The Solid Phase Extraction of Some Heavy Metal Ions Using Dodecylamine Pillared Mg-Al Layered Double Hydroxides

Abstract

Pillared host-guest material or layered double hydroxide (LDHs) of the type Mg-Al-CO_3 with dodecylamine (DA) has been synthesized. The sorption capacities have been investigated for the removal of some heavy metal ions Ni(II), Cd(II), Co(II), Cu(II), Pb(II) and Cr(III) from natural water samples. The new LDHs compound Mg-Al-DA was characterized by fourier transform infrared spectroscopy (FT-IR), powder x-ray diffraction (PXRD) and scanning electron microscope (SEM). The analytical parameters such as pH, volume, the amount of sample and adsorption capacity for the quantitative recoveries of the ions using Mg-Al-DA was investigated. Effect of some common Interfering cations and anions that might be present in the water with the analyte on recovery was also examined. The recovery values of metal ions in natural water with relatively large sample volume of 100-1000 mL were greater than 95%. The determination of the heavy metal ions was carried out using atomic absorption spectroscopy.

Keywords: Layered Double Hydroxides; Adsorption; Heavy Metals; Extraction; Natural Waters**.**

1. Introduction

Determination and removal of trace heavy metal ions in environmental samples and especially in natural waters are an object of great interest that led to the ongoing search for the discovery and design of new materials [1-5]. The most common materials used in solid phase extraction were organic adsorbents such as sephiolits, thiol cotton, activated carbon, spent green tea leaves, microcrystalline naphthalene, cellulose, and Diaion HP-20 [6-11]. In the last decade, chelating resins from the commercial adsorption resins have been popular [12-15]. Drinking water is also an important source of heavy metals for humans. The difference between the quantity being acceptable or toxic is very limited. Therefore, trace levels of heavy metal ions in natural drinking water should be accurately evaluated in order to prevent any toxic or harmful effects. To do an accurate and precise analysis, it is advised to use inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES), x-ray fluorescence spectrometry, and graphite furnace atomic absorption spectrometry (GFAAS). However, these instruments are expensive and difficult to use. The separation or determination by flame atomic absorption spectrometry (FAAS) is a good alternative for these techniques due to low cost and ease in usage [16]. The nanoparticles of synthetic inorganics such as zeiolites or clays used as ion exchangers or adsorbents have shown a marked resistance to high temperatures, radiation, and high selectivity for a number of ions that to be removed from environmental samples. A variety of these materials which also include metal phosphates, heteropolyacids, and hydrous metal

oxides, have also been used for the separation of ionic and different molecular species [17-20].

Layered double hydroxides (LDHs) or what is called anionic clays, are an important type of materials that currently receiving much attention [21]. They consist of positively charged metal oxide sheets balanced by intercalated anions and water molecules [22], which lead to the possible exchange of the anion and subsequent incorporation of other guest molecules. Several LDHs have been structurally characterized in which some divalent metal cations have been substituted by trivalent ions with general formula:

$[M^{2+}_{1-X} M^{3+}_x (OH)_2]$ [x/nA^{n-}]. mH$_2$O. Where, M^{2+} and M^{3+} are metal cations. Possible M^{2+} and M^{3+} species include Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}or Ca^{2+} and Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, or Li^{3+}, respectively, x is equal to the ratio $M^{3+}/(M^{2+}+ M^{3+})$ and A^{n-} is an exchangeable anion of charge n$^-$ [22-24]. Miyata [25] reported that a hydrotalcite-like LDH transforms into a mixed magnesium aluminum oxide after heat treatment at 500-800 ^{0}C, which rehydrates and combines with anions to reform an LDH in the presence of water and anion. This property of LDHs can provide an effective synthetic route for incorporating inorganic and organic anions into LDHs. An advantage of this method is that the incorporation of inorganic counter anions into the LDH is prevented, although the inclusion of a small amount of carbonate from the atmosphere can not be ruled out. The ease and extent of reconstruction of the calcined LDH are controlled by the properties of the matrix ions and the temperature of calcination. Recent research focuses on the intercalation of some organic anions into LDHs, such as o-carboxylic acid, dodecylsulphates, sebacic acid, toluene-p-sulphonic acid and sulmanic acid [26, 27]. These compounds have proved to exhibit a remarkable complexing behavior for anionic species or cation – anion pairs and higher capacity for selective uptake of heavy metal ions. LDHs are decorated with hydroxyl groups at both layer surfaces. Since the closely related hydroxyl groups of kaolinite are amenable to several chemical modifications, surface LDHs hydroxyl groups are also expected to be susceptible to the same type of reactions, and showing higher reactivity due to the higher availability of reaction sites for metal ions [28]. Surfactants can drastically change the properties of the LDH. Studies of adsorption of single surfactant as well as mixtures of various types along with the mechanisms involved were studied. The adsorption systems along with structure–property relationships for industrial applications and for drug delivery systems in particular were recently reviewed [30]. The choice of dodecyleamine surfactant esteemed from its role as an important industrial agent such as its uses as antistatic agent in fabric softeners and hair rinse formulas. It is used in textile manufacturing to delay dye adsorption. Its action as a corrosion inhibitor in an acid environment in which it competes with H$^+$ ions. In addition, the intercalated dodecylamine will present a suitable site for complex formation with metal ion; such compound being incorporated within the layers of LDHs would open a new era for many industrial applications. In continuation of our previous work [29], and based on the reactions with the host material of the heat treated Mg-Al-LDH pillared dodecylamine guest molecule [C$_{12}$H$_{25}$NH$_2$], was prepared and subsequent uptake or extraction/removal of heavy metal ions from environmental or natural water samples is presented in this work.

