
Determination of Pb and Ni in natural water samples after solid phase extraction with layered double hydroxide (LDH) nano-particles

Saeedeh sepehrikiya¹, Donya arefi^{2,*}

¹Laboratory Expert, Mashhad University of Medical Science, Khorasan-Razavi, Iran

²Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Zabol University of Medical Sciences, Zabol, Iran

Email address:

Sepehrikiya@yahoo.com (S. sepehrikiya), Donya_arefi@yahoo.com (D. arefi)

To cite this article:

Saeedeh sepehrikiya, Donya arefi. Determination of Pb and Ni in Natural Water Samples after Solid Phase Extraction with Layered Double Hydroxide (LDH) Nano-Particles. *American Journal of Nanoscience and Nanotechnology*. Vol. 1, No. 4, 2013, pp. 83-86.

doi: 10.11648/j.nano.20130104.12

Abstract: Due to the industrialization, especially in the developing countries, the emission of the heavy metals as lead, cadmium, chromium, nickel, arsenic, and mercury are highly concerned to public and aquatic health. Lead is released with the effluent from the paint, batteries, and automobiles manufacturing units. Lead is one of the toxic metals and largely affects the central, peripheral nervous system. In this study, a suitable and reliable method for the direct determination of Pb and Ni ions in environmental water is proposed. Pb and Ni ions were extracted and preconcentrated with layered double hydroxides (LDHs) nano-particles. LDHs, relatively inexpensive and simply prepared material, was synthesized and used as a solid phase extraction (SPE) adsorbent to quantitatively determine the concentration of Pb and Ni ions in natural water samples. Several factors affecting the extraction efficiency, such as, eluent type, eluent volume, flow rate of sample, sample volume, and amount of adsorbent, were investigated and optimized in detail. Pb and Ni ions can be quantitatively retained by LDH nano-particles, then eluted completely by 1 mL of CO_3^{2-} (1.5 mol L^{-1}) and 1 mL EtOH (65% v/v), respectively. The detection limit of this method for Pb and Ni ions was 17 ng mL^{-1} with an enrichment factor of 100, and the relative standard deviation (RSD) was 1.4%.

Keywords: Pb, Ni, Nano-Particle, Solid Phase Extraction, Layered Double Hydroxide (LDH)

1. Introduction

Trace metal ions have important roles in our life functioning in a wide spectrum. Thus, the determination of trace metal ions is becoming increasingly important because of the increased interest in environmental samples including water, soil and plant, etc.

Toxic heavy metals constantly released into the environment. They are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in environment and in food chains [1-2]. The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, metal finishing industries, tanneries, chemical manufacturing, mine drainage and battery manufacturing [3].

Layered Double Hydroxides (LDHs), also called anionic clays, are clay-like materials that show promising properties for a large number of applications. These materials exhibit

unique physical and chemical properties such as high specific surface area, swelling property, memory effect, high anion exchange capacity, and dispersive property. Moreover, LDHs have many pharmaceutical properties such as improving solubility of poorly water-soluble drugs and also barrier properties similar to those of gastric mucosa. Anionic clays are promising materials for the immobilization of biomolecular and development of biosensor electrodes due to their anion exchange and intercalation capacity, hydrophilicity, and adsorption of biomolecular such as proteins and enzymes. Also, they are nontoxic and show good biocompatibility.

Clays can be divided into two main classes: cationic clays that have negatively charged aluminosilicate layers; and anionic clays, with positively charged hydroxide layers. The neutrality of these materials is ensured by intercalation of cations or anions in the interlayer space. Layered Double

Hydroxides (LDHs), also called anionic clays, are clay-like materials that show promising properties for a large number of applications.

