

## A novel thermodynamic approach for the complexation study of toxic metal cations by landfill leachate

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Landfill leachates can contaminate nearby aquifers. The hazard deriving from this contamination also depends on the chemical speciation of various contaminants. A novel approach is proposed here to face-up this problem from a chemical thermodynamics point of view. The complexing ability of the soluble fraction of a landfill leachate (collected from Bellolampo, Palermo, Italy) towards  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  has been investigated at  $T = 298.15 \text{ K}$  in  $\text{NaCl}_{\text{aq}}$  at  $I = 0.1 \text{ mol dm}^{-3}$ . The soluble fraction of the landfill leachate was first characterized by different analytical techniques. Then, its acid-base properties were studied by ISE- $\text{H}^+$  potentiometric titrations and modelled by the so-called diprotic-like model. Successively, Differential Pulse Anodic Stripping Voltammetry (DP-ASV) titrations of metal ion aqueous solutions with diluted landfill leachate were carried out in order to determine the stability constants of leachate-metal complexes. The stability of  $\text{Pb}^{2+}/\text{OH}^-$  and  $\text{Pb}^{2+}/\text{Cl}^-$  complexes was also studied by the same technique. Finally, the sequestering ability of leachate towards the investigated metal cations has been quantified by the calculations of various  $\text{pL}_{0.5}$  values in different pH conditions. Results proved that landfill leachate is a good sequestering agent toward those cations, reducing the fraction of the free cations in solution, and that it can be a selective sequesterant at different pH.

### Introduction

Most of municipal solid wastes is worldwide stored in sanitary landfills. As a consequence of rain, leachates of extremely variable composition are produced in those landfills, depending on several factors, such as the type of wastes, the age of landfill, the pH, the redox potential.<sup>1-5</sup> Nevertheless, leachate components can be ascribed to four main categories: dissolved organic matter (DOM), xenobiotic organic compounds, inorganic macrocomponents and heavy metals.<sup>3</sup> The least category mainly includes arsenic, cadmium, copper, lead and mercury, with concentrations ranging from few  $\mu\text{g dm}^{-3}$  and up to some  $\text{mg dm}^{-3}$ .<sup>6</sup> Though the leachate should be ideally confined in the landfill, it often happens that, because of imperfections and/or possible damages of landfill liners, it contaminates superficial and ground waters in the proximity of the landfill, causing serious environmental pollution and human health risks, especially related to the presence of the above-cited toxic heavy metal ions. These risks depend, in turn, on the species that each metal forms with other leachate and ground-water components, *i.e.*, on their chemical speciation.

In fact, not all the species formed by toxic metal ion present in water are "bioavailable" to biota.<sup>7</sup> Several models have already been developed in order to know the bioavailability of a toxic metal in aquifer systems, such as the Free Ion Activity Model and the Biotic Ligand Model.<sup>8,9</sup> These models, as the speciation model here proposed, are currently used although these paradigms do not always account for experimental observations, and there are several exceptions.

Leachate DOM plays a critical role, since a variable but significant fraction of it is constituted by humic- and fulvic-like compounds, originated by a series of biological and chemical processes involving DOM itself (especially during the methanogenic phase of wastes decomposition).<sup>3,4</sup> Since these substances contain a great number of binding sites (mainly carboxylic and phenolic groups, but N-donor too), they strongly interact and bind several metal ions,<sup>2</sup> modifying their speciation in both the landfill and the receiving groundwater. That is why classical studies on the sole quantification of toxic metals in both leachates and groundwaters are not sufficient, alone, to evaluate the environmental impact of leachate contamination. On the contrary, a novel approach is necessary to face-up these issues, in which an accurate thermodynamic investigation of the complexing ability of landfill leachate towards heavy metal ions is crucial to assess their chemical speciation and, consequently, to make more critical evaluations about the real environmental and human health risks. To this end, here we report the results of a thermodynamic investigation (by ISE- $\text{H}^+$  potentiometry and Differential Pulse Anodic Stripping Voltammetry, DP-ASV) of both the acid-base properties and the complexing ability of the soluble fraction of landfill leachate towards  $\text{Cd}(\text{II})$ ,  $\text{Pb}(\text{II})$  and  $\text{Cu}(\text{II})$  ions. In particular, leachate samples were collected in the solid waste sanitary landfill of Bellolampo (close to Palermo, Italy), created in 1960s and become a controlled dump site in 1980s. The potentiometric and voltammetric titrations were carried out in  $\text{NaCl}_{\text{aq}}$ , at  $I = 0.1 \text{ mol dm}^{-3}$ , in order to simulate the possible conditions of some groundwater/leachate systems. The voltammetric titrations of metal ions solutions with leachate (diluted or as it is) were

carried out at pH = 5.0. Potentiometric data related to the acid-base properties of leachate have been elaborated by the so-called Diprotic-Like model,<sup>10</sup> while its complexing ability towards metal cations has been evaluated by the determination of some metal – leachate complex formation constants from DP-ASV data,<sup>11</sup> The global sequestering ability of leachate towards the investigated cations has then been quantified by the calculation of various  $pL_{0.5}$  values in different conditions.<sup>12</sup> The hydrolytic behaviour of  $Pb^{2+}$  and its chloride complexes were further investigated in  $NaCl_{aq}$  at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$  by DP-ASV.

## Experimental

### Reagents

Cadmium(II), copper(II) and lead(II) ion solutions were prepared by weighing the  $Cd(NO_3)_2 \cdot 4H_2O$ ,  $Cu(NO_3)_2 \cdot H_2O$  and the  $Pb(NO_3)_2$  salts, respectively, and were standardized by EDTA standard titrations.<sup>13</sup> NaCl used to fix the ionic strength of the solutions at the desired value was weighed after drying in oven at  $T = 383.15 \text{ K}$  for 2 hours. Hydrochloric acid and sodium hydroxide solutions used to adjust the pH of the metal ion solutions and in the ISE- $H^+$  potentiometric titrations were prepared by diluting concentrated ampoules, and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. Standard solutions of lead(II), copper(II) and cadmium(II) ions used for calibration curves were prepared by diluting  $1000 \text{ mg dm}^{-3}$  standard solutions in 2 %  $HNO_3$ . All reagents were purchased from Sigma-Aldrich, Italy, and its various brands, and all were of the highest available purity. All the solutions were prepared using freshly,  $CO_2$ -free ultra-pure water ( $\rho \geq 18 \text{ M}\Omega \text{ cm}^{-1}$ ) and grade A glassware.