2. Experimental

2.1 Reagents

All the starting chemicals and solvents were from Merck (standard analytical grade). Stock solutions of all metal ion salts were freshly prepared with the demineralized water (DMW). The buffer solutions of ammonium acetate (0.10M) were prepared by adding an appropriate amount of acetic acid to ammonium acetate to form solutions of pH 2-6 and ammonium chloride solution with ammonia to form a buffer of pH 8-10. The dodecylamine hydrochloride was prepared by mixing equal molar amounts of dodecylamine and 0.10N hydrochloric acid, following reported procedure. The mixture was heated to aid dissolution. Additional hydrochloric acid/ dodecylamine was added until the solution maintained a pH of 7.

2.2 Instrumentation

Powder x-ray diffraction (PXRD) pattern was recorded using a Philips APO 1700 instrument, with Ni-filtered Cu-Kα radiation. The FT-IR spectra of the material were recorded on a Perkin-Elmer FT-IR 1730 spectrophotometer. The pH measurements were recorded using an Elico-pH meter. A mechanical shaker was used for batch experiments. Shimadzu 6501 FAAS flame atomic absorption spectrometer was employed for determination of metal ions using an air/ acetylene flame.

2.3 Synthesis of Mg-AL-DA

The synthesis of Mg-Al-CO$_3$ LDHs host material was prepared first by taking 0.01mol of Mg(NO$_3$)$_2$.6H$_2$O and 0.05 mol of Al(NO$_3$)$_3$.9H$_2$O in 70 ml of deionized water was added with vigorous stirring to a solution of 0.35 mol of NaOH and 0.09mol of Na$_2$CO$_3$ (anhydrous) in 100 ml of demineralized water (DMW). The pH was maintained close to 10. After drying, the material was then calcined in air at 450°C. The calcined LDH was added to a 0.05-0.1mol solution of dodecylamine(DA) in about 100 ml of decarbonated distilled water [28].

2.4 Column preparation

The glass column containing a stopcock and a porous disk at the bottom with glass wool support was 25 cm long and 1.0 cm in diameter. Then, 1.0 g of Mg-Al-DA was packed into the column. It was washed successively with water and acetone, and then conditioned by passing 100 ml 2.0 % HCl through the column. All experiments were carried out at a flow rate 2-3 ml/min.

2.5 Sample preparation and pre-concentration procedure

Prior to the determination, laboratory sample solutions were prepared for testing the column method. 100 ml of solution containing 10-20 μg of the metal ion of interest was added to 10 ml buffer of desired pH, and then passed over the column at a flow rate of 2 ml/min. After passing of this solution, the column was rinsed twice with water. The adsorbed metal on the column was eluted with 10 ml portions of 2.0 M HCl. The eluent was later evaporated over a hot plate to dryness. The residue was dissolved in 5 ml of 1.0 M HCl, and then analyzed for metal concentration by FAAS.

2.6 Analysis of natural water samples

The water samples were collected in clean prewashed polyethylene bottles, filtered, then acidified to 1% with nitric acid and stored in 1 liter polyethylene bottles at 4°C. A sample of this water was taken and the above column separation method was applied. The investigated metal ions in the final solutions were then determined by flame AAS.

3. Results and discussion

3.1 *Characterization of Mg-Al-DA*

The x-ray powder diffraction studies figure 1 a) shows the prepared material after incorporation of dodecylamine and in figure 1 b) the host Mg-Al-CO$_3$ LDH as prepared in which a d$_{003}$ reflection gave a sharp peaks corresponding to a basal spacing shift from 7.7 Å to 13.2 Å, given that the interlayer thickness of a brucite layer is 4.8 Å. In figure 1 c) the amorphous nature of the material is shown after heat treatment at 450 °C.
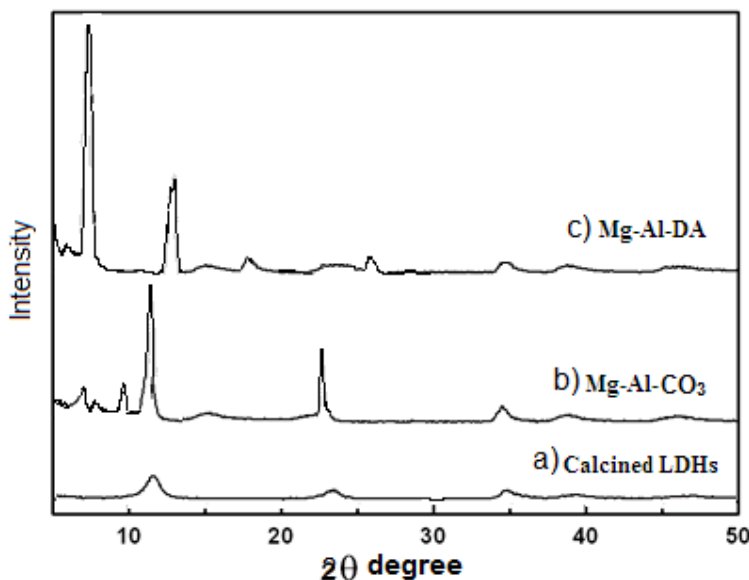

Figure 1: XRD for the a) calcined LDH at 450 °C, b) parent (host) as prepared and c) the intercalated LDHs with dodecylamine.

