

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

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This supporting information contains 6 appendixes:

Appendix 1: Thermogravimetric and Differential Thermal analysis.

Appendix 2: Scanning electron images (SEM) of MgAl-Cl.

Appendix 3: Calculation limiting currents.

Appendix 4: Estimation of the removal by adsorption (blank).

Appendix 5: Electrochemical removal of Cd(II) and Pb(II), electrodes without LDH.

Appendix 6: Stability of Ag in CdCl₂ and PbCl₂ solutions.

1. Thermogravimetric and Differential Thermal Analysis.

Thermogravimetric and Differential Thermal analysis were performed to calculate the content of water molecules to propose an experimental formula of the LDHs. Fig. S1 shows the thermograms obtained.

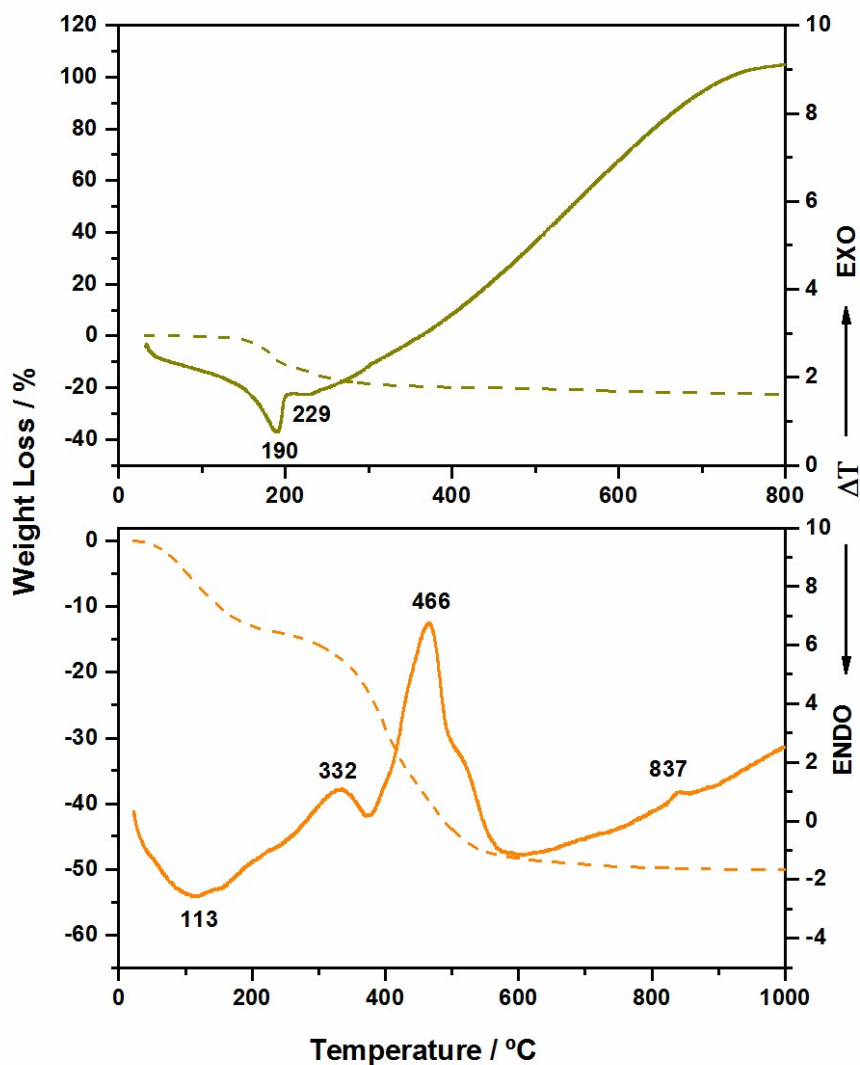


Fig. S1. Thermogravimetric and Differential Thermal analysis of ZnAl-CO₃ (top), and MgAl-Cl (bottom).

2. Scanning Electron Image (SEM) of MgAl-Cl.

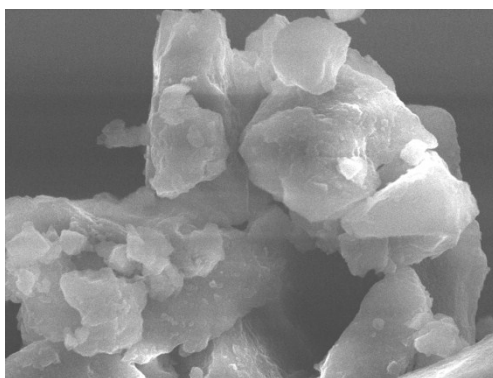


Fig. S2. Scanning Electron Image (SEM) of MgAl-Cl.

