

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Capturing Cd(II) and Pb(II) from contaminated water sources by electro-deposition on Hydrotalcites-like Compounds

M. A. González^a, R. Trócoli^b, I. Pavlovic^a, C. Barriga^a, F. La Mantia^{b,c}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Two different hydrotalcite-like compounds were prepared and used as substrates for the electrochemical removal of extremely toxic pollutant cations, such as Cd(II) and Pb(II), from aqueous solutions, and their posterior recovery for further potential applications. By deposition on the hydrotalcite electrode, it was possible to remove 75% of Cd(II) contained in a starting 5.2 mM solution of CdCl₂, which was subsequently recovered and concentrated up to 14.3 mM in a single step. A removal of almost 100% was obtained in the case of Pb(II). Its recovery was largely hindered by the formation of several inert phases, among which some stable formation of hydroxycarbonate. Our results suggest that the removal of these contaminants by hydrotalcite-like compounds occurs by the combination of two parallel processes: electro-deposition and adsorption. It was possible to achieve a removal capacity for Cd(II) and Pb(II) equal to 763 mg/g_{a.m.} and 1039 mg/g_{a.m.}, respectively. These removal capacities, accompanied by an excellent posterior eluent-free recovery of Cd(II), suggest that this new method could be an environmentally friendly alternative to the conventional adsorption wastewater treatment.

Introduction

Heavy metals are extremely toxic pollutants, which are directly or indirectly discharged into the natural water from different sources, such as metal plating, mining operations, pesticides, textile and dyeing, paper industries, and battery manufacturing, as well as natural rock mineralization processes. Many of them are soluble in water and therefore become more available for living organisms. Their toxicity lies in their bio-accumulation characteristics, i.e. they are not biodegradable and thus accumulate in living systems. Lead and cadmium are recognized to be the most hazardous pollutants to various ecosystems and human health^[1] since they bind to soft tissues and bones,^[2] thus inducing complex changes in plants at genetical, biochemical and physiological levels and leading to phytotoxicity.^[3] World Health Organization drinking water guideline values for Cd and Pb are 0.003 and 0.01 mg/l respectively. Therefore, several remediation technologies such as adsorption by complex formation,^[4] co-precipitation,^[5] flotation,^[6] ion exchange,^[7] coagulation,^[8] inverse osmosis, nanofiltration,^[9] electrolysis,^[10] biosorption,^[11] etc. have been applied to remove the pollutants from contaminated water. Notwithstanding that in many places two or more techniques can work synergistically for better results, new processes can improve the efficiency and functionality of the waste water treatment. Among the different techniques applied with this aim in mind, the most extensively used is the precipitation of

metals as insoluble metal hydroxides, obtained by increasing the pH of the solution. However, this process consumes large amount of chemicals and produces large volumes of low density sludge, which is difficult to dispose. One of the most promising emerging technologies in this field is the biological or biochemical techniques but there are several challenges related to the extreme complexity of soil chemistry.^[12] Even active carbons, which have been widely used as adsorbent, present several disadvantages, among which its high cost and difficulty to be separated from the aquatic system after utilization.^[13]

Electro-deposition is an attractive technology due to its high efficiency. The electrochemical treatment techniques offer good removal yields, rapidity, lower volume of sludge, eco-friendly processing, and the possibility to obtain excellent removal capacities even at high concentration of pollutants.^[14] The substrate used to deposit heavy metals from wastewaters plays an important role during the electrochemical process, affecting the formation of dendrites, the occurrence of side reactions (H₂ evolution), and the stability of the process. So, it is necessary to find a low-cost and non-toxic material as substrate with the purpose to get a good electrochemical performance. At this aim, some of the most promising materials are the hydrotalcite-like compounds (layered double hydroxides, LDH). These materials have attracted attention because of their interesting applications in many fields, due to their singular structural characteristics and properties.^[15-19] The LDHs exist as minerals, as well as synthetic phases, and their structure could be derived from those of brucite with some Al-for-Mg substitution, which is resulting in an excess of positive layer charge that is balanced by interlayer carbonate anions. LDHs have the general chemical formula [M(II)_{1-x}M(III)_x(OH)₂]_nX_{(n-x)/n}·mH₂O, where M(II), M(III) and Xⁿ⁻ are divalent (Mg²⁺, Zn²⁺, Ni²⁺, etc.), trivalent (Al³⁺, Fe³⁺, Cr³⁺, etc.) cations, and the interlayer anion, respectively.^[20, 21] Thus, it is possible to obtain a huge variety of LDH compounds by modifying the nature of these three components.

^a Dpto de Química Inorgánica e Ingeniería Química, Campus de Excelencia Internacional Agroalimentario (CeiA3), Universidad de Córdoba, Córdoba, Spain.

^b Semiconductor and Energy Conversion, Zentrum für Elektrochemie – CES, Ruhr-Universität Bochum, Germany.