The interlayer height generated is close to 8.4 Å which gives clear evidence of the incorporation of DA between the layers of the double hydroxide sheets. In addition to the basal spacing for the d$_{0012}$ and d$_{012}$ with low intensities at higher angle confirming the presence of dodecylamine [28].
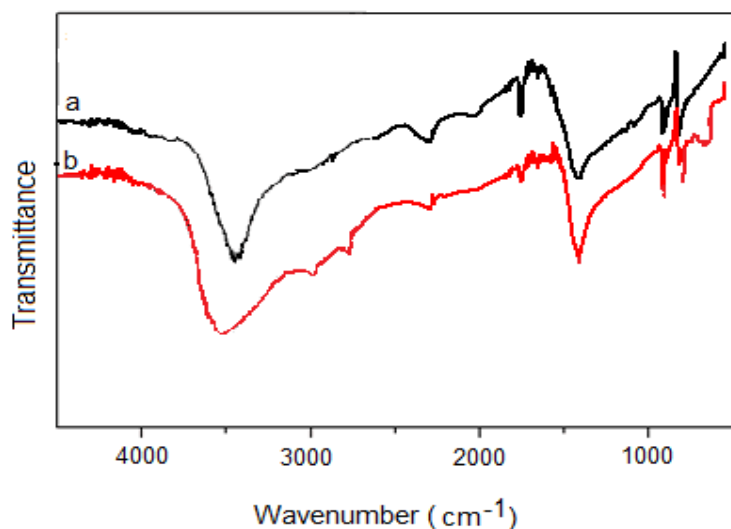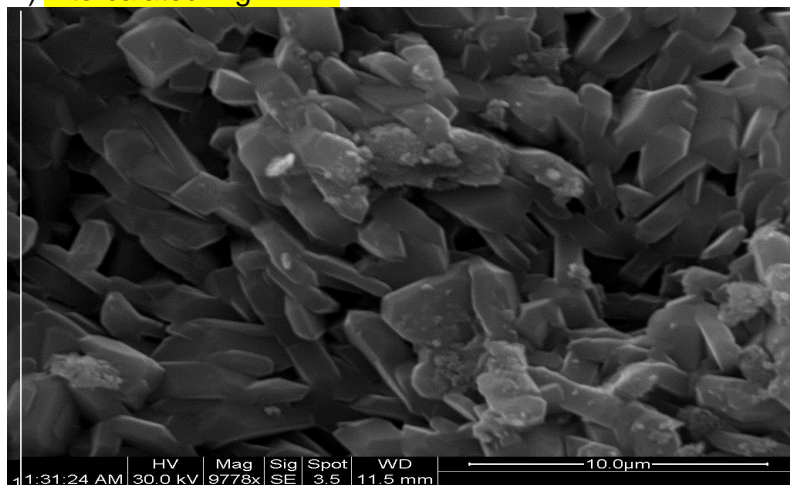
Figure 2: FT-IR for: a) Mg-Al-CO$_3$ and b) Intercalated compound of Mg-Al-DA.

When the infrared spectra of Mg-Al-CO$_3$ and Mg-Al-DA were compared, **Fig. 2**, four additional bands were observed, two sharp bands at 2933 and 2856 cm^{-1} are assigned to the C-H stretching vibrations. A sharp, strong band at 1400 cm^{-1} and a broad band at 600 cm^{-1} are observed characteristic of the C-N stretching mode. These situations also agree with our previous studies [28]. A series of 500 mg of Mg-Al-DA were saturated with each metal ion, separately in the optimal conditions. Their FT-IR spectra were recorded and compared with FT-IR spectra of Mg-Al-DA. The characteristic band due to C-N group gave a change in the frequency from 1400 to 1384 cm^{-1} when a metal ion was adsorbed on the Mg-Al-DA. This suggests that the coordination of the metal ions with the amino group is responsible for their complexing behavior and subsequent sorption onto the Mg-Al-DA material. The scanning electron microscope (SEM) in **Fig. 3** for Mg-Al-DA shows a belt-like structure with average particle size less than 5.0 μm. The calcination at 450 °C resulted in the removal (dehydroxilation) of the intercalated dodecylamine and subsequent collapse of the layer structure of the LDH with only metal oxide product.
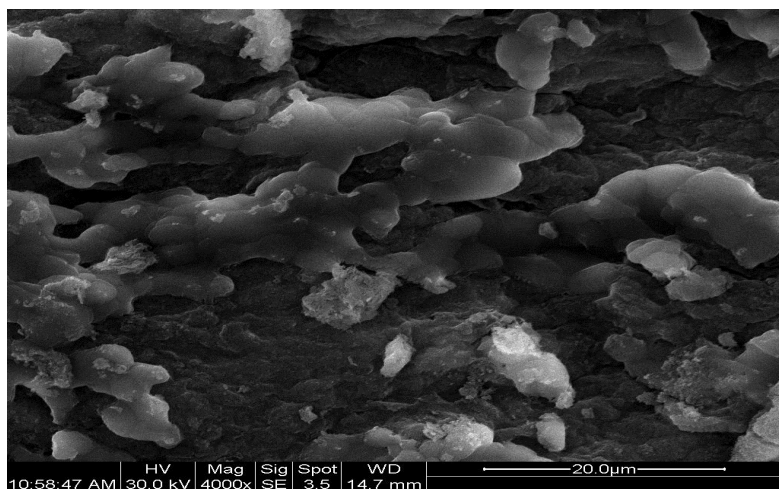
A) Intercalated Mg-Al-DA

