{C_e}{Q_0} \tag{1}$$

$$q_e = B \ln k_T + B \ln C_e \tag{2}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

Where Q_0 is the highest Mo(II) ions sorption capacity at Fe@Mg-Al LDH (mg/g) and b are the constant of the Langmuir Equation, k_t and B are the constants of

the Temkin Equation, K_f and n are the constants of the Freundlich Equation, C_e (mg/L) is the concentration of the adsorbate in the liquid phase after reaching equilibrium, and q_e (mg/L) is the amount of the adsorbate per unit mass of Fe@Mg-Al LDH.

The parameters of isotherm models are deposited in Table 1. The correlation coefficient of Langmuir isotherm for Mo(II) ions is 0.917, while this value of the Freundlich and Temkin isotherms is 0.808 and 0.847, respectively. The results show that the Langmuir model can be considered as a monolayer adsorption mechanism of Mo(II) metal ions on the Fe@Mg-Al LDH.

Determination of thermodynamic parameters
Thermodynamic parameters include changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔG), which are the most important features of an adsorption process for practical applications. Thermodynamic equations help to better understand the process of adsorption, that is, to increase the adsorption efficiency. According to Table 4, since all ΔGs were positive for Mo(II) ions, it could be concluded that all adsorption processes by the Fe@Mg-Al LDH were non-spontaneous. Additionally, if the ΔG was between 0 and 20, the adsorption processes were chemical. The positive enthalpy of adsorption reactions on the Fe@Mg-Al LDH indicated that these processes were endothermic. The entropy changes in adsorption by Fe@Mg-Al LDH were positive, indicating that the degree of freedom at the solid-solution phase in adsorption increased.

The standard free energy change (ΔG⁰) can be calculated from the following equation (Eq. 4):

$$\Delta G^0 = -RT LnK \tag{4}$$

Where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K is the sorption equilibrium constant. The standard entropy change (ΔS⁰) can

Table 1. Langmuir, Temkin, and Freundlich isotherms constants for the adsorption of Mo(II) ions by Fe@Mg-Al LDH

Freundlich isotherm			Langmuir isotherm			Temkin isotherm		
n	K_f (L/g)	R^2	Q_0 (mg/g)	b (L/mg)	R^2	k_t (L/g)	B (J/mol)	R^2
1.60	0.947	0.809	160.14	0.105	0.917	0.247	0.068	0.846

Table 2. Thermodynamic parameters

$T(K^0)$	lnK	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol K)
283	-1.65	3.9	14.371	0.037
293	-1.45	3.53		
303	-1.2	3.04		

be calculated according to the following equation or by plotting lnK versus 1/T (lnK=ΔS^0/R - ΔH^0/RT) [32, 33]. The parameters of Thermodynamic are deposited in Table 2.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

Interference Effects

The preconcentration protocols of trace metal ions can be strongly affected by other ions. For this reason, the effects of matrix ions were researched under optimal conditions. The results revealed that the Fe@Mg-Al LDH behaves as a neutral ionophore in the pH range 8 [45-50] so that the Mo ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the solid phase extraction of Mo(II) ions. The influence of the concentration of sodium acetate ion on Mo recovery was investigated, and the results are given in Table 3. As seen, the percent recovery of Mo^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative. Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation, thus, in the solid phase extraction experiments, there was no need for the addition of any buffer solution.The tolerance limit of coexisting ions was given in Table 5. The experiments

Table 3. Separation of Mo from binary mixtures [a]

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Mo^{2+} ion
Na^+	92.4	1.15(2.4)[b]	97.7(1.7)
K^+	92.5	1.32(2.3)	97.4(2.9)
Mg^{2+}	14.4	0.7(1.2)	97.9(1.7)
Ca^{2+}	26.3	2.24(3.0)	97.4(1.6)
Sr^{2+}	2.44	2.74(2.4)	98.4(2.2)
Ba^{2+}	2.66	3.16(2.1)	98.3(2.3)
Mn^{2+}	2.66	1.74(2.2)	97.3(2.8)
Co^{2+}	2.16	1.4(2.3)	99.1(2.9)
Ni^{2+}	1.64	2.2(2.4)	98.4(2.6)
Zn^{2+}	2.78	1.97(2.1)	98.4(2.2)
Cd^{2+}	2.45	1.92.2)	97.2(2.7)
Pb^{2+}	0.44	2.7(1.9)	97.3(2.7)
Hg^{2+}	0.44	2.71(2.1)	97.7(2.7)
Ag^+	2.63	3.45(2.9)	96.6(2.9)
Cr^{3+}	1.73	2.92(2.3)	97.3(2.4)
UO^{2+}	2.74	2.7(2.1)	97.3(2.7)

[a] Initial samples contained 10µg Mo^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).