### Treatment and characterization of landfill leachate

The experiments were carried out using the same leachate samples of Bellolampo landfill used in Amorello *et al.*<sup>14</sup> The leachate samples were filtered through  $0.45 \mu\text{m}$  filters and the filtrates were stored at  $T = 277.15 \text{ K}$  for no more than one week before the analysis.

The organic and inorganic residues of leachate were determined as follows:  $200 \text{ cm}^3$  of filtered leachate were placed in a porcelain crucible and dried in an oven at  $T = 453.15 \text{ K}$  to quantify the total organic, and inorganic compounds. Then the residue was incinerated in muffle furnace at  $T = 823.15 \text{ K}$  to quantify the inorganic fraction. In both cases the weight was measured after a constancy was reached. The procedure was repeated on five samples and the mean values of the organic and inorganic residues of leachate (g) have been reported,  $\pm 95 \%$  confidence interval.

The pH of leachate samples was measured by an ISE- $H^+$  glass electrode (Ross type 8102, from Thermo-Orion) connected to a potentiometer (Metrohm, model 713). The electrode was previously calibrated carrying out strong standard acid – strong standard base titrations under the same medium and ionic strength conditions, with the aim of determining  $E^0$ .

The chloride content was determined on leachate ash, previously solubilised with  $HNO_3$ , by using the Volhard method.  $NH_4^+$  and total N were determined by acid - base titration, upon distillation at alkaline pH and by the Kjeldahl method, respectively.

FT-IR spectra of leachate residues at  $T = 453.15 \text{ K}$  were registered by using a Jasco 420 FT-IR spectrometer. Pellets were prepared by mixing 1.6 mg of the sample powder with 140 mg of KBr oven-dried at  $T = 378.15 \text{ K}$ . Then the mixture was mixed in an agate mortar to obtain a homogeneous, finely grained powder and pressed at 12 tons for *ca.* 10 min. Spectra were recorded at a resolution of  $4 \text{ cm}^{-1}$  and are reported as percentage of transmittance (T%) vs. wavenumber ( $\lambda^{-1}$ ) after baseline correction.

The amount of Pb, Cd, Cu, Al, Cr, Mn, Fe, Co, Ni, Zn and Sn in the previously filtered leachate was measured by ICP-OES technique (Perkin Elmer - Model Optima 2100, equipped with a autosampler model AS-90) after digestion with a microwave oven (Milestone - model MLS-1200 Mega, Milestone Laboratory System, Italy). About 5 mL of leachate were transferred in Teflon vessels and 5 mL of 69 %  $HNO_3$  and 1 mL of 30 %  $H_2O_2$  were added. The following instrumental conditions were used: 1 min at 250 W, 1 min at 0 W, 5 min at 250 W, 5 min at 450 W, 3 min at 600 W and 5 min at 300 W.

### Procedure and equipment for potentiometric measurements

The acid–base properties of landfill leachate were studied by using the potentiometric technique, in  $NaCl_{aq}$  at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . A potentiometric titration system (Metrohm, Model 888 Titrando) controlled by the Tiamo software (Metrohm) and equipped with a combination ISE- $H^+$  glass electrode (Ross type 8102, from Thermo-Orion) was used. Estimated accuracy was 0.2 mV and  $0.003 \text{ cm}^3$  for electromotive force (e.m.f.) and titrant volume readings, respectively. All potentiometric titrations were carried out in a thermostatted cell under magnetic stirring, bubbling purified presaturated  $N_2$  through the solution in order to remove dissolved  $O_2$  and  $CO_2$ . For each titration,  $25 \text{ cm}^3$  of solution containing the soluble fraction of landfill leachate ( $5, 8$  or  $10 \text{ cm}^3$  in  $100 \text{ cm}^3$ ) and NaCl were titrated with a standardized solution of NaOH in the pH range  $2.0 \leq \text{pH} \leq 12.0$ . The titrand solutions were acidified with known amounts of HCl in order to start the titrations from  $\text{pH} \sim 2.0$ . For each experiment, independent strong standard acid – strong standard base titrations were carried out under the same medium and ionic strength conditions, with the aim of determining  $E^0$ . In this way, the pH scale used was the free scale,  $\text{pH} = -\log [H^+]$ , where  $[H^+]$  is the free proton concentration (not activity). The reliability of measurements in the alkaline pH range was checked by calculating the appropriate  $pK_w$  values. 80-100 points for each titration were collected.

### Procedure and equipment for voltammetric measurements

Voltammetric titrations were performed to investigate the hydrolysis and chloride complexes of  $Pb^{2+}$ . Measurements were performed on  $25 \text{ cm}^3$  of solutions containing known amounts of  $PbCl_2$  ( $c_{Pb} = 10^{-6} - 10^{-8} \text{ mol dm}^{-3}$ ), and suitable

amounts of HCl and NaNO<sub>3</sub> in order to obtain the pre-established pH and ionic strength values. Two different sets of measurements were carried out. The first consisted of the addition of different amounts of NaCl (up to ~1 mol dm<sup>-3</sup>) to the solution containing Pb<sup>2+</sup> at 1.5 ≤ pH ≤ 2.0, in order to investigate the formation of PbCl<sub>r</sub> stepwise species. In that pH range, the formation of hydrolytic species of Pb<sup>2+</sup> does not occur. The second set was performed as follows: the solution containing Pb<sup>2+</sup> was titrated with standard NaOH solution (also in the presence of different amounts of NaCl) and, for each point of the titration, both the pH values and voltammograms were recorded. This kind of procedure allowed us to determine the formation of the different simple Pb(OH)<sub>q</sub> and mixed PbCl(OH) hydrolytic species. For each titration, 30 to 40 voltammograms were recorded in the pH range 2.0 ≤ pH ≤ 9.0. In order to check the repeatability of the system, the measurements were carried out by two operators.