B) Calcined Mg-Al-DA

Figure 3: SEM image for: A) Intercalated Mg-Al-DA and B) Calcined Mg-Al-DA at 450 °C.

3.2 Effect of pH on the retentions

Fig. 4 shows the results of the influence of pH on the retention behavior of Ni(II), Co(II), Cu(II), Cd(II), Pb(II) and Cr(III) on the Mg-Al-DA in the pH range of 2-11. 50 ml test solutions containing 20 µg of each analyte ion were adjusted by buffer solutions given in the experimental section to give the final desired pH value. The addition of the buffer at pH ~2-7 gave a slow release profile plots indicating the less recovery of the metal ions which may be attributed to the presence of gibbsite-like form in the LDHs at this range of pH, and subsequently decreases the influence of dodecylamine. These investigations showed that the metal ions could be recovered quantitatively in the pH range of 8.5-10. In the light of the above observations, and as expected, that the pH should have a marked effect on the sorption of metal ions as well as on the recovery, an increase in pH markedly reduces the amount of hydroxides, and therefore increases the average charge on the LDHs layer making the dodecylamine more strongly protonated, giving rise to excess positive charge and hence the smooth release of metal ions. The volume of the buffer solution had no much influence on recoveries. In all further experiments a 10 ml ammonium chloride buffer solution of pH 10 was used.
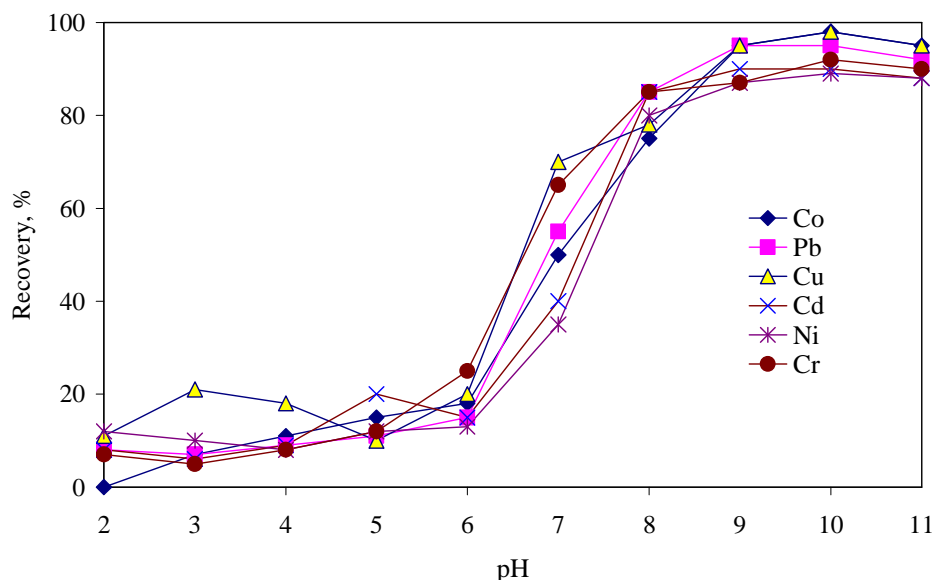
Figure 4: Effect of pH in the retention of metal ions on LDH-DA material

3.3 Effect of eluent type and volume

Table 1 shows the results of the influence of eluent type on recoveries of metal ions. It is well known that the type of eluent is an important factor in the solid phase extraction. The effect of 20 ml of various eluents, namely nitric acid, hydrochloric acid, ammonia and ammonium nitrate with a concentration ranging from 1 M to 2 M solution was studied. From these results it is clear that selective recoveries of metal ions are possible for a number of eluents. The best eluent chosen was 2 M HCl in acetone for all metal ions. Note that some other eluent could be used for specific metal ion(s) like 1 M HNO_3 which is suitable for Ni(II), Co(II) and Cu(II) ions. The volume of the eluent investigated in the range 5-20 ml. Quantitative recovery (>95%) were obtained after 10 ml of the eluent volume was used.

Table 1: Effect of various eluent types and concentration on the recoveries of metal ions from the Mg-Al-DA column.