^c Energiespeicher- und Energiewandlersysteme, Universität Bremen, Germany.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Recently, these materials have found increasing interest also in electrochemistry because of their layered structure^[22] and many attractive properties, such as magnetic, redox, and catalytic functions.^[23] The LDHs have been used as anode material in Zn-Ni secondary batteries, showing lower corrosion, better reversibility and superior electrochemical stability in galvanostatic charge/discharge processes.^[24]

For these multiple reasons, this work deals with the incorporation of LDH materials as substrate component of the electrodes used in the electrochemical deposition of heavy metals. The control of secondary reactions, the metal concentration in the electrolyte, amount of LDH, current rate, etc. are crucial parameters during the removal process which should be optimized. Therefore, a first aim of this work was to find out an effective removal method based on the electrochemical deposition of Pb(II) and Cd(II) and using LDH compounds as substrate. Based on the previously developed mixed entropy, desalination and lithium recovery technologies,^[25-28] the second objective of this study was to investigate the possibility to recover and concentrate the removed metals in a recovery water stream, which could be used for other industrial purposes, such as production of Pb and Ni-Cd batteries, metallic coatings, dyes, stabilizers for plastics, alloys, fertilizers, etc. At this aim, two different hydrotalcite-like materials were prepared: one consisting of Zn/Al layers with carbonate as the balancing anion (ZnAl-CO₃), and another with an organic anion humate (H) between the Mg/Al layers (MgAl-H).

Materials and Methods

All the reagents were of analytical grade products and purchased from Sigma-Aldrich. To synthesize the Mg-Al-H, distilled water previously boiled and purged with N₂ to prevent CO₂ presence was used.

Preparation of ZnAl-CO₃ and MgAl-H.

The hydrotalcite [Zn₄Al(OH)₁₀]₂(CO₃)·nH₂O, named ZnAl-CO₃, was synthesized by the previously reported coprecipitation method at room temperature.^[29] A mixed aqueous solution of 0.40 M Zn(NO₃)₂·6H₂O and 0.10 M Al(NO₃)₃·3H₂O were dropped from a funnel into 50 mL of water solution of 1.5 M NaOH and 0.2 M Na₂CO₃, under vigorous agitation and maintaining the basic pH. The suspension obtained was hydrothermally treated at 85 °C for 24 h, separated by centrifugation, washed with distilled water, and dried overnight at 60 °C. The hydrotalcite [Mg₃Al(OH)₈]₂(H)·nH₂O, named MgAl-H, was prepared in two steps: chloride intercalated precursor (Mg₃Al-Cl) was synthesized by the coprecipitation method, which was afterwards dispersed (second step) in a sodium humate solution obtaining the final product by anion exchange. Mg₃Al-Cl was prepared by drop-wise addition of a 200 mL aqueous solution of 0.75 M of MgCl₂·6H₂O and 0.25 M of AlCl₃·6H₂O to a 0.25 M of NaCl solution under vigorous agitation and constant pH = 8, set by addition of 1 M NaOH solution. The synthesis was performed in N₂ atmosphere in order to avoid atmospheric CO₂ dissolution and consequently carbonate incorporation to the solid. The suspension obtained was hydrothermally treated at 80°C for 24 h, separated by centrifugation, and washed. A portion of the precipitate was dried

at 60°C to obtain Mg₃Al-Cl, while the remaining slurry was suspended in a 0.13 M sodium humate solution under vigorous stirring and a constant pH = 8 for 24 h.

Characterization Zn/Mg-Al hydrotalcites.

X-ray diffraction patterns (XRD) of powder samples were recorded using a Siemens D-500 diffractometer with CuKα radiation (λ = 1.54050 Å). The Fourier-transform infrared (FT-IR) spectra were registered in a Perkin Elmer Spectrum One Spectrometer using the KBr disc method. Elemental chemical analyses for Zn, Mg and Al were determined by inductively coupled plasma mass spectrometry (ICP-MS) in a Perkin Elmer ELAN DRC-e instrument. The samples were dissolved in concentrated HNO₃. Thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded on a Setaram Setsys Evolution 16/18 apparatus in an oxidizing atmosphere under the heating rate of 5 °C/min. Scanning electron microscopy (SEM) images were recorded using a Quanta 3D FEG instrument equipped with energy dispersive X-ray analyser (EDAX). Cadmium concentrations were determined by atomic absorption spectroscopy (AAS) in an Analytik Jena AAS 6 Vario instrument and lead concentrations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) by Wessling GmbH according to the ISO 11885A standard.

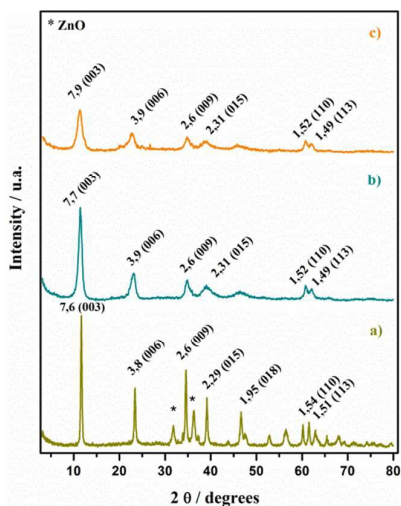
Preparation of electrodes based on Zn/Mg-Al hydrotalcites.

To prepare the electrodes, a slurry consisting of active material (LDH or Ag), C65 carbon black (Timcal Super P C60), polyvinylidene fluoride (Solef S5130, Solvay) binder solution in N-methyl pyrrolidone (25 mg ml⁻¹), and graphite (Timcal SFG6) in a 75:10:15 and 80:9:9:2 by weight proportion for LDH and Ag respectively were mixed thoroughly for 30 min at 4000 r.p.m. using an ultra-turrax disperser (Ika). The electrodes, with an approximate area of 2.9 cm², were prepared by hand-painting on carbon cloth (Fuel Cell Earth) current collector with a mass loading of 7 mg of LDH per cm² for the removal process from a solution 5.2 mM of CdCl₂, and 7 and 14 mg of LDH per cm² when a solution 2.5 mM and 5 mM of PbCl₂ were respectively used. Prior to use, the electrodes were dried at 60°C.