[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table 4. Mo^{2+} ions determination in actual water samples (number of repetitions 3 times)

Samples	Spiked (µg/L)	Found (µg/L)	Relative recovery (%)
	0.0	ND	-
Tap water	5.0	5.07 ± 1.18[a]	98.62 ± 2.17
	15.0	20.48 ± 1.80	97.62 ± 1.88
	0.0	6.37 ± 1.59[a]	98.52 ± 1.25
Well water	5.0	12.18 ± 1.98	98.52 ± 2.06
	15.0	22.69 ± 1.47	99.62 ± 1.67
	0.0	6.80 ± 2.20	98.36 ± 2.88
Industrial wastewater	5.0	12.29 ± 2.59	97.75 ± 2.99
	15.0	22.95 ± 2.60	98.07 ± 2.45

[a] Mean ± standard deviation

ND: not detected.

Table 5. Comparison of this adsorbent with another method for Mo^{2+} ions extraction

Approach	q_m (mg/g)	pH	Equilibrium time	Ref.
Magnetic Fe@Mg-Al LDH adsorbent	29.74	8	8 min	This work
Amino functionalized magnetic graphenes composite	27.95	6	200 min	[10]
Magnetic biochar composite	26.08	5	120 min	[11]
Magnetized and non-magnetized biochar from Douglas fir	25.29	5	180 min	[29]
Bimetallic coordination polymer adsorbent	175	4	30 min	[16]

indicated that, no further sample treatment or masking reagents are needed.

Measurement of Mo^{2+} ions in real water samples
To test the applicability of the presented method for measuring Mo^{2+} ions in actual samples, the concentration of Mo^{2+} ions was measured in different aqueous samples with a volume of 200 mL. Regarding this, the water samples, such as tap water (collected in Varamin on April 15, 2023, after running the water for 10 minutes), well water (taken in Tehran on April 22, 2023), and industrial wastewater (taken in Charmshahr on March 18, 2023), (Table 4). The measuring of the Mo^{2+} ions concentration was done using the graphite furnace atomic spectrometer.

Comparison of this technique with another method
The employed methodology is superior to the approaches because it has a high Mo^{2+} ion loading, performs extraction near neutral pH, and has a low equilibrium time. Magnetic Fe@Mg-Al LDH adsorbent may be easily separated using a magnet instead of centrifuges or filtrations. Additionally, the use of pricey and dangerous organic solvents is decreased when using the magnetic Fe@Mg-Al LDH adsorbent with extraction in an aqueous sample (Table 5) [10, 11, 16, 29].

CONCLUSION

To increase the extraction properties and Mo^{2+} ions adsorption in the current study, a magnetic Fe@Mg-Al LDH adsorbent was employed to effective extraction heavy metal ions from water samples. The structure of magnetic Fe@Mg-Al LDH adsorbent was then examined using an analytical approach, and different amounts of magnetic Fe@Mg-Al LDH adsorbent were used to effectively extract Mo^{2+} ions from a variety of water samples. The qmax for Mo^{2+} ions was 29.74 mg/g at pH=8. According to the adsorption isotherms, the Freundlich model was the most useful one to explain the sorption of Mo^{2+} ions by the magnetic Fe@Mg-Al LDH adsorbent. According to the R^2=0.99, the pseudo-second-order model is more suited to explain the Mo(II) sorption onto the magnetic Fe@Mg-Al LDH adsorbent. In the conclusion, the recommended approach offers an effective way to measure trace levels of lead ions in a variety of water samples. Notable features include high efficiency, rapid separation rate, high adsorption capacity, and good recovery. The magnetic Fe@Mg-Al LDH adsorbent may be used up to three more times since it works well at removing Mo^{2+} ions from aqueous solutions.

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