Eluent type	Recovery (%)*					
	Ni^{2+}	Cd^{2+}	Co^{2+}	Cu^{2+}	Pb^{2+}	Cr^{3+}
1 M HCl	100±2	78±2	98±2	104±2	101±3	85±2
2 M HCl	89±3	67±2	94±2	92±3	103±2	77±3
1 M HCl in acetone	89±3	68±2	94±1	92±2	103±2	78±3
2 M HCl in acetone	101±2	96±2	100±2	98±2	102±2	97±2
1 M HNO_3	100±2	95±2	102±2	99±3	85±3	88±4
2 M HNO_3	98±2	96±3	94±2	96±1	84±2	92±2
1 M HNO_3 in acetone	103±2	89±2	100±3	104±2	101±3	85±2
2 M HNO_3 in acetone	96±3	72±2	68±3	84±2	73±3	73±1
1 M NH_3	18±2	20±2	<10	<10	17±2	<10

2 M NH$_3$	22±3	17±2	15±1	<10	<10	<10
1 M NH$_3$ in acetone	<10	<10	<10	16±2	<10	<10
2 M NH$_3$ in acetone	<10	<10	16±2	14±2	<10	<10
1 M NH$_4$NO$_3$	<10	<10	<10	<10	<10	<10
2 M NH$_4$NO$_3$	13±1	21±2	24±2	<10	16±2	<10
1 M NH$_4$NO$_3$ in acetone	<10	<10	<10	<10	15±2	<10
2 M NH$_4$NO$_3$ in acetone	18±3	21±2	11±2	<10	<10	12±2

The value following ± is the standard deviation (n = 3). Elution volume 20 ml.

3.4 Influence of Mg-Al-DA amount

The influence of the amounts of Mg-Al-DA material filled in the column, on the recoveries of the investigated metal ions. With the increasing amount of Mg-Al-DA above 400 mg an increase in the recovery can be achieved. The results are shown in **Fig. 5**. The material amounts were taken in the range of 400-1200 mg. The recoveries were not quantitative up to 600 mg of the material. With the amount of material increase above 600 mg, efficient extractions and a quantitative recovery were observed. For further studies 1000 mg amount was chosen as it shows the maximum efficiency (>95%) for most metal ions under investigation.
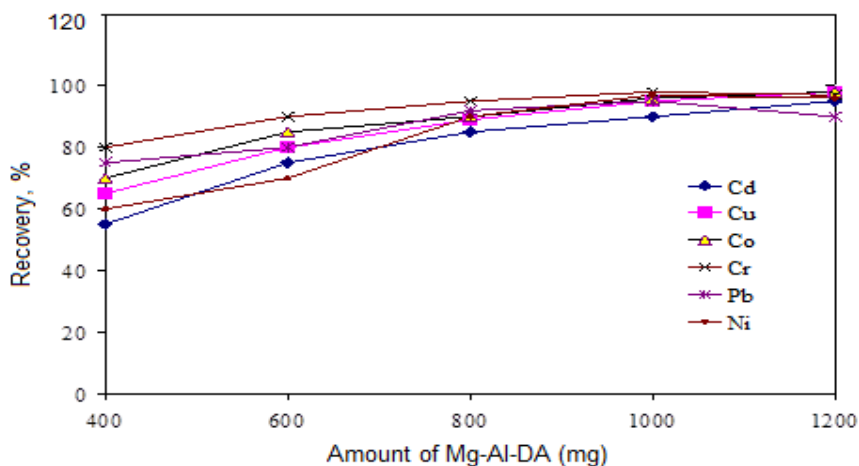

Figure 5: Influence of Mg-Al-DA amounts on the recoveries of investigating ions (using 2 M HCl in acetone)

3.5 Effect of sample volume on the recoveries

To study the effect of larger volumes of sample, environmental samples, 20 μg of the analyte ions was taken as sample test solutions. The amount of metal ion is taken constant while increasing the sample volume. Due to low concentration of heavy metals in the real environmental samples, preconcentrations have been done on large volume. **Fig. 6** shows the results of the effect of sample volume in the range of 100-1200 ml on the sorption of metal ions by passing these volumes through the

column packed with 1000 mg Mg-Al-DA material. <mark>The recoveries of the analyte ions were quantified</mark> and the adsorption of metal ions was not affected by the sample volume until 1000 ml.
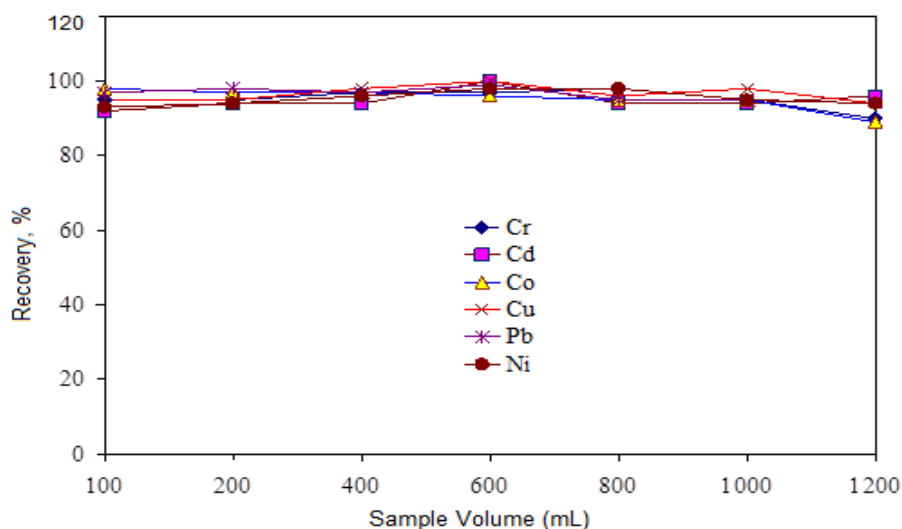