Electrochemical measurements.

Electrochemical deposition of metals was performed on a flooded three-electrode cell containing 40 ml of the respective solution (5.2 mM CdCl₂, 2.5 mM PbCl₂ or 5 mM PbCl₂), LDH-based electrode as working electrode, Ag as counter electrode, and Ag/AgCl (3 M KCl) as reference electrode. Prior to the electro-deposition process, argon was bubbled for 10 minutes in solution, and a slow flow was kept during the measurements to avoid the presence of oxygen. After the deposition process, the volume of the cell was reduced to 10 mL and the same configuration described above was used for the recovery process. For the calculation of the current density, the amount of cations in the starting solution was used. Current rates of C/5.2 and C/20.8 were applied for reduction/oxidation of cadmium and C/20 in the case of lead, where a rate of C/n represents a complete reduction (deposition step) or oxidation (recovery step) of all the amount of cations in n hours. Electrochemical measurements were performed with Biologic VSP-300 instrument.

Fig 1. X-ray patterns of ZnAl-CO₃ (a), MgAl-Cl (precursor of MgAl-H) (b) and MgAl-H(c) hydroxaltes.



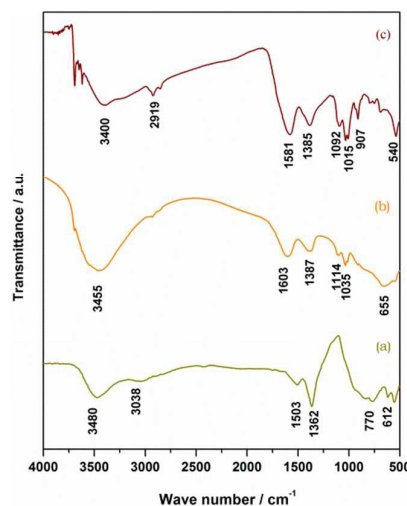
Results and discussion

Structural characterization of the hydroxaltes.

The ZnAl-CO₃, MgAl-Cl and MgAl-H samples were characterized by XRD powder method. Their XRD patterns, included in Fig. 1, correspond to hydroxaltes-like compounds with rhombohedral symmetry and a basal spacing of 7.6 Å for ZnAl-CO₃, 7.7 Å for MgAl-Cl and 7.9 Å for MgAl-H samples. The XRD reflections of ZnAl-CO₃ were sharper and more symmetric than MgAl-H, showing a good crystallized system. The modification of the hydroxaltes with the organic anions (humate) caused a broadening of the diffraction lines and a decrease of the intensities in the hydroxaltes-system. The basal spacing, d_{003} obtained for ZnAl-CO₃ (7.6 Å) corresponds to carbonate containing hydroxaltes,^[30] for MgAl-H the basal spacing was 7.9 Å, close to MgAl-Cl used as precursor.^[31] The slight modification of the interlayer spacing during the exchange was consistent with other humic acid containing LDHs.^[32-34] The FT-IR spectra of the ZnAl-CO₃ and MgAl-H samples are given in Fig. 2. The broad absorption peak in both spectra between 3600 and 3300 cm⁻¹ is due to the u(OH) mode of the hydroxy groups, both from the brucite-like layers and from interlayer water molecules. Interlayer water also gives rise to the broad, medium-intensity, absorption between 1600-1500 cm⁻¹, $\delta(\text{H}_2\text{O})$. Hydrogen bonding of the water with interlayer carbonate anions also shows a shoulder at 3038 cm⁻¹ in the spectrum of ZnAl-CO₃ sample. The very intense absorption band at 1362 cm⁻¹ in the spectrum of Fig. 2a corresponds to the ν_3 mode of the carbonate species. Absorptions below 800 cm⁻¹ are due to lattice vibrations, involving metal-oxygen stretching modes and, in the case of ZnAl-CO₃ sample, also modes ν_2 (out-of-plane deformation) and ν_4 (in plane bending) of carbonate at 868 and 670 cm⁻¹ respectively.^[35] In the case of MgAl-H, the bands at 1114 and 1035 cm⁻¹ confirmed the presence of humate anions in the hydroxaltes and the bands at 1603 cm⁻¹ and 1387 cm⁻¹ were

associated to antisymmetric and symmetric vibration of the carboxylate groups.^[31, 36]

Fig 2. FT-IR spectra of ZnAl-CO₃ (a) and MgAl-H (b) hydroxaltes. A pattern of humic acid solution salt was added for comparison (c).



