

# Kaolinite sorption of Cd, Ni and Cu from landfill leachates: influence of leachate composition

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**Abstract** Heavy metal speciation in landfill leachates plays a significant role in determining the mobility during the percolation through soils. The complexation characteristics of landfill leachate directly affects heavy metal solubility and the extent of the interaction with soils, lowering or raising the sorbed amount depending on the relative affinity of the complexed metal and uncomplexed form to soil adsorption sites. In this paper, the adsorption of Cd, Ni and Cu onto kaolinite from three leachates (collected from landfill at different fermentation stage) is studied, also in comparison with metal speciation by two different operative procedures. The heavy metals, at their natural concentration, were divided into operational classes according to an exchange-based procedure and by fractionation on the basis of molecular weight (exchange onto Chelex100 resin and ultrafiltration, respectively). All the experiments were performed also on synthetic solutions designed according to leachate composition and theoretical speciation. The experimental results have shown leachate complexing capacity is strongly dependent on landfill age, and that broad parameters such as COD, DOC, pH, ionic strength and VFA concentration are not able to predict it. It is noteworthy that the strong complexing capacity of leachate can cause extraction of metals from the solid phase instead of adsorption from the liquid one.

**Keywords** Heavy metals; kaolinite; landfill leachates; sorption; speciation

## Introduction and aims

Landfilling is still extensively used in waste management. Indeed, increasing quantities of both industrial and municipal solid wastes are dumped on the soil in uncontrolled tips. One of the major problems associated with this disposal technology is the generation of large quantities of highly polluted leachate, which can percolate through soils and become a potential threat for ground water quality (Lema *et al.*, 1988). Leachate migration is often slow and the effects of an improper management of landfills might become evident only after a long time. The composition of landfill leachate is affected by several factors which include the composition of the disposed wastes, the climate, the landfill conditions at the site, as well as the landfill management and the hydrogeological conditions. Considering the high variability of these factors, large variations in leachate composition are often encountered especially with reference to the organic fraction (Ghassemi *et al.*, 1984, Oman and Hynning, 1993).

Among the different pollutants occurring in landfill leachates, heavy metals can be particularly dangerous. Their movement through soils is largely affected by the interaction at the solid – liquid interface which is controlled by the composition of both phases in contact. As largely reported in the scientific literature, heavy metal's adsorption onto soil is strongly affected from the liquid phase composition. The effects of metal concentration, pH, ionic strength and presence of inorganic competing ions have been intensively studied, especially with reference to pure solid phase (such as clays and oxides). When dealing with landfill leachates the occurrence of organic compounds which can bind heavy metals with different strength and stability has to be accounted for as one of the most significant mechanisms affecting the interaction with the solid phase (Majone *et al.*, 1998). Depending

of the age of the landfill, organic compounds with different molecular weights and different complexing capacity may be present. The complexation characteristics of the landfill leachate may increase the heavy metal solubility (thus increasing the metal extraction ability from the solid wastes) and influence the adsorption onto soil, lowering or raising the sorbed amount depending on the relative affinity to the soil of the complexed metal and the uncomplexed form (Knox and Jones, 1979, Harmsen, 1983, Christensen, 1989, Majone *et al.*, 1993).

The aim of this work was to study the adsorption of several heavy metals (Cd, Ni and Cu) from three leachates collected from landfill at different fermentation stages onto kaolinite, and to compare the experimental behaviour with metal speciation. Two different operative procedures were used to determine the metal distribution in different classes according to their behaviour with respect to an exchange-based and molecular weight-based procedure (exchange onto Chelex 100 resin and ultrafiltration, respectively).

## Materials and methods

### Analytical methods

Major cations (Na, K, Ca and Mg) and Fe were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Jobin Yvon JY38 Plus) following the procedure optimised by Petrangeli Papini *et al.* (1994) after microwave mineralisation. Due to the low concentration in the leachates, Cd, Pb, Cu and Ni were determined by graphite furnace atomic absorption spectrophotometry (Thermo Jarrel Ash – Smith Hieftje, furnace CTF 188) on the previously mineralised samples. Dissolved carbon (DC) and dissolved inorganic carbon (DIC) were determined according to standard procedure by a total carbon analyser (Strholein CMAT 550 pc). Dissolved organic carbon (DOC) was obtained as difference. Inorganic anions were determined by ion chromatography with chemical suppression and conductimetric detection (Dionex 2000i, AG4 guard column and AS4 analytical column, eluent  $\text{NaHCO}_3$   $1.7 \text{ mmol L}^{-1}$  –  $\text{Na}_2\text{CO}_3$   $1.8 \text{ mmol L}^{-1}$ , regenerant  $\text{H}_2\text{SO}_4$   $50 \text{ mmol L}^{-1}$ , eluent flow rate  $1.5 \text{ mL min}^{-1}$ ). Volatile fatty acids were determined by gas chromatography according to Ottenstein and Bartley (1971). Phenolic substances were measured by the spectrophotometric method of Folin-Ciocalteau (Box, 1983) in terms of salicylic acid. Kjeldahl nitrogen (inorganic and organic) and chemical oxygen demand (COD) were measured using standard procedures.

### Leachates

The leachates used for this research were collected from three different municipal landfill sites located in central Italy. The “LA” leachate was collected from the leachate collection system of a young landfill in use for one month; the “LM1” leachate was collected from a landfill operating for a few years, whereas the “LM2” leachate was sampled from the leachate reservoir of an old (more than ten years) and inactive landfill. The leachate samples were stored in polyethylene bottles at  $4^\circ\text{C}$ . Table 1 reports the analytical characterisation of the three leachates after separation of the suspended matter by centrifugation at