3. Calculation limiting currents.

As we indicated in the main article, the diffusion limiting current affects considerably the removal process. In order to evaluate such effect, the diffusion limiting currents (I_l) of the Cd(II) and Pb(II) were calculated according to the following equation:

$$I_l = nFAD\frac{C_b}{\delta} \quad (S1)$$

where A is the geometrical surface area, D the diffusion coefficient of Cd(II) or Pb(II), c_b the concentration of Cd(II) or Pb(II) in the bulk of the solution, and δ the diffusion layer thickness (estimated around 100 μm for systems subject only to natural convection). The values of D are $4.6224 \times 10^{-6} \text{ m}^2\text{h}^{-1}$ and $5.29 \times 10^{-6} \text{ m}^2\text{h}^{-1}$ for Cd and Pb respectively. ^[S1]

The table S1 shows the diffusion limiting current obtained for the respective concentration of metal, and the currents used in the deposition step in every case.

Table S1. Diffusion current under the experimental conditions, and currents applied during the deposition step.

Concentration (mM)	Diffusion limiting current (mA)		Current used (mA)		
	Cd	Pb	Cd (C/5.2)	Cd (C/20.8)	Pb (C/20)
2.5	-	2.06	-	-	0.26
5	3.73	4.11	2.14	0.53	0.52

The current applied for the removal of Pb(II) was 790 times smaller than the diffusion limiting current what permitted its elimination in a potential close to the predicted by the Nernst equation and obtaining higher percentages of removal than in the case of Cd(II). For this metal, the current used was 58 % and 14.2 % of the diffusion limiting current what is in agreement with the polarization observed in deposition process (Fig. 4 main article) and the lower eliminations of pollutant reached.

[S1] Ana C.F. Ribeiro, Joselaine C.S. Gomes, Luís M.P. Veríssimo, Carmen Romero, Luis H. Blanco, Miguel A. Esteso. *J. Chem. Thermodynamics*, 2013, **57**, 404–407.

4. Estimation of the removal by adsorption (blank).

The differences observed in the concentrations predicted by electrochemistry and the one measured by AAS and ICP-MS were attributed in the main article to the metal adsorption capacity of the substrate employed, the adsorption property of the LDHs is well known. The Table S2 shows the variations in the concentration of a 5.2 mM CdCl₂ solution by the immersion of the electrodes for a time equivalent to the one employed in the electro-deposition process. It is important to consider that the experimental conditions during the electro-deposition step could be quite different with respect to the one existing during these measurements of removal by immersion, because the applied current could generate strong modifications in the chemical composition of the solution in the surrounding of the electrode. In any case, there is a good correlation between the removal values observed in the adsorption process and the difference between electrochemical data and chemical analysis (Table 2 main article).

Table S2. Analysis of concentrations of cadmium (mmol L⁻¹) in the electrolyte after the adsorption process by ZnAl-CO₃ and MgAl-H under different contact times (C_{iel} = 5.20 mM).

BLANKS	CONTACT TIME (h)	ΔC_A (mM)
<i>ZnAl-CO₃</i>	5	-0.16
	20	-0.32
<i>MgAl-H</i>	5	-0.5
	20	-0.71

Similar results were obtained when the electrodes were submerged in 2.5 mM and 5 mM PbCl₂ solutions for 20 hours (Table S3). Higher removed amounts were obtained for higher concentrations of pollutant. The high values observed in the case of ZnAl-CO₃ are in agreement with the low concentrations reached during the recovery process. As we described in the main article, the Pb(II) generated was re-adsorbed by the hydrotalcite following three possible mechanisms. The data obtained with these blank measurements confirm the high

affinity of the LDHs towards lead and its precipitation as hydroxycarbonate that can be observed as majority phase in the X-ray analysis (Fig. 6 main article).

Table S3. Analysis of concentration of lead (mmol L⁻¹) in the electrolytes after the adsorption process by ZnAl-CO₃ and MgAl-H hydrotalcites. Ci_{el} indicates the initial concentration of the electrolyte. Contact time = 20 h.

BLANKS	Ci_{el} (mM)	ΔC_A (mM)
<i>ZnAl-CO₃</i>	2.5	-1.45
	5	-3.24
<i>MgAl-H</i>	2.5	-0.83
	5	-1,02

5. Electrochemical removal of Cd(II) and Pb(II), blank without LDH.

To confirm the critical role of the LDHs on the electrochemical deposition of Cd and Pb 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 done using an electrode formed by these components but without the presence of LDH (Figure S3 a) at a slow current rate, namely C/20. The deposition of Cd showed a decrement of the concentration of 0.34 mM starting from a solution of 5.20 mM of CdCl₂, reducing the initial concentration of just 6.5%. For the electro-deposition of Pb from a 5mM PbCl₂ solution, the decrease of its concentration using an electrode without LDH was 0.22 mM, equal to just 4.4 % removal. This removal capacities obtained in absence of LDHs clearly manifests the critical role of the LDH as substrate for the electrochemical removal of these highly toxic metals.