The chemical analysis of the ZnAl-CO₃ and MgAl-H hydroxaltes are shown in Table 1. The molar ratio Zn:Al was approximately 4, close to the one of the starting solution used to prepare the sample, which evidenced that the co-precipitation was practically complete. The results for MgAl-H indicated that a partial dissolution of Mg²⁺ could have occurred in the sample with respect to the composition of the precursor MgAl-Cl used during the synthesis.^[31] The number of water molecules has been calculated from the total loss weight in the TG curves (appendix 1 SI, Fig. S1) attributed to the loss of physically adsorbed and interlayer water, dehydroxylation and decarbonation of the sample ZnAl-CO₃, and for the MgAl-H hydroxaltes was calculated from the first loss water, in the TG curves. In the latter case, two assumptions were used to define the extreme value of the hydration range: all humate molecules are substituting the chlorides in the interlayer; humate is sitting only on the surface.^[31, 37]

SEM images of the substrates containing different matrix of LDHs are included in Fig. 3. The ZnAl-CO₃ showed thin platelets and regular shape, which is consistent with a good crystallized structure. The primary particle size was in the range 85-250 nm. The morphology of MgAl-H sample kept the structural homogeneity after the incorporation of humate anions but a loss of crystallinity, and an aggregation of the layered particles was observed (SEM image of MgAl-Cl, precursor of MgAl-H is included in appendix 2 SI, figure S2).

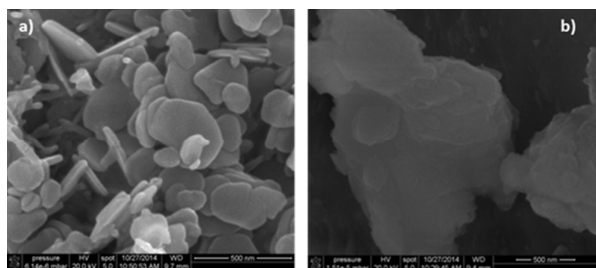
Table 1. Chemical analysis results of ZnAl-CO₃ and MgAl-H hydroxaltes.

	% wt		Atomic ratio		Proposed Formula
	M(II) ^a	Al	M(II)/Al		
ZnAl-CO ₃	50	5.4	3.8		[Zn _{0.79} Al _{0.21} (OH) ₂](CO ₃) _{0.105} ·0.33H ₂ O
MgAl-Cl	20	8	2.8		[Mg _{0.74} Al _{0.26} (OH) ₂](Cl) _{0.26} ·0.83H ₂ O

MgAl-H	15	7	2.4	$[\text{Mg}_{0.71}\text{Al}_{0.29}(\text{OH})_2(\text{X})_{0.29/m}\text{mH}_2\text{O}^b]$
--------	----	---	-----	---

^a M= Zn or Mg; ^b X= Cl and/or H (n= 1 and/or 2; m= 0.58-0.71)

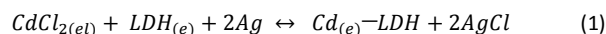
Fig 3. SEM images of ZnAl-CO₃ a) and MgAl-H b) hydroxaltes.



Finally, the aggregation of the primary particles can reach a size of more than 300 nm, likely due to the presence of humate anions.

Electrochemical removal of cadmium.

Fig. 4 shows the electrochemical deposition of the Cd(II) on both ZnAl-CO₃ and MgAl-H, at two different current densities. The process can be described by the following reaction:



where the subscripts (e) and (e) indicate the electrolyte and electrode phases respectively. When a negative current was applied, Cd²⁺ was reduced on the LDH to Cd⁰ (from left to right in the reaction 1) and simultaneously 2 Ag were oxidized in the counter electrode. Under the experimental conditions used in this study, the limiting diffusion current is 3.73 mA (more details in appendix 3 SI). The current applied for the electro-deposition under C/5.2 was close to this value and equal to 2.14 mA, which implies that an high concentration overpotential is required to reduce Cd²⁺ in these measurements. This effect was evidenced in Fig. 4, where the initial overvoltage was 43 mV ($E_{\text{eq}} = -0.471$ V vs. NHE) for both double layered hydroxides when a rate of C/20.8 was used, but it increased to 119 mV and 248 mV when the current rate was raised to C/5.2, for ZnAl-CO₃ and MgAl-H, respectively.

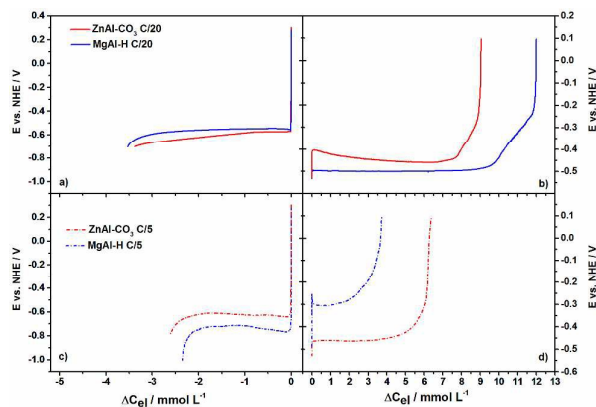


Fig 4. Electrochemical removal of cadmium at C/5.2 (a) and C/20.8 (c) and their posterior recovery (b and d).