DP-ASV has also been used in the study of the complexing ability of landfill leachate towards Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup> ions. Voltammetric titrations of metal ion solutions ( $c_M = 10 - 15 \text{ mg dm}^{-3}$ ,  $c_{\text{NaCl}} = 0.1 \text{ mol dm}^{-3}$ , initial pH = 5.0) by concentrated or diluted (1:20 or 1:50) landfill leachate were carried out for each metal ion. The peak current and potential values after each titrant addition were collected.

The metal ion concentration in the titrand solutions was determined by Differential Pulse Anodic Stripping Voltammetry (DP-ASV) technique. The voltammetric apparatus was constituted by a Metrohm 663 VA stand combined with the Autolab potentiostat in conjunction with the IME663 interface and was controlled by NOVA v. 1.10 software.<sup>11, 15</sup>

The VA stand was equipped with a three-electrode system consisting of i) a Multi Mode Electrode Pro (Metrohm, code 6.1246.120) working in the Static Mercury Drop Electrode (SMDE) mode, ii) a glassy carbon auxiliary electrode (code 6.1247.000), and iii) a double junction Ag/AgCl/KCl (3 mol·dm<sup>-3</sup>) reference electrode (code 6.0728.030). The DP-ASV measurements were performed after bubbling purified N<sub>2</sub> gas into the solutions for 150 s. The error of ± 1 mV was experimentally determined for the potential readings. For ten replicate experiments the standard error is ± 0.3 mV.

The experimental electrochemical conditions, reported in Table 1, were chosen in order to optimize the quality parameters, as signal/noise ratio, repeatability, accuracy and to avoid interferences.

Calibration curves of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup> ions were done in the same experimental conditions used in the experiments. 25 cm<sup>3</sup> of aqueous solutions containing NaCl at  $I = 0.1 \text{ mol dm}^{-3}$  and at pH = 5 were placed in the voltammetric cell. A voltammogram of the solution was recorded as blank. Then, the peak current values after the addition of different aliquots of the standard solution (100 mg·dm<sup>-3</sup>) of the metal ion at the same pH and

**Table 1.** Instrumental parameters of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> DP-ASV measurements

Parameters	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>
Deposition potential <sup>a</sup>	-0.75	-0.55	-0.15
Deposition time <sup>b</sup>	1	1	1
Equilibration time <sup>b</sup>	10	10	10
Potential interval <sup>a</sup>	-0.80 / -0.40	-0.55 / -0.20	-0.15 / 0.20
Scan rate <sup>c</sup>	0.01	0.01	0.01
Step potential <sup>d</sup>	3	3	3
Modulation amplitude <sup>d</sup>	50	50	50
Modulation time <sup>b</sup>	0.01	0.01	0.01

<sup>a</sup> V; <sup>b</sup> s; <sup>c</sup> V s<sup>-1</sup>; <sup>d</sup> mV

ionic strength were collected. The calibration curves were carried out in the range 0.75 to 16 mg·dm<sup>-3</sup>. Considering that the pH of metal ion solutions was not buffered, during the experiments, the pH was monitored using the same potentiometric apparatus reported in previous section. The ISE-H<sup>+</sup> glass electrode was previously calibrated at the same experimental conditions of the experiments.

#### Calculations and equations used to fit experimental data

The nonlinear least-squares computer program ESAB2M was used for the refinement of all the parameters of the acid – base potentiometric titration, such as the standard electrode potential ( $E^0$ ), the ionic product of water ( $K_w$ ), the acidic junction potential ( $E_j = j_a [H^+]$ ), and the analytical concentration of reagents. The BSTAC and STACO software was used to refine the protonation constants of leachate functional groups from ISE-H<sup>+</sup> potentiometric titrations. In particular, the acid – base properties of leachate were studied assuming that the DOM was prevalently constituted by humic like substances (HS). As in the case of fulvic and humic acids of soils and sediments, -COOH and phenol -OH groups have been considered as the main functional groups of HS, though some N-donor and other titrable and/or binding groups are also present (this aspect will be commented in next sections). Their acid – base equilibria fall in two different pH ranges. For this reason, two distinct types of units were considered and were individually studied: one accounting for the carboxylic -COOH groups ( $L_1$  units) and another for the phenol -OH groups ( $L_2$  units). The Diprotic-Like model, successfully used to study the protonation equilibria of natural and synthetic polyelectrolytes,<sup>10, 16</sup> has been used to elaborate the ISE-H<sup>+</sup> potentiometric data of the two units. This model considers each unit as a di-functional unit whose acid-base properties can be defined by two protonation constants ( $K_1$  and  $\beta_2$ ), independent of the dissociation degree of the polyelectrolyte ( $\alpha$ ). The Diprotic-Like model can be used with a negligible loss of precision when, in the range  $0.1 \leq \alpha \leq 0.9$ , the variation of protonation constant of the considered functional groups is not very large ( $\sim 2.5 \log$  units). On the basis of the obtained results, the protonation constants of  $L_1$  units are given by (all charges of  $L_1$  and  $L_2$  species are omitted for simplicity):

$$K_1 = \frac{[HL_1]}{[L_1][H^+]} \quad (1)$$

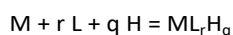
$$\beta_2 = \frac{[H_2L_1]}{[L_1][H^+]^2} \quad (2)$$

The negligible variation of protonation constants of the phenol -OH groups of  $L_2$  units with  $\alpha$  suggests that their acid-base properties are well defined by only one protonation constant:

$$K_1 = \frac{[HL_2]}{[L_2][H^+]} \quad (3)$$

An exhaustive explanation of the Diprotic-Like model is reported in refs. <sup>10, 17</sup>.