2. Methods

Layered double hydroxides (LDHs) have been known for over 150 years since the discovery of the mineral hydrotalcite. They are a broad class of inorganic lamellar compounds with high capacity for anion intercalation. LDHs are also widely known as hydrotalcite-like compounds due to their structural similarities to hydrotalcite, a mineral with the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ which was first studied by Manasse in 1915. The X-ray diffraction (XRD) studies on mineral samples were carried out by Allmann and Taylor. The hydrotalcite structure results from the stacking of brucite-like layers $[Mg(OH)_2]$ containing extra positive charge due to the partial isomorphous substitution of Mg^{2+} by Al^{3+} . This positive excess charge is balanced by carbonate anions, which exist in the interlamellar spaces [4-6]. The structure of LDHs is represented by the general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} (An)_{x/n} \cdot mH_2O$ where M^{2+} and M^{3+} can be any divalent and trivalent metal ions (whose ionic radius is not so different from that of Mg^{2+}), which can be accommodated in the octahedral sites in the brucite-like layers and x is the metal ratio $M^{3+}/(M^{2+}+M^{3+})$. An- in the interlamellar region can be any anion (organic or inorganic) and m is the amount of water in mol, present in the same region. The amount of water in the interlayer region can be determined by factors such as the nature of the anions, the water vapor pressure and temperature [7].

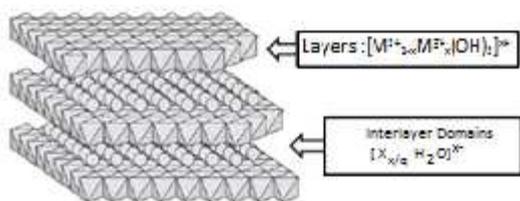


Fig 1. Structure of LDH

The accurate and precise determination of metal ions at trace levels is an important field in analytical and environmental chemistry [8-11], because of their roles in the human body and environment. Inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES), graphite furnace (GFAAS) and flame (FAAS) atomic absorption spectrometry are the main analytical instruments used currently [12-14]. Element concentrations those are low relative to the detection limits of ICP-OES and atomic absorption spectrometry. Even $ng L^{-1}$ level of trace metal could be determined by ICP-MS, the interference effects caused by the matrix components of real samples is problematic for ICP-MS, ICPOES and GFAAS [15-18]. These difficulties can generally be avoided by using enrichment-separation techniques such as solvent

extraction, cloud point extraction, membrane filtration, coprecipitation and electrodeposition [19-22]. Solid phase extraction (SPE) is a cost-effective and important preconcentration-separation technique for separation enrichment of trace metal ions that offers important advantages, including simplicity, rapid analysis, and simple adaptation to automation [23-27]. Solid phase extraction also performs well in the preconcentration of trace metals with respect to minimizing solvent waste generation and the adsorption of analytes on the adsorbent in a more stable chemical form [28-31]. Adsorbents are preferred for the SPE of metal ions from environmental samples and these should have the following properties: the possibility for extracting a variety of metal ions over a wide pH range, high surface area, fast and quantitative adsorption and easy elution, ultra purity, repeated usability and accessibility [32-36]. Carbon nanotubes possess these properties and their use for enrichment and separation of metal ions at trace levels has been very popular in recent years.

3. Results and Discussion

Trace concentrations of metals were determined by FAAS using a WFX210 Model Atomic absorption spectrometer. The air-acetylene flame was adjusted according to the manufacturer's recommendations. A Hanna Instrument pH 211 microprocessor pH meter equipped with a combined glass calomel electrode was used for the pH adjustment. All solutions were delivered to pass through the glass column, having a stopcock and a porous disk was 10 cm long and 1.0 cm in diameter packed with Chromosorb 105.

The first prepared different concentrations of the sample after solid phase extraction were added to the sample layered double hydroxide (LDH) nano-particles finally were read absorption the samples with AAS. Pb and Ni ions can be quantitatively retained by LDH nano-particles, then eluted completely by 1 mL of CO_3^{2-} ($1.5 mol L^{-1}$) and 1 mL EtOH (65% v/v), respectively. Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance, is the main instrument in the research laboratories for determining a variety of heavy metals. The detection limit of this method for Pb and Ni ions was $17 ng mL^{-1}$ with an enrichment factor of 100, and the relative standard deviation (RSD) was 1.4%.

References

- [1] Sari A, Tuzen M and Soylak M, J. Hazard. Mater, 2007,144,41- 46.
- [2] Bulut Y and Baysal Z, J. Environ. Manage, 2006, 78,107-113.
- [3] Matheickal J T and Yu Q, Miner Eng. ,1997, 10 ,947-957.
- [4] Khan, A., O'Hare, D., "Intercalation chemistry of layered double hydroxides: recent developments and applications", J.

- Mater. Chem., vol.12, 2002, p.p. 3191–3198,
- [5] Miyata, S., “The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties”, *Clays and Clay Minerals*, vol.23, 1975, p.p. 369-375.
 - [6] Miyata, S., “Anion exchange properties of hydrotalcite-like compounds”, *Clays and Clay Minerals*, vol.31, 1983, p.p. 305-311.
 - [7] Hou, X., Bish, D., Wang, S., Johnston, T., Kirkpatrick, R.; “Hydration, expansion, structure, and dynamics of layered double hydroxides”, *American Mineralogist*, vol.88, 2003, p.p. 167–179.
 - [8] Soy lak M, Karatepe AU, Elci L, Dogan M (2003) Column Preconcentration/Separation and Atomic Absorption Spectrometric Determinations of Some Heavy Metals in Table Salt Samples Using Amberlite XAD-1180. *Turk J Chem* 27:235–242
 - [9] Popa C, Bulai P, Macoveanu M (2010) The study of iron (II) removal from 34% calcium chloride solutions by chelating resin purolite S930. *Environ EngManag J* 9:651–658
 - [10] Soy lak M, Turkoglu O (1999) Trace metal accumulation caused by traffic in agricultural soil near a Motorway in Kayseri-Turkey. *Journal of Trace and Microprobe Techniques* 17:209–217
 - [11] Khadem M, Golbabaie F, Rahimi-Froushani A, Shahtaheri SJ (2010) Optimization of solid phase extraction for trace determination of cobalt (II) using Chromosorb 102 in biological monitoring. *Int J Occupational Hygiene* 2:11–17
 - [12] Uluozlu OD, Tuzen M, Mendil D, Soy lak M (2007) Trace metal content in nine species of fish from the black and Aegean seas, Turkey. *Food Chem* 104:835–840.
 - [13] Kazi TG, Baig JA, Shah AQ, Kandhro GA, Khan S, Afridi HI, Kolachi NF, Wadhwa SK, Shah F, Mehmood Baig A (2011) Determination of arsenic in scalp hair samples from exposed subjects using microwave-assisted digestion with and without enrichment based on cloud point extraction by Electrothermal Atomic Absorption Spectrometry. *J AOAC Int* 94:293–299
 - [14] Soy lak M, Elci L (2000) Solid phase extraction of trace metal ions in drinking water samples from Kayseri-Turkey. *J Trace Microprobe Techniques* 18:397–403
 - [15] Kamau JN, Ngila JC, Kindness A, Bush A (2011) Equilibrium and kinetic studies for extracting Cu, Mn, and Fe from Pulp wastewater onto a C-18 Column with Acetylaceton Complexing Ligand. *Anal Lett* 44:1891–1906.
 - [16] Aydin FA, Soy lak M (2007) A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples. *Talanta* 73:134–141.
 - [17] Li C, Zhang Z, Pan J, Gao J, Zhao G, Guan W, Yan Y (2010) Synthesis and characterisation of sodium trititanate whisker surface Cd(II) ion-imprinted polymer and selective solid-phase extraction of cadmium. *Int J Materials Structural Integrity* 4:291–307.
 - [18] Ciopec M, Negrea A, Davidescu CM, Negrea P, Muntean C, Popa A (2010) Use of Di-(2-Ethylhexyl) Phosphoric Acid (DEHPA) Impregnated XAD-8 Copolymer Resin for the Separation of Metal Ions from Water. *Chem Bull “POLITEHNICA” Univ (Timisoara)* 55:127–131
 - [19] Soy lak M, Sahin U, Elci L (1996) Spectrophotometric determination of molybdenum in steel samples utilising selective sorbent extraction on Amberlite XAD-8 Resin. *Anal Chim Acta* 322:111–115.
 - [20] Khosravan M, Vaezi M (2011) Synthesis, characterization of silica gel phases chemically immobilized with 2-Aminothiophenol and the use of it for preconcentration and determination of trace amounts of lead and batch studies by Flame Atomic Absorption Spectrometry. *Eur J Sci Res* 48:614–620
 - [21] Ezoddin M, Shemirani F, Khani R (2010) Application of mixed micelle cloud point extraction for speciation analysis of chromium in water samples by electrothermal atomic absorption spectrometry. *Desalination* 262:183–187.
 - [22] Duran C, Gundogdu A, Bulut VN, Soy lak M, Elci L, Senturk HB, Tufekci M (2007) Solid phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) Ions from Environmental Samples. *J Hazard Mater* 146:347–355
 - [23] Soy lak M, Narin I, Dogan M (1997) Trace enrichment and atomic absorption spectrometric determination of lead, copper, cadmium and nickel in drinking water samples by Use of an Activated Carbon Column. *Anal Lett* 30:2801–2810.
 - [24] Sahnurova A, Turkmenler H, Ozbas EE (2010) Biosorption Kinetics and isotherm studies of Cd(II) by Dried Enteromorpha compressa Macroalgae Cells from Aqueous Solutions. *Clean* 38:936–941.
 - [25] Soy lak M, Elci L, Dogan M (1996) Determination of some trace metal impurities in refined and unrefined salts after Preconcentration on to activated carbon. *Fresen Environ Bull* 5:148–155
 - [26] Khani R, Shemirani F (2010) Determination of trace levels of nickel and manganese in soil, vegetable and water. *Clean* 38:1177–1183.
 - [27] Novaes CG, Santos JS, Ferreira SLC, Lemos VA (2010) Synthesis of a new solid-phase extractor and its application to Preconcentration and determination of lead in water samples. *J AOAC Int* 93:1609–1615
 - [28] Topuz B, Macit M (2010) Solid phase extraction and preconcentration of Cu(II), Pb(II), and Ni(II) in environmental samples on chemically modified Amberlite XAD-4 with a proper Schiff base. *Environ Monit Assess* 173:709–722.
 - [29] Karaaslan NM, Senkal BF, Cengiz E, Yaman M (2010) Novel polymeric resin for solid phase extraction and determination of lead in waters. *Clean* 38:1047–1054.
 - [30] Narin I, Soy lak M, Kayakirilmaz K, Elci L, Dogan M (2002) Speciation of Cr(III) and Cr(VI) in Tannery wastewater and sediment samples on Ambersorb 563 Resin. *Anal Lett* 35:1437–1452.
 - [31] Noei-Aghaei MA, Mohammadhosseini M, Zamani HA, Nekoei M (2010) A comparative investigation on efficacy of two methodologies of solid phase extraction for separation and pre-concentration of trace copper in aqueous samples prior to flame atomic absorption spectrometric determination. *J Chin Chem Soc* 57:363–370
 - [32] Soy lak M, Elci L, Dogan M (1997) Determination of trace amounts of cobalt in natural water samples as

- 4-(2-Thiazolylazo) Resorcinol Complex after Adsorptive Preconcentration. *Anal Lett* 30:623–631.
- [33] Mimura AMS, Vieira TVA, Martelli PB, Gorgulho HF (2010) Utilization of rice husk to remove Cu²⁺, Al³⁺, Ni²⁺ and Zn²⁺ from wastewater. *Quim Nova* 33:1279–1284
- [34] Kapakoglou NI, Giokas DL, Tsogas GZ, Vlessidis AG (2010) Analytical application of surface-affinity polymerized vesicular membranes to trace metal analysis by electrothermal atomic absorption spectrometry. *Microchim Acta* 169:99–107.
- [35] Kutahyalı C, Şert S, Çetinkaya B, Inan S, Eral M (2010) Factors affecting lanthanum and cerium biosorption on *Pinus brutia* leaf powder. *Sep Sci Technol* 45:1456–1462.
- [36] Ghaedi M, Niknam E (2010) Application of Triton X-100 Coated Poly Vinyl Chloride as new solid phase for Preconcentration of Fe³⁺, Cu²⁺ and Zn²⁺ Ions and their flame atomic absorption spectrometric determinations. *Bull Chem Soc Ethiop* 24:11–20