Table 2 summaries the modifications in the concentration of cadmium after the electro-removal process (ΔC_{el}). The value of ΔC_{el} was calculated from the charge flow using the Faraday law. The amount of cadmium in solution decreased of 3.38 and 3.53 mM when ZnAl-CO₃ and MgAl-H were respectively used at C/20.8. These values indicate reduction of the pollutant ions of 65.0 % and 67.8 %, respectively. Increasing the current rate, the percentage of cadmium removal decreased to 50.3 % (ZnAl-CO₃) and 45 % (MgAl-H), respectively. These lower values are in agreement with the fact that the electro-deposition process was controlled by diffusion limitation at this current rate. It is noteworthy to mention that the duration required in the faster experiments was 4 times smaller than when a rate of C/20.8 was used. Therefore, it is possible to select the current rate in order to reach the desired objective, i.e. shorter times or higher removal fraction. Additionally, the combination of different current densities permits achieving multiple targets, for example, a high initial current to decrease very fast the concentration of pollutant, followed by a low current to increase the total amount of removed metal ions. Furthermore, if higher percentages of removal are desired, it is enough that a lower current density is applied. It would be possible also to combine this technology with the previous reported adsorption process based on similar LHDs,^[31, 37] which effectiveness is limited to concentration of pollutants lower than 2.5 mM. Therefore, after the electro-deposition step it could be possible to use an adsorption step, to remove all the remaining pollutants from the solution. To measure the real variation of the concentration in the electrolyte, the solutions after and before the electrochemical processes were analysed by AAS. In all the cases, the values of cadmium elimination observed by means of AAS (ΔC_{A} , table 2) were higher than the value of ΔC_{el} . It would have been expected that the value of ΔC_{el} would be larger than ΔC_{A} , due to a non-unitary efficiency in the electrochemical process, maybe caused by hydrogen evolution. The observed differences were associated to the adsorption properties of the double layered hydroxides, able to remove a fraction of cadmium by simple contact of the electrode with the electrolyte. An estimation of the contribution of the adsorption process to the total removal of metal is described in appendix 4 SI. When this effect is taken into account, an efficiency lower than 1 was obtained for the electrochemical process. The electrochemical removal capacities were equal to 622 mg/ g_{a.m.} (g_{a.m.} = gram of active

material) and 518 mg/g_{a.m.} when ZnAl-CO₃ and MgAl-H were respectively used as substrate with a current rate of C/5.2. These values increased to 749 mg/g_{a.m.} and 763 mg/g_{a.m.} when the current rate was equal to C/20.8. These removal capacities are considerably higher than the traditional values obtained by adsorption process alone, which generally ranges from 10⁻³ mg/g to 270 mg/g of adsorbent.^[38] The presence of pollutant was reduced of 61.2% and 73.8 % for ZnAl-CO₃, and 50.9% and 75.2 % for MgAl-H, when the current rate was equal to C/5.2 and C/20.8, respectively. To confirm the critical role of the LDHs on the electrochemical deposition of Cd and to evaluate the contribution of the current collector (carbon cloth) and additives used to prepare the electrodes (carbon black, polyvinylidene fluoride, and graphite), a removal process was performed using an electrode composed only by carbon black, graphite, and binder at a current rate C/20.8 (SI, Figure S3 a, appendix 5). The electro-deposition of Cd with such substrate was limited to just 6.5% of the initial amount, confirming that the LDH plays a critical role. (Table 2).

Table 2: Analysis of variation of the concentrations of cadmium (ΔC) in the electrolyte after deposition and recovery processes on ZnAl-CO₃ and MgAl-H at different rates, ($C_{el} = 5.20$ mM).

Sample	Rate	Deposition		Recovery	
		ΔC_{el} (mM)	ΔC_{el} (mM)	ΔC_A (mM)	ΔC_A (mM)
ZnAl-CO ₃	C/5.2	-2.62	6.37	-3.18	6.65
ZnAl-CO ₃	C/20.8	-3.38	9.04	-3.84	10.55
MgAl-Cl	C/5.2	-2.34	3.72	-2.65	2.75
MgAl-H	C/20.8	-3.53	11.99	-3.91	14.33

After the removal process, the volume of the cell was reduced to 10 mL and the cadmium was recovered by applying a positive current (from right to left in the reaction 1, Fig. 5). A recovery of 60.7 % and 39.7% of the cadmium deposited was obtained when ZnAl-CO₃ and MgAl-H were used at C/5.2, respectively. When the current applied was decreased to C/20.8, values of 84.2% and 66.8% were achieved. These percentages are greater than the recovery obtained (close to 38 %) with adsorption methods that have removal capacities similar to the ones of this work.^[39] This methodology permitted to increase the concentration of cadmium up to 14.33 mM, 4.5 times higher than that obtained by other effective absorbents, and without the need to use any eluent.^[40] The recovery solution could be used for other applications, such as reactant in flow cadmium batteries; this technology permits to convert wastewater to an added-value product. Additionally, the reduction of the volume used for the recovery process and the possibility to reuse the same solution would permit to increase the concentration of cadmium to desired values, as we previously demonstrated in an equivalent method for lithium recovery from brines.^[27, 28]

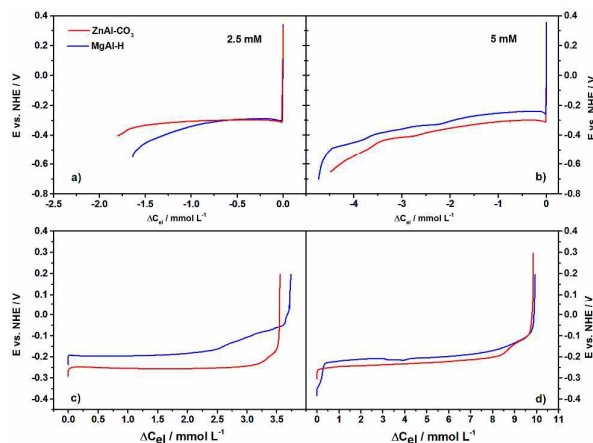


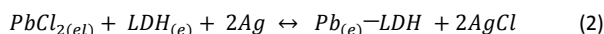
Fig 5. Electrochemical removal of lead from 2.5 mM (a) and 5 mM PbCl₂.