Figure 6: Effect of sample volume on the recoveries of metal ions (eluent: 2 M HCl in acetone).

3.6 Adsorption capacity of Mg-Al-DA material

The study of metal ion absorptive capacity on Mg-Al-DA was carried out using batch method. 0.5 g of the material and 25 ml of metal ion solution containing 10 mg of the ion of interest at pH 10 were mixed and kept for 1 hour under intermittent shaking. The mixture was then filtered off and the supernatant solution was determined by atomic absorption spectrometer. The capacities for Ni(II), Co(II), Cu(II), Cd(II), Pb(II) and Cr(III) were 3.6, 3.8, 3.5, 4.0, 3.8, and 4.0 mg/g Mg-Al-DA, respectively.

3.7 Effect of <mark>foreign</mark> cations and anions

Table 2 shows the <mark>results of the effect of possible matrix ions influence in the environmental samples including some transition metal ions. These cations and anions that might be present in natural water samples, normally do not interfere with the analysis under the experimental conditions used. The recovery of metal ions under such conditions evaluated the possibility of selective recovery.</mark> To do that, 100 ml solution containing ions like Ca^{2+}, Mg^{2+}, K^+, and Na^+ with the analyte ion <mark>was</mark> used. It can be seen that quantitative recoveries were obtained for each metal ion, except a low recovery found with Ca^{2+}. The concentrations of these salts were found significantly low in the eluent solutions, giving a suitable determination and a potential application of natural or <mark>environmental water samples with results that is independent from the matrix effects.</mark>

9

Table 2: Effect of some common Interfering cations and anions on recovery

Interfering Ion (added as)	Added (mg/L)	Found (mg/L)	Recovery (%)*					
			Ni^{2+}	Cd^{2+}	Co^{2+}	Cu^{2+}	Pb^{2+}	Cr^{3+}
Na^+ (NaCl)	1000	15	102±2	97±1	95±1	94±2	99±2	100±2
	500	8	102±2	98±2	95±2	93±3	102±2	98±1
K^+ (KCl)	1000	11	100±3	97±2	102±3	96±1	99±2	97±2
	500	-	97±2	96±2	98±2	98±2	98±2	95±1
Mg^{2+} (MgCl$_2$)	1000	14	101±2	99±1	98±2	99±2	102±2	95±2
	500	10	99±1	96±2	95±2	96±2	101±3	97±2
Ca^{2+} (CaCl$_2$)	250	30	95±1	95±2	98±1	101±2	97±2	99±2
	100	12	97±2	96±2	102±2	100±2	96±1	95±2
Cl^- (NH$_4$Cl)	500	-	100±3	101±2	98±1	100±3	99±1	97±2
	250	-	101±2	100±2	96±2	98±2	96±2	96±2
SO_4^{-2} ((NH$_4$)$_2$SO$_4$)	500	-	98±2	95±2	98±1	102±2	94±1	95±2
	250	-	97±1	96±2	97±2	98±2	97±1	96±1

The value following ± is the standard deviation (n = 3).

3.8 Procedure accuracy for natural water samples

In order to estimate the accuracy and reliability of the presented method was checked by doing a spiking experiments, variable amounts of investigated metal ions were added to 500 ml of drinking water samples collected from Tafila Technical University and the main city center. **Table 3** shows the results of recovery when compared between the added and measured metal ion amounts. The recovery values obtained for the added and measured analyte amounts gave a good agreement with direct analysis. This confirm the accuracy of the proposed procedure and the effectiveness of Mg-Al-DA material.

Table 3: Recovery of Ni(II), Cd(II), and Cu(II) from tap water samples

Metal ion	Added (µg)	College		City	
		Found (µg)	Recovery (%)*	Found (µg)	Recovery (%)*
Ni^{2+}	0	4.2±0.3	-	-	-
	20.0	23.6±0.2	96±1	19.3±0.4	98±2
Cd^{2+}	0	2.9±0.2	-	3.2±0.1	-
	20.0	23.8±2	102±3	23.3±0.4	102±1
Co^{2+}	0	-	-	-	-
	20.0	22.3±0.9	98±4	20.2±0.5	100±4
Cu^{2+}	0	4.2±0.2	-	8.6±0.5	-
	20.0	24.5±0.5	102±3	28.5±0.6	99±4

Pb^{2+}	0 20.0	- 20.2±2	- 101±2	12.6±0.8 32.5±0.7	- 99±4
Cr^{3+}	0 20.0	- 20.2±0.6	- 101±2	- 20.4±0.5	- 102±2

* Average of five determinations. 500 ml sample volume, final volume: 5 ml.