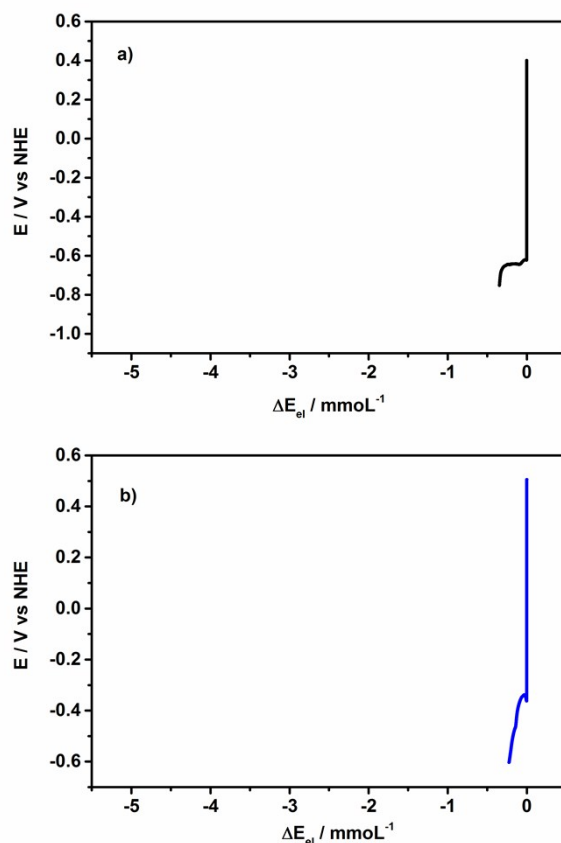


Fig. S3. Electrochemical removal of Cd (a) and Pb (b) using electrodes without LDH.

6. Stability of Ag in CdCl₂ and PbCl₂ solutions.

The stability of silver in 5.2 mM CdCl₂ and 5 mM PbCl₂ was analysed. Figure S4 shows that the capacity was stabilized after 25 cycles to around 60 mAh g⁻¹ in the case of use PbCl₂ as electrolyte, when CdCl₂ was used, a similar capacity was obtained immediately from the 1st cycle. In both cases it was possible to reuse the silver electrode at least 30 times, that proves its possible utilization as chloride capturing electrode during the electrochemical removal of metals. Its electrochemical performance and low voltage reaction makes Ag an ideal candidate as counter electrode for the electrochemical removal process, however the possible commercial applicability of this technique required undoubtedly the substitution of silver by another materials due to the elevate cost of this noble metal.

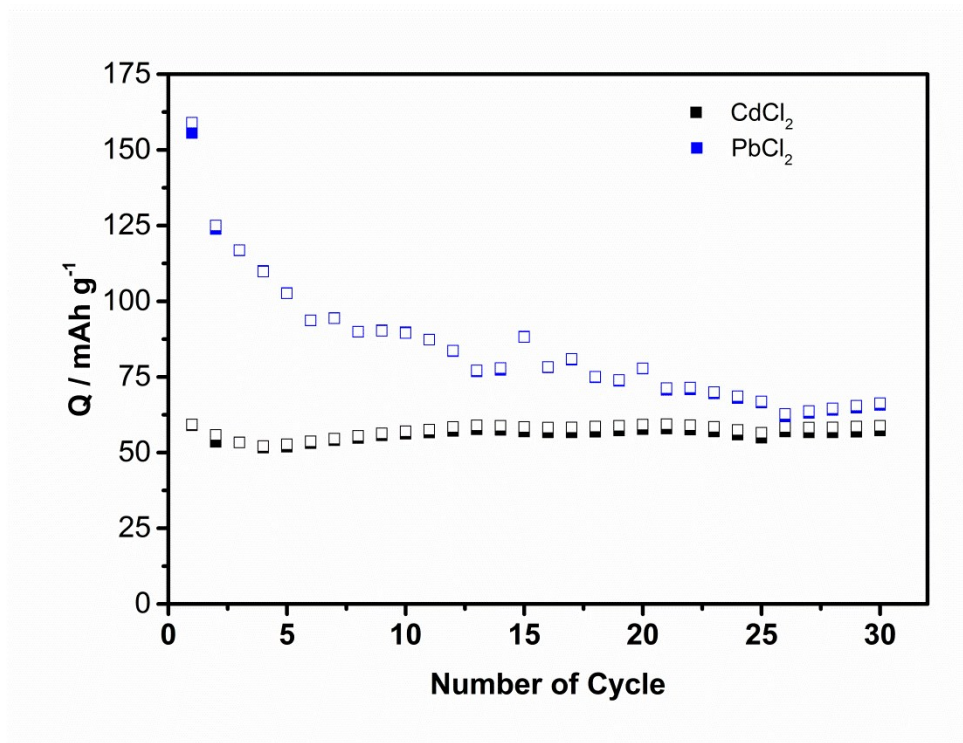


Fig. S4. Electrochemical stability of Ag in CdCl₂ (black) and PbCl₂ (blue).