Table 3. Analysis of the variation of the concentrations of lead (ΔC) after deposition and recovery process on ZnAl-CO₃ and MgAl-H at different concentrations of electrolyte (C_{el}).

Sample	C_{el}	Deposition		Recovery	
		ΔC_{el} (mM)	ΔC_{el} (mM)	ΔC_A (mM)	ΔC_A (mM)
ZnAl-CO ₃	2.5	-1.80	3.56	-2.09	1.31
ZnAl-CO ₃	5	-4.48	9.85	-4.60	0
MgAl-Cl	2.5	-1.64	3.73	-1.95	2.16
MgAl-H	5	-4.73	9.93	-5.07	3.32

Electrochemical removal of lead.

Fig. 5 shows the electrochemical deposition of the Pb(II) on both, ZnAl-CO₃ and MgAl-H hydrotalcites, at two different concentrations of electrolyte. Similar than reported previously in the case of cadmium, the process can be described by the following reaction:



where the subscripts (*el*) and (*e*) indicate the electrolyte and electrode phases respectively. When a negative current was applied Pb²⁺ was reduced on the LDH to Pb⁰ (from left to right in the reaction 2) and simultaneously 2 Ag were oxidized in the opposite electrode. In the case of lead, the applied current was always far from the diffusion limiting current, thus the polarization observed at lower concentrations of Pb(II) can be attributed to the deposition mechanism itself, which is kinetically slow. The variations of lead concentration are summarized in Table 3. The Pb(II) concentration was reduced of 1.8 mM and 1.64 mM when ZnAl-CO₃ and MgAl-H were respectively used in a solution containing an initial concentration of 2.5 mM of PbCl₂, decreasing the starting amount of Pb(II) by 72 % and 65.6 %, respectively.

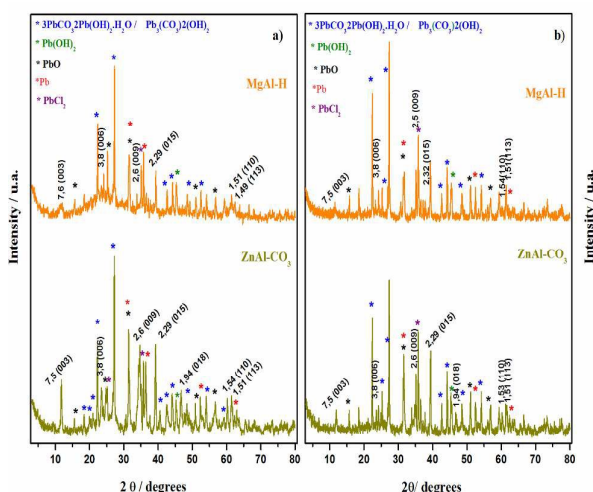


Fig. 6. X-ray diffractograms of the substrates after the recovery process from 2.5 mM (a) and 5 mM (b) lead solutions as electrolyte.

When a solution with initial concentration equal to 5 mM was used, it was possible to decrease the concentration of pollutant by 4.48 mM (ZnAl-CO₃) and 4.73 mM (MgAl-H), reaching percentages of removal equal to 89.6 % and 94.6%. The concentration of Pb(II) in the solution after the removal process was analyzed by ICP-MS. Again, lower values of ΔC_A were obtained with respect to the values of ΔC_{el} calculated from the Faraday law. These differences were in the same range of the one observed for Cd, and it was verified that they were due to the inevitable adsorption process occurring during the contact of the hydroxycarbonate with the solution containing the pollutant (more details in appendix 4 SI). Considering the combination of the electrochemical removal process and the adsorption effect, the percentages of Pb eliminated from a 2.5 mM solution reached values of 83% and 78% for ZnAl-CO₃ and MgAl-H respectively, these values increased up to 92 % and 100 % when a 5 mM solution was used, achieving a nearly total removal of Pb(II). The highest removal capacity was obtained by the sample MgAl-H from a 5 mM Pb(II) solution, reaching 1039 mg/g_{a.m.}, 2.7 times higher than the best adsorption method.^[41] As in the case of the electro-deposition of Cd, the presence of LDH in the electrode was vital to the process. Without LDH in the electrode a removal of Pb(II) equal to just 4.4% was achieved when a 5 mM PbCl₂ solution was treated with a current rate of C/20. This clearly shows that LDHs plays a critical role in the electro-deposition of these highly toxic metals. After the removal process, the volume of the cell was reduced to 10 mL and lead was recovered by applying a positive current (from right to left in the reaction 2, Fig. 5). Although from Fig. 5 c and d, it could be supposed that the recovery of the deposited lead was successful, the ICP analysis (Table 3) showed that there was no or little recovered lead, so that the final solution after recovery had a lower concentration than the initial one. With the aim to clarify the mechanism of lead depletion during the recovery process, the electrodes were analyzed by X-ray diffraction (Fig. 6). The XRD patterns showed a complex system containing several phases: lead metal, oxide, hydroxide, hydroxycarbonate, and chloride of lead. Three possible mechanisms of re-adsorption of Pb(II) on LDHs during the recovery process, or the combination of

them, could explain the differences observed between the electrochemical and ICP-MS data, as they are schematically shown in Fig. 7. The first mechanism is given by precipitation as hydroxycarbonate of lead. The presence of carbonate as interlayer anion in the structure of the hydroxycarbonate helps to produce this compound. The lower values of recovery obtained using the ZnAl-CO₃ (Table 3) comparing with the MgAl-H are in agreement with