Formation constants of complex species formed by  $L_1$  and  $L_2$  units with the metal ions are given according to the equilibria:



where M is  $Pb^{2+}$ ,  $Cd^{2+}$  or  $Cu^{2+}$  and L is the  $L_1$  or  $L_2$  unit.

Voltammetric titration data were elaborated as reported elsewhere. <sup>11, 18</sup> For a ligand L and a metal cation M at fixed  $c_L:c_M$  ratios and varied pH, the peak potential shift due to the formation of labile complex species at any pH value is given by:

$$\Delta E_p = \Delta E_p^{free} - \Delta E_p^{comp} = \frac{RT}{nF} \ln \frac{c_M}{[M]} + \frac{RT}{nF} \ln \frac{i_p^{comp}}{i_p^{free}} \quad (4)$$

where  $\Delta E_p$  is the peak shift due to the difference between the peak potential of the free metal ( $E_p^{free}$ ) and the metal in the presence of the ligand ( $E_p^{comp}$ );  $i_p^{comp}$  and  $i_p^{free}$  are the peak heights (current intensities) with and without ligand in solution, respectively. The  $c_M$  and  $[M]$  are the analytical and the free metal ion concentrations, respectively, and  $n$  is the number of electrons involved in the redox process. The left-hand side of the equation and the term relative to the peak intensities are directly obtained from experimental data, while that containing the free metal concentration is given by solving the mass balance equations. Working with high  $c_L:c_M$  ratios and at relatively low metal concentrations, the assumption that no polynuclear species are formed is reasonable. By taking into account this assumption, the free cation concentration  $[M]$  at any pH value is given by:

$$[M] = \frac{c_M}{1 + \sum \beta_{ML_rH_q} [L]^r [H]^q} \quad (5)$$

with

$$[L] = \frac{c_L}{1 + \sum \beta_q [H]^q} \quad (6)$$

where  $\beta_q$  represents the overall protonation constant of the ligand. Eq. (6) is only valid in this form when  $c_L \gg c_M$  and complex species can be neglected in the mass balance equation of the ligand. When  $q < 0$ , the summation in eq. (5) takes into account the formation of simple ( $r = 0$ ) or mixed ( $r \neq 0$ ) hydrolytic species. Both the right and the left-hand sides of

eq. (4) are pH dependent and are valid for a fixed  $c_L:c_M$  ratio. Some examples of application of this procedure to the determination of complex formation constants of various systems are reported, *e.g.*, in refs. <sup>11, 18-21</sup>. The LIANA software was used to calculate the formation constants of  $M^{2+}$  - leachate species from voltammetric titration data. The ES4ECI software was used to draw speciation and sequestration diagrams and to calculate species formation percentages. Details on the computer programs used are given in ref. <sup>22</sup>.

## Results and discussion

### Characterization of landfill leachate

The residue after drying the filtrate leachate at  $T = 453.15$  K was  $12.24 \pm 0.05$  g  $dm^{-3}$  (organic and inorganic compounds), whilst the residue after incineration at  $T = 823.15$  K was  $9.67 \pm 0.04$  g  $dm^{-3}$  (inorganic compounds). As consequence, the organic fraction of filtrate leachate resulted  $2.57 \pm 0.05$  g  $dm^{-3}$ . The pH of filtrate leachate was  $8.5 \pm 0.2$ . This value is in the typical pH range (7.5 – 9.0) of landfill leachates in the methanogenic phase. In this phase of decomposition, most of DOM consists of humic-like substances. <sup>3, 4</sup> The predominance of humic-like substances has been confirmed by the FT-IR spectrum of leachate residue at  $T = 453.15$  K, reported in Figure 1. The spectrum has the typical bands of leachate humic acid, <sup>2, 23, 24</sup> *e.g.*:  $3400 - 3300$   $cm^{-1}$  (OH and NH stretching),  $\sim 2900$   $cm^{-1}$  (aliphatic C-H stretching)  $\sim 1580$   $cm^{-1}$  (aromatic C=C, C=O and COO<sup>-</sup>),  $\sim 1400$   $cm^{-1}$  (C-O stretching of phenol -OH and -COO<sup>-</sup> asymmetric stretching). The presence of humic and fulvic-like substances in Bellolampo landfill leachate has been also demonstrated by the three dimensional excitation-emission fluorescence spectra reported in ref <sup>14</sup>, which exhibit the unique fluorescence signals with excitation-emission position of the peak representative of the leachate sample. A systematic study on the metals content and on other important chemical parameters of different samples of Bellolampo landfill leachate has been carried out (unpublished data). The concentrations of 11 metals in the leachate sample used in this study together with other chemical parameters values are reported in Table 1S of Supplementary Material. As can be seen,  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  ions concentrations were below  $10$   $\mu g$   $dm^{-3}$ . The  $NH_4^+$  and the total N concentrations are 99 and 118  $mmol$   $dm^{-3}$ , respectively. Considering the reducing properties of leachate (COD = 9330  $mg$   $dm^{-3}$   $O_2$ ), no nitric and nitrous N should be present and the difference between total N and  $NH_4^+$  should be organic N.

### Acid-base properties of soluble humic-like substances of landfill leachate

The humic-like substances represent the most important part of dissolved organic fraction of leachate in terms of its complexing ability towards metal ions. As known, they are natural polyelectrolytes whose formation is due to a series of

reactions that involve the organic substances present in the landfill.<sup>2</sup> The knowledge of the protonation equilibria of the functional groups of the organic fraction of leachate is mandatory to study its complexation capacity towards metal ions. The main binding groups of organic soluble fraction of leachate are supposed to be the carboxylic -COOH and the -OH phenol groups, in analogy with humic and fulvic fractions of humic substances of soils and sediments<sup>10, 25-27</sup>.

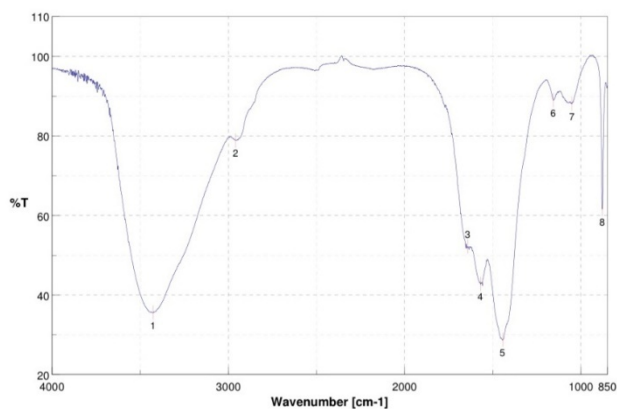


Figure 1. FT-IR spectrum of leachate residue at 453.15 K

The content of -COOH and of -OH groups of leachate was checked by direct potentiometric titrations (by NaOH) of leachate solutions prepared as above described. Afterwards, to confirm the concentration values of the main two functional groups, the classical calcium acetate and barium hydroxide methods were used.<sup>28</sup> The following mean carboxylic and phenolic group concentrations were determined (in parenthesis the results of indirect titrations):

$$c_{\text{COOH}} = 0.010 \pm 0.002 \text{ (} 0.011 \pm 0.007 \text{)} \text{ mol dm}^{-3}$$

$$c_{\text{OH}} = 0.160 \pm 0.005 \text{ (} 0.163 \pm 0.008 \text{)} \text{ mol dm}^{-3}$$

These values should be only considered as a rough estimation of the functional groups concentration, being the obtained values the sum of all the titrable binding groups in the same pH range of both -COOH and -OH groups, respectively. In particular, protonation/deprotonation equilibria of amino groups, usually present in the humic fraction of leachate in higher concentration than soil or aquatic humic substances,<sup>27</sup> can be in the same pH range of phenol groups. Nevertheless, due to the predominant amount of carboxylic and phenolic binding groups, these groups can be taken as main representatives of the two main fractions of leachate in the study of their acid – base and binding properties (named  $L_1$  and  $L_2$  for -COOH -OH groups, respectively).

The deprotonation of -COOH groups of  $L_1$  unit occurs, with a good approximation, in the pH range 2.5 – 6.5, while the deprotonation of -OH groups of  $L_2$  units starts at pH > 7.5. For this reason, the acidic and the alkaline parts of the potentiometric titrations have been analysed in two different steps by STACO and BSTAC computer programs. Moreover, as a supplementary check of the content of -COOH and -OH

groups, each potentiometric dataset was furtherly re-analysed by refining their concentrations simultaneously with the corresponding protonation constants (with and without constraints: the details about all possibilities and features of BSTAC and STACO programs can be found in ref.<sup>22</sup>). In the experimental conditions considered ( $I = 0.1 \text{ mol dm}^{-3}$  in  $\text{NaCl}_{\text{aq}}$

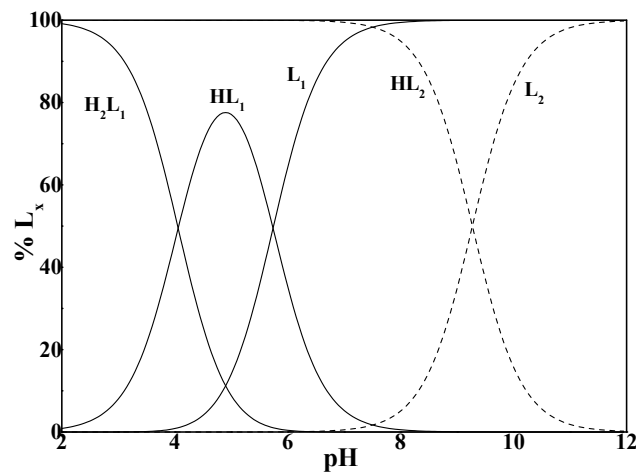


Figure 2. Distribution diagram of protonated and unprotonated species of  $L_1$  (continuous lines) and  $L_2$  (dotted lines) units of humic like substances of landfill leachate vs. pH in  $\text{NaCl}_{\text{aq}}$  at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ .

and  $T = 298.15 \text{ K}$ ) the protonation constants determined were  $\log K_1 = 5.746 \pm 0.005$  and  $\log \beta_2 = 9.80 \pm 0.01$  for  $L_1$ , and  $\log K_1 = 9.267 \pm 0.001$  in the case of  $L_2$ . As an example, in Figure 1S of Supplementary Material a acid – base titration curve of leachate is reported together with the fit curve obtained with the proposed speciation model with BSTAC program. The distribution of these species as a function of pH is shown in the speciation diagram of Figure 2, obtained considering a concentration of  $L_1$  (dashed lines) and  $L_2$  (continuous line) units of 10 and 160  $\text{mmol dm}^{-3}$ , respectively, as those determined during leachate analysis.

#### Hydrolysis of metal cations

For an accurate speciation study of aqueous systems containing metal cations, their acid-base properties (*i.e.*, their hydrolysis) must be known in the same conditions as the systems to be investigated. Often, in the literature, the hydrolysis constants of the metal cations are available, but they were generally obtained at relatively high concentrations of cations ( $c_M > 10^{-4} \text{ mol dm}^{-3}$ ), thus having a complex speciation among mononuclear and polynuclear species. In this work, the concentration of the cations in the experiments are much lower ( $c_M = 10^{-6} - 10^{-8} \text{ mol dm}^{-3}$ ), therefore the main species in solution are the mononuclear ones, with stoichiometry  $\text{M}(\text{OH})_q$ . Concerning both  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , available literature data (*e.g.*, stability constants, models, equations) were sufficient to derive a comprehensive set of hydrolysis and/or chloride complex formation constants, able to define with sufficient accuracy the solution behaviour of these cations in the conditions adopted in this work (*i.e.*,

NaCl<sub>aq</sub> at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ ).<sup>29-33</sup> The same did not happen for Pb<sup>2+</sup>, for which there are few data relative to the mononuclear species (except for the PbOH) and only at  $I = 0$  and at  $I \geq 3 \text{ mol kg}^{-1}$ , so that we decided to perform new voltammetric measurements in order to define the speciation of Pb<sup>2+</sup> at  $T = 298.15 \text{ K}$ , in NaCl<sub>aq</sub> in the ionic strength range  $0 < I / \text{mol dm}^{-3} \leq 1.0$ . The analysis of the experimental data allowed us to determine the stability of three simple Pb<sup>2+</sup>/Cl<sup>-</sup> species, three simple Pb<sup>2+</sup>/OH<sup>-</sup> species and one mixed Pb<sup>2+</sup>/OH<sup>-</sup>/Cl<sup>-</sup> species. The dependence of the corresponding stability constants on ionic strength has been taken into account by a classical extended Debye-Hückel equation:

$$\log K = \log K^0 - z^* \cdot 0.51 \cdot I^{0.5} / (1 + 1.5 \cdot I^{0.5}) + C \cdot I \quad (7)$$

with

$$z^* = \sum z_{\text{react}}^2 - \sum z_{\text{prod}}^2$$

where  $\log K^0$  is the stability constant at infinite dilution,  $z$  is the charge of each ion involved and  $C$  is an empirical parameter, reported in Table 2 for each species.

Worth mentioning is that the proposed speciation scheme has been obtained by a voltammetric technique, using very low total metal concentrations. This hampered the formation of polynuclear species, which becomes significant at the typical concentration range of other experimental techniques, such as potentiometry (the most used technique in the determination of stability constants, in which typical measurements are performed at millimolar analytical concentrations). For example, at  $c_{\text{pb}} \sim 5.0 \text{ mmol dm}^{-3}$ , the main species are the Pb<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> (maximum formation percentage 65% at pH  $\sim 7.0$ ), the Pb<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> (20% at pH  $\sim 6.5$ ) and the Pb<sub>6</sub>(OH)<sub>8</sub><sup>4+</sup> (30% at

**Table 2.** Ionic strength dependence parameters of the Pb<sup>2+</sup>/OH<sup>-</sup>, Pb<sup>2+</sup>/Cl<sup>-</sup>, and Pb<sup>2+</sup>/OH<sup>-</sup>/Cl<sup>-</sup> species.

Equilibrium	$\log K^0$	$z^*$	$C$
Pb <sup>2+</sup> + Cl <sup>-</sup> = PbCl <sup>+</sup>	$1.50 \pm 0.03^a$	4	$0.37 \pm 0.02$
Pb <sup>2+</sup> + 2 Cl <sup>-</sup> = PbCl <sub>2</sub>	$2.10 \pm 0.12$	6	$0.55 \pm 0.03$
Pb <sup>2+</sup> + 3 Cl <sup>-</sup> = PbCl <sub>3</sub> <sup>-</sup>	$1.8 \pm 0.1$	6	$0.55 \pm 0.03$
Pb <sup>2+</sup> + H <sub>2</sub> O = Pb(OH) <sup>+</sup> + H <sup>+</sup>	$-6.47 \pm 0.03$	2	$0.18 \pm 0.01$
Pb <sup>2+</sup> + 2 H <sub>2</sub> O = Pb(OH) <sub>2</sub> + 2 H <sup>+</sup>	$-16.12 \pm 0.01$	2	$0.18 \pm 0.01$
Pb <sup>2+</sup> + 3 H <sub>2</sub> O = Pb(OH) <sub>3</sub> <sup>-</sup> + 3 H <sup>+</sup>	$-28.4 \pm 0.1$	0	$0.01 \pm 0.03$
Pb <sup>2+</sup> + H <sub>2</sub> O + Cl <sup>-</sup> = Pb(OH)Cl + H <sup>+</sup>	$-7.0 \pm 0.3$	4	$0.36 \pm 0.02$

<sup>a</sup>  $\pm 95\%$  confidence interval.

pH  $\sim 8.0$ ), meaning that the stability of the mononuclear species cannot be potentiometrically determined with sufficient accuracy. On the contrary, species with low nuclearity, determined in this work, are the most important at low Pb<sup>2+</sup> concentrations ( $c_{\text{pb}} < 10^{-5} \text{ mol dm}^{-3}$ ), as can be those typical of many trace metal cations in natural waters and biological fluids. In addition, a new species, present in chloride media, has been determined, *i.e.*, the mixed Pb(OH)Cl. This species, determined for other metal cations, such as Sn<sup>2+</sup><sup>20</sup> and Cd<sup>2+</sup>,<sup>15</sup> is important at high chloride concentration, such as the conditions of brines. The results reported in this work are in a fairly good agreement with literature data collected in

Martell *et al.*<sup>31</sup> and Baes and Mesmer<sup>29</sup>, especially considering the differences in the experimental conditions (differences are less than one order of magnitude).

### Complexing ability of landfill leachate towards Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup>

Experimental voltammetric data were elaborated by the LIANA software, taking into account the protonation constants of leachate binding groups and the hydrolysis constants of metal ions. The initial pH of the titrand solutions was always around 5.0 and, during the titrations with leachate solutions, it increased, reaching values depending on the leachate concentration, but never as high as pH = 8.5. In this pH range, only the carboxylic groups of L<sub>1</sub> units of the humic fraction of leachate are deprotonated (Figure 2), supporting the assumption that only L<sub>1</sub> units are available to bind the metal ions. Nevertheless, experimental data have been elaborated proposing a wide number of speciation schemes, considering various ML<sub>r</sub>H<sub>q</sub> species for both L<sub>1</sub> and L<sub>2</sub>, as well as mixed ML<sub>1r</sub>L<sub>2r</sub>H<sub>q</sub> species. The possible formation of species involving the L<sub>2</sub> ligand (*e.g.*, ML<sub>2</sub>) was unsuccessfully tested, because they may exist at pH > 8.5. The accepted model, for all the three investigated metal cations, is reported in Table 3 together with the corresponding stability constants. Concerning the model selection, it is important to stress that rigorous criteria should be always followed, and various results should be critically analysed from different points of view, going beyond the simplistic comparison of fitting parameters. A detailed description of some of these criteria, applied to different cases, could be found, *e.g.*, in refs.<sup>34, 35</sup>. Comparing results of Table 3 for the three investigated cations, it can be observed that the ML<sub>1</sub> species, common to all cations, has the lowest stability for Cd<sup>2+</sup>, while that of PbL<sub>1</sub> and CuL<sub>1</sub> species is similar. The ML<sub>1</sub>OH species was determined for both Pb<sup>2+</sup> and Cu<sup>2+</sup>, while the protonated ML<sub>1</sub>H species is only formed by Pb<sup>2+</sup> (see distribution diagrams reported in Figures S2-S4 of Supplementary Material). The comparison of the stability constants of the three metal cations–leachate species suggests that, in the investigated pH range, oxygenated groups of leachate are involved in metal ion complexation. In fact, the stability of complex species formed by N-donor groups with Cu<sup>2+</sup> ions is usually greater than those of the other two metal cations, while it is comparable for carboxylate complexes (Table 4). Using the NICA-Donnan model, Milne *et al.*<sup>36</sup> calculated that the affinity trend for the metal cation under study is Cu<sup>2+</sup> > Pb<sup>2+</sup> > Cd<sup>2+</sup>.

In this context, it must be reminded that the numerical results of this study (*e.g.*, equilibrium constants, pL<sub>0.5</sub>) are valid at  $I = 0.1 \text{ mol dm}^{-3}$ . This value simulates the conditions of some ground water /leachate systems, to which the data here reported may be directly applied. If the ionic strength is significantly different than this value, some corrections must be done, taking into account Debye-Hückel, SIT or Pitzer equations.

**Table 3.** Stability constants between metal cations and soluble fraction of Bellolampo landfill leachate obtained by differential pulse anodic stripping voltammetry at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ .

Equilibrium	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$
$\text{M} + \text{L}_1 = \text{ML}_1$	$5.9 \pm 0.3^a$	$4.91 \pm 0.03^a$	$6.1 \pm 0.1^a$
$\text{M} + \text{HL}_1 = \text{ML}_1\text{H}$	-	-	$6.30 \pm 0.09$
$\text{M} + \text{L}_1 = \text{ML}_1\text{OH} + \text{H}$	$-0.49 \pm 0.07$		$-0.9 \pm 0.1$
m.d. <sup>b</sup>	0.031	0.012	0.021

<sup>a</sup>  $\pm 95\%$  confidence interval; <sup>b</sup> mean absolute deviation of the fit (see ref. <sup>37</sup>).

**Table 4.** Comparison among the stability constants <sup>a</sup> of some ligands towards  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ .

Ligand	$\log K_{\text{ML}}$		
	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$
Ethylenediamine	5.1	10.5	5.4
1,3-diaminopropane	6.3	9.7	4.5
Acetic acid	2.1	1.8	1.5
Succinic acid	3.1	2.7	2.0
Oxalic acid	4.2	4.9	2.6

<sup>a</sup> data from Martell *et al.* <sup>31</sup>.

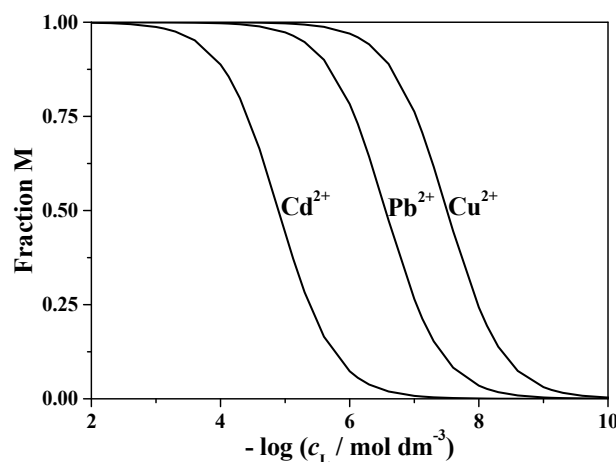
#### Quantification of the sequestering ability of landfill leachate towards $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$

Data reported in Table 3 for the three investigated cations in the presence of landfill leachate showed that  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  have three different speciation schemes. Moreover, their hydrolytic behaviour and their interactions with chloride ion change as well. This means that, even in simplified models, the simple analysis of the stability constants of complexes with the same stoichiometry (*e.g.*, the  $\text{ML}_1$  in our case) may not be sufficient alone to make accurate comparisons and speculations about the ability of a ligand to “sequester” different cations. It is always useful, especially for not-specialized readers, to emphasize that the whole sequestration process of a cation by a ligand/chelant in a multicomponent solution (such as many real systems) is not only dependent on the simple complexing ability of the selected ligand, but it is affected by many other factors, such as all the competing reactions involving both the cation and the ligand (*e.g.*, hydrolysis, protonation, formation of other complexes). That is why many approaches and models have been proposed during the years to face up the problem of the sequestration. <sup>12, 38</sup> Here, the evaluation of the sequestering ability of the leachate is quantified by determining the  $\text{pL}_{0.5}$  (or  $\text{pL}_{50}$ ), a semiempirical parameter proposed since some years <sup>12</sup> to numerically quantify this capacity, showing a series of advantages with respect to other approaches (*e.g.*,  $\text{pM}$ ). <sup>12, 38</sup> Briefly, a so-called “sequestration diagram” is built by plotting the molar fraction (or the percentage if one refers to  $\text{pL}_{50}$ ) of the investigated metal cation (as trace,  $10^{-12} \text{ mol dm}^{-3}$  in our case) complexed by the ligand of interest as a function of the analytical concentration of the ligand itself (expressed as  $-\log$

$c_L$ ). The resulting curve is similar to a dose-response curve, which can be fitted by a Boltzmann type equation:

$$x = \left[ \frac{1}{1 + 10^{(\text{pL} - \text{pL}_{0.5})}} \right] \quad (8)$$

The value of  $\text{pL}$  at  $x = 0.5$  is called  $\text{pL}_{0.5}$ . The higher the  $\text{pL}_{0.5}$ , the higher the sequestering ability is. This approach can be used for the comparison of the sequestering ability of different ligands towards the same cation and *vice versa*, and it is simple to calculate and advantageous. Among its various features,

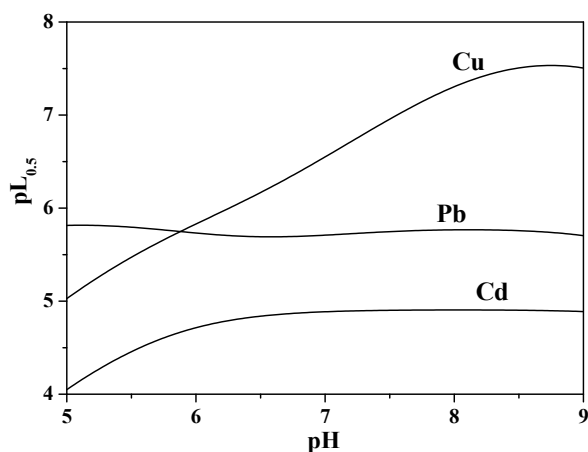


**Figure 3.** Sequestration diagrams of the  $\text{L}_1$  ligand towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  at  $\text{pH} = 8.5$ ,  $T = 298.15 \text{ K}$  and  $I = 0.1 \text{ mol dm}^{-3}$  in  $\text{NaCl}_{\text{aq}}$ .

worth mentioning is the fact that it takes into account all the side reactions (ligand protonation, metal cation hydrolysis, presence of other ligands and cations) that can occur in a system, since the molar fraction of complexed metal can be determined by classical programs for the calculation of the species distribution in different experimental conditions (*e.g.*,  $\text{pH}$ , ionic strength, temperature) and in the presence of many other ligands and cations. In Figure 3, the sequestration diagram of the  $\text{L}_1$  towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  is shown at  $\text{pH} = 8.5$ ,  $T = 298.15 \text{ K}$  and  $I = 0.1 \text{ mol dm}^{-3}$ . The  $\text{pL}_{0.5}$  has been calculated in the  $\text{pH}$  range 5.0–9.0 and its trend for the three cations as a function of  $\text{pH}$  is shown in Figure 4. As can be observed, the leachate may selectively sequester one of the investigated cations in the presence of the others just varying  $\text{pH}$ . For example,  $\text{Cu}^{2+}$  can be sequestered at  $\text{pH} > 7.0$  (ideally  $\text{pH} \sim 8.5$ – $9.0$ , where  $\Delta\text{pL}_{0.5} \sim 1.5$  and  $2.5$  with respect to  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ ), while  $\text{L}_1$  is selective for  $\text{Pb}^{2+}$  at  $\text{pH} < 6.0$  ( $\Delta\text{pL}_{0.5} \sim 1.0$  and  $2.0$  with respect to  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  at  $\text{pH} \sim 5.0$ ). To give an idea of the order of magnitude, the  $\text{pL}_{0.5}$  of EDTA, ethylenediamine, leachate and succinic acid towards  $\text{Cu}^{2+}$  is 17.1, 9.5, 7.5 and 2.2, respectively (in the same experimental conditions of Figure 3).

## Conclusions

The absence or the damage of waterproofing liners can cause a serious contamination of the aquifers near the landfills due to the release of leachate in soils. The hazard certainly depends on the chemical composition of leachate, but also on the speciation of its components in the experimental conditions of the contaminated aquifer. That is why the sole quantification of various contaminants in the leachate and in the groundwaters only gives partial information about the severity of contamination. Here, a thermodynamic approach based on procedures and models already used for humic and fulvic acids of different origin has been applied for the first time to humic-like substances of leachate. By evaluating the solution behaviour and the complexing ability of landfill leachate toward some environmentally relevant metal cations (*i.e.*,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ ). A detailed speciation study of the soluble fraction of a landfill leachate has been performed, starting from the evaluation of its acid-base behaviour, and going through the study of its complexing and sequestering



**Figure 4.** Dependence on pH of  $pL_{0.5}$  values for the sequestration of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by  $L_1$  ligand in  $\text{NaCl}_{\text{aq}}$ , at  $I = 0.1 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ .

ability towards  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . In particular, according to the Diprotic-Like model<sup>10</sup>, two soluble leachate fractions have been considered in modelling its acid-base properties: the first ( $L_1$ ) mainly refers to the carboxylic groups of leachate, while the second ( $L_2$ ) mainly accounts for its hydroxo- groups. Overall, two protonation constants for  $L_1$  and one for  $L_2$  were sufficient to describe the protonation/deprotonation of leachate over a wide pH range. Successively, results obtained in the investigated conditions proved that in the first fraction (*i.e.*,  $L_1$ ) is the main responsible for leachate complexation towards  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in the pH range 5.0 – 8.5, with different species formed. Finally, the  $pL_{0.5}$  values calculated in various conditions showed that leachate itself is a good sequestering agent towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , reducing the amount of the free aquo-ions in solution. Moreover, results demonstrated that the sequestration process by  $L_1$  can be selective toward one or another cation just varying pH (highest

selectivity is observed for  $\text{Pb}^{2+}$  at  $\text{pH} \sim 5.0$ , and at  $\text{pH} \sim 8.5$  for  $\text{Cu}^{2+}$ ).

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was supported by MIUR (Grant PRIN 2015 - 2015MP34H3) for partial funding.

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