The detection limits of the investigated ions based on the standard deviation and evaluated as the concentration corresponding to three times of ten runs of the blank solution, measurements were between 0.065 to 0.382 µg/L for 100 ml sample volume. In **Table 4**, the results of the method for the separation of the metal ions studied in natural water samples collected from different parts of a local city. These results were obtained and calculated on the assumption of 100% recovery and zero interference for working elements.

Table 4: Concentration of metal ions in the natural water samples taken from different sites in a local city.

Sample	Concentration (µg/L)*					
	Ni^{2+}	Cd^{2+}	Co^{2+}	Cu^{2+}	Pb^{2+}	Cr^{3+}
Campus	3.0±0.2	-	1.4±0.2	5.9±0.2	4.7±0.3	-
Al-Eas	-	-	1.2±0.1	5.4±0.2	4.4±0.3	1.8±0.1
City Market	4.6±0.2	0.8±0.1	1.5±0.2	4.3±0.1	5.1±0.4	2.4±0.3
Qadesia	3.5±0.3	-	5.2±0.1	5.9±0.2	2.8±0.2	-

* Average of five determinations

4. Conclusion

Based on the practical results found in this study, it can be concluded that the use of Mg-Al-DA material gave a simple and effective procedure for the separation/solid phase extraction of heavy metal ions in natural water samples or environmental samples in general. The quantitative investigations showed more than 95 % recovery for all metal ions in the pH range of 8.5 -10. The capacities for Ni(II), Co(II), Cu(II), Cd(II), Pb(II) and Cr(III) were 3.6, 3.8, 3.5, 4.0, 3.8, and 4.0 mg/g Mg-Al-DA, respectively. The ease of preparation and cost effect of Mg-Al-DA material gave another advantage for this method. Our next work will focus on dodecylamine incorporated in LDHs. The material will be considered as the model corrosion inhibitor. The electrochemical and surface analysis methods will be adopted to investigate the adsorption behavior and inhibition mechanism of dodecylamine at different pH values, and further to probe the influence of pH value on the inhibition performance of dodecylamine on metal surface.

References

[1] Ghaedi, M. Rezakhani, M. Khodadoust, S. Niknam, K. and Soylak, M. The Solid Phase Extraction of Some Metal Ions Using Palladium Nanoparticles Attached to Silica Gel Chemically Bonded by Silica-Bonded N-Propylmorpholine as New Sorbent prior to Their Determination by Flame Atomic Absorption Spectroscopy. The Scientific World Journal Volume 2012; Article ID 764195, 9 pages doi:10.1100/2012/764195

[2] Jamhour,Rasheed M.A.Q. and Al-Mazaideh G. M. Treatment of Chromium(III) in Tannery Wastewater Using LDH Incorporated With EDTA. Journal of Environment and Earth Science. 2014; 4, 8: 98-104.

[3] Ghaedi, M. Tavallali, H. Montazerozohori, M. Mousavi, S. D. Khodadoust, S. Soylak, M. A novel nanometer pore size acorn based activated carbon modified with 2-(4-methoxybenzylideneamino) thiophenol for the preconcentration of copper and zinc ions and their determination in some food samples. Fresenius Environmental Bulletin. 2011; 20: 2783–2793.

[4] Ghaedi, M. Shokrollahi, A. Kianfar, A. H. Mirsadeghi, A. S. Pourfarokhi, A. and Soylak, M. The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon. Journal of Hazardous Materials. 2008; 154, 1–3: 128–134.

[5] Tuzen, M. Soylak, M. Evaluation of Metal Levels of Drinking Waters from the Tokat-Black Sea Region of Turkey. Polish J. of Environ. Stud. 2006; 15, 6: 915-919.

[6] Soylak, M.and Tuzenb, M. Diaion SP-850 resin as a new solid phase extractor for preconcentration-separation of trace metal ions in environmental samples. Journal of Hazardous Materials. 2006; 137, 3: 1496–1501.

[7] Lia, Z. Changa, X. , Hua, Z. Huanga, X. Zoua, X. Wua, Q. Niea. R. Zincon-modified activated carbon for solid-phase extraction and preconcentration of trace lead and chromium from environmental samples. Journal of Hazardous Materials. 2009; 166,1: 133–137.

[8] Ko ,D. C. K. Tsang , D. H. K. Porter , J. F. and McKay, G. Applications of Multipore Model for the Mechanism Identification during the Adsorption of Dye on Activated Carbon and Bagasse Pith. Langmuir. 2003; 19, 3: 722–730.

[9] Zuorro, A. and Lavecchia, R. Adsorption of Pb(II) on Spent Leaves of Green and Black Tea. American Journal of Applied Sciences. 2010; 7, 2: 153-159.

[10] Shabany, M. Haji Shabani, A. M. Dadfarnia,S. Gorji, A. Ahmadi, S. H. Solid phase extraction of zinc with octadecyl silica membrane disks modified by N,N'-disalicylidene-1,2-phenylendiamine and determination by flame atomic absorption spectrometry. Eclet. Quím. 2008; 33, 2: 61-66.

[11] Yebra, M.C, García, A. Carro, N. Moreno-Cid, A. Puig, L. Design of a field flow preconcentration system for cadmium determination in seawater by flow-injection-atomic absorption spectrometry. Talanta. 2002; 56, 4: 777–785.

[12] Saracoglu, S. Divrikli, U. Soylaki, M. and Elci, L. Determination of Copper, Iron, Lead, Cadmium, Cobalt and Nickel by Atomic Absorption Spectrometry in Baking Powder and Baking Soda Samples after Preconcentration and Separation. Journal of Food and Drug Analysis. 2002; 10, 3: 188-194.

[13] Tikhomirova, T.I; Kuznetsov, M.V; Dubovik, D.B; Tsizin, G.I; Zolotov, Y.A. Preconcentration of arsenic(V) as molybdoarsenic heteropoly acid by dynamic sorption. J. Anal. Chem. 2000; 55,9: 846-850.

[14] Pana, B.C. Menga, F.W. Chena, X.Q. Pana, B.J. Lia, X.T. Zhanga, W.M. Zhanga, X. Chena, J.L. , Zhanga, Q.X. Sun, Y. Application of an effective method in predicting breakthrough curves of fixed-bed adsorption onto resin adsorbent. Journal of Hazardous Materials. 2005; 124, 1–3: 74–80.

[15] Tewari, P.K. and Singh, A.K. Amberlite XAD-7 Impregnated with Xylenol Orange: A chelating Collector for Preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) Ions Prior to Their Determination by Flame AAS. Fresen. J. Anal. Chem. 2000; 36, 7: 562-566.

[16] Ghaedi, M. A. F. and Soylak, M. Simultaneous preconcentration of copper, nickel, cobalt and lead ions prior to their flame atomic absorption spectrometric determination. Annali di Chimica. 2007; 97, 5-6: 277–285.

[17] Chen, W. Feng, L. and Qu, B. Preparation of Nanocomposites by Exfoliation of ZnAl Layered Double Hydroxides in Nonpolar LLDPE Solution. Chem. Mater. 2004; 16,3: 368–370.

[18] Gunjakar, J.L. Kim,T. W. Kim, H. N. Kim, I. Y. and Hwang, S.J. Mesoporous Layer-by-Layer Ordered Nanohybrids of Layered Double Hydroxide and Layered Metal Oxide: Highly Active Visible Light Photocatalysts with Improved Chemical Stability. J. Am. Chem. Soc. 2011; 133 , 38: 14998–15007
.
[19] Boclair, J. W. and Braterman, P. S. Layered Double Hydroxide Stability. 1. Relative Stabilities of Layered Double Hydroxides and Their Simple Counterparts. Chem. Mater. 1999; 11, 2: 298–302.

[20] Alcantara, A. C. S. Aranda, P. Darder, M. Ruiz-Hitzky, E. Bionanocomposites based on alginate–zein/layered double hydroxide materials as drug delivery systems. J. Mater. Chem. 2010; 20: 9495–9504.

[21] Sels, B. F. De Vos, D. E. Grobet, P. J. Preparation and mechanical properties of polypropylene-clay hybrids. Nature. 1999; 400: 855–857.

[22] Lu, Z. Xu, W. Zhu, W. Yang, Q. Lei, X. Liu, J. Li, Y. Sun, X. and Duan, X. Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction. Chem. Commun. 2014; 50: 6479–6482.

[23] Xiang, X. Li, F. Huang, Z. Recent advances in layered double hydroxide-based materials as versatile photocatalysts. Rev. Adv. Sci. Eng. 2014; 3: 158–171.

[24] Wang, Q. O'Hare, D. Recent Advances in the Synthesis and Application of Layered Double Hydroxide (LDH) Nanosheets. Chem. Rev. 2012; 112: 4124–4155 and references therein.

[25] Miyata, S. Physico-Chemical Properties of Synthetic Hydrotalcites in Relation to Composition. Clays and Clay Minerals. 1980; 28, 1: 50-56.

[26] Newman, S. P. and Jones, W. Synthesis, characterization and applications of layered double hydroxides containing organic guests. New J. Chem. 1998; 22: 105-115.

[27] Zhang, R. and Somasundaran P. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. Adv. Colloid Interface Sci. 2006; 123-126: 213–229.

[28] Qureshi, S.Z. Jamhour, R.M.A.Q. Rahman, N. Intercalation of Dodecylamine and Sulfamic acid into Layered Double Hydroxide. Annales de Chimie. Fr. 1996; 21: 231-236.

[29] Jamhour, R. M. A. Q. and Almazaideh, G. M. Treatment of chromium(III) in tannery wastewater using LDH incorporated with EDTA. Journal of environment and earth science. 2014; 4, 8: 98-104.

[30] Zhang, K. Xu, Z. P. Lu, J. Tang, Z. Y. Zhao, H. J. Good, D. A. and Wei, M.Q. Potential for Layered Double Hydroxides-Based, Innovative Drug Delivery Systems. Int. J. Mol. Sci. 2014; 15, 5: 7409–7428.