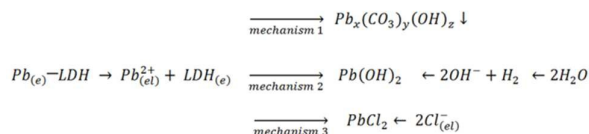


Fig. 7. Possible mechanisms of lead depletion during the recovery process.

the higher amount of carbonate inside the ZnAl-CO₃, so the possibility to remove this anion to form hydroxycarbonate of lead is plausible. This assumption was confirmed by the blank measurements, which showed higher removal values of this HT (more details in table S2, supporting information). Pavlovic et al. also found PbCO₃ precipitated in ZnAl-LDH intercalated with DMSA ligands and Park et al. in Mg/Al-LDH.^[21, 42] The humate anion contained in the MgAl-H could contribute to the sorption process via complexation/chelation between the metallic cation and the functional groups of humate. This mechanism was confirmed by XRD, several peaks associated to this phase are shown in Fig. 6. The uptake of lead by precipitation as hydroxide on the LDH is the second mechanism proposed. The local increase of pH caused by possible H₂ evolution during the deposition process could induce its precipitation. Finally, the third mechanism involves the formation of PbCl₂. During the recovery process the concentration of Pb(II) in the surrounding of the electrode increases and simultaneously Cl⁻ anions are attracted from the bulk owing to the positive current applied, generating locally an oversaturated solution and the precipitation of PbCl₂. However, there was neither a clear evidence of the presence of hydroxide nor chloride of lead, which could happen in a negligible amount or could be rebalanced very rapidly, once the current is interrupted. The identification of both phases could also be complicated by the fact that the main peaks of the XRD pattern are overlapping with the diffraction lines of different species of hydroxycarbonate, which phase is the majority. In any case the XRD patterns indicate the high complexity of these systems that hinder the recovery of lead and its concentration to values higher than 3.3 mM.

Due to the nature of the reactions involved in the removal process investigated in this study (reactions 1 and 2), the integrity of the LDHs is not compromised by oxidation/reduction of their components or structural stress. Therefore we expect a long cycle life and good stability of the LDHs, similar that reported by Huang et al.^[24] The authors demonstrated that LDH-based electrodes had a cycle life superior to 500 cycles. The silver electrode showed a good stability, and was cycled at least 30 times in 5.2 mM CdCl₂ and 5 mM PbCl₂ at least 30 times (appendix 6 SI, Figure S4), reaching a capacity close to 60 mAh g⁻¹.

Conclusions

The electrochemical method for the removal of Cd(II) and Pb(II) developed in this article is based on the use of ZnAl-CO₃ and MgAl-H hydrotalcites as substrates. The structural characterization of these compounds confirms the hydrotalcite-like structure with a good crystallization of the samples. The utilization of these materials permits the elimination of pollutants by two simultaneous processes; electrochemical reduction of M²⁺ to M⁰, and adsorption. This combined methodology shows removal values of 763 mg/g_{a.m.} and 1039 mg/g_{a.m.} of Cd(II) and Pb(II), respectively, removing 75% and 100 % of the heavy metals from the water stream. These values are considerably higher than the traditional values obtained by using other materials as adsorbents. We have shown that the presence of the LDH is vital to the electro-deposition process, and only negligible removal is reached in electrodes that do not contain the hydrotalcite-like compounds. Additionally, it was possible to recover 27% of the removed lead in a separate solution; in the case of cadmium it was possible to reach a recovery value of 84.2%, thus obtaining a solution with a concentration of 14.3 mM, 4.5 times higher than the best cadmium recovery method using adsorbents and without the need to use any eluent. This recovery solution could be used for other applications, such as reactant in flow cadmium batteries, without further treatment. The lower amount of lead recovered was attributed to the formation of different species of this metal resorbed on the LDH. This was also confirmed by XRD. Future work should focus on replacing silver as counter electrode with more suitable materials, in terms of cost and effectiveness.

Acknowledgements

The financial support from: the Spanish Junta de Andalucía (research group FQM214) and MCYT (Project CTM2011-25325), the Federal Ministry of Education, Research (BMBF) in the framework of the project "Energiespeicher" (FKZ 03K3005), and the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft (DFG) are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at ...

References

- [1] S. Mol. *Biol. Trace Elem. Res.*, 2011, **143**, 974.
- [2] G. Yuan S. Dai, Z. Yin, H. Lu, R. Jia, J. Xu, X. Song, L. Li, Y. Shu, X. Zhao. *Food Chem. Toxicol.*, 2014, **65**, 260.
- [3] Gordana Drazic and N. Mihailovic. *Plant Science*, 2005, **168**, 511.
- [4] M.R. Pérez, I. Pavlovic, C. Barriga, J. Cornejo, M.C. Hermosin and M.A. Ulibarri, *Appl. Clay Sci.*, 2006, **32**, 245.
- [5] K.G. Karthikeyan, H.A. Elliot and F.S. Cannon, *Environ. Sci. Technol.*, 1997, **31**, 2721.
- [6] J. Rubio, M.L. Souza and R.W. Smith, *Miner. Eng.*, 2002, **15**, 139.
- [7] S.Y. Kanga, J.U. Leeb, S.H. Moona and K.W. Kima, *Chemosphere*, 2004, **56**, 141.
- [8] Q. Chang and G. Wang, *Chem. Eng. Sci.*, 2007, **62**, 4636.
- [9] H.A. Qdais and H. Moussa, *Desalination*, 2004, **164**, 105.

- [10] A.T. Heijne, F. Liu, R. Weijden, J. Weijma, C.J.N. Buisman, and H.V.M. Hamelers, *Environ. Sci. Technol.*, 2010, **44**, 4376.
- [11] N. Ahalya, T. V. Ramachandra and R. D. Kanamadi, *Res. J. Chem. Environ.*, 2003, **7**, 71.
- [12] M.A. Hashim, S. Mukhopadhyay, J.N. Sahu, B. Sengupta. *J. Environ. Manage.* 2011, **92**, 2355.
- [13] Q. Jiuhui, *J. Environ. Sci.*, 2008, **20**, 1.
- [14] F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407.
- [15] A. E. Palomares, J.-M. López-Nieto, F.J. Lazaro, A. Lopez and A. Corma, *Appl. Catal. B.*, 1999, **20**, 257.
- [16] D.G. Evans and X. Duan, *Chem. Commun.*, 2006, **5**, 485.
- [17] J.-H. Choy, S.-J. Choi, J.-M. Oh and T. Park, *Appl. Clay Sci.*, 2007, **36**, 122.
- [18] F. Bruna, I. Pavlovic, R. Celis, C. Barriga, J. Cornejo and M.A. Ulibarri, *Appl. Clay Sci.*, 2008, **42**, 194.
- [19] R. Extremera, I. Pavlovic, M.R. Pérez and C. Barriga, *Chem. Eng. J.*, 2012, **213**, 392.
- [20] P.S. Braterman, in *Handbook of Layered Materials*, ed. S. M. Auerbach et al., Marcel Dekker, Inc., New York, Basel, 2004, pp. 373-474.
- [21] I. Pavlovic, M.R. Pérez, C. Barriga and M.A. Ulibarri, *Appl. Clay Sci.*, 2009, **43**, 125.
- [22] P. Vialat, F. Leroux, C. Taviot-Gueho, G. Villemure and C. Mousty, *Electrochim. Acta*, 2013, **107**, 599.
- [23] C. Obayashi, M. Ishizaka, T. Konishi, H. Yamada and K. Katakura, *Electrochemistry*, 2012, **80**, 879.
- [24] T. Wang, Z. Yang, B. Yang, R. Wang and J. Huang, *J. Power Sources*, 2014, **257**, 174.
- [25] F. La Mantia, M. Pasta, H. D. Deshazer, B.E. Logan and Y. Cui, *Nano Lett.*, 2011, **11**, 1810.
- [26] M. Pasta, C.D. Wessells, Y. Cui and F. La Mantia, *Nano Lett.*, 2012, **12**, 839.
- [27] M. Pasta, A. Battistel and F. La Mantia, *Energy Environ. Sci.*, 2012, **5**, 9487.
- [28] R. Trócoli, A. Battistel and F. La Mantia, *Chem. Eur. J.*, 2014, **20**, 9888.
- [29] W.T. Riechle, *Solid State Ionics*, 1986, **22**, 135.
- [30] I. Crespo, C. Barriga, V. Rives and M.A. Ulibarri, *Solid State Ionics*, 1997, **101-103**, 729.
- [31] M.A. González, I. Pavlovic, R. Rojas-Delgado and C. Barriga, *Chem. Eng. J.*, 2014, **254**, 605.
- [32] Y. Seida and Y. Nakano, *Water Res.*, 2000, **34**, 1487.
- [33] S.J. Santosa, E.S. Kunarti and Kamato, *Appl. Surf. Sci.*, 2008, **254**, 7612.
- [34] S. Vreysen and A. Maes, *Appl. Clay Sci.*, 2008, **38**, 237.
- [35] V. Rives, *Layered Double Hydroxides: Present and Future*, Nova Science Publishers, Inc., New York, 2001.
- [36] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
- [37] M.A. González, I. Pavlovic and C. Barriga, *Chem. Eng. J.*, 2015, **269**, 221.
- [38] D. Purkayastha, U. Mishra and S.A. Biswas, *Journal of Water Process Engineering journal*, 2014, **2**, 105.
- [39] V. Singh, A.K. Sharma and S. Maurya, *Ind. Eng. Chem. Res.*, 2009, **4**, 4688.
- [40] K.C. Justi, V.T. Fávere, M.C.M. Laranjeira, A. Neves and R.A. Peralta, *J. Colloid Interface Sci.*, 2005, **291**, 369.
- [41] K. Kesenci, R. Say and A. Denizli, *Eur. Polym. J.*, 2002, **38**, 1443.
- [42] M. Park, C.L. Choi, Y.J. Seo, S.K. Yeo, J. Choi, S. Komarneni and J.H. Lee, *Appl. Clay Sci.*, 2007, **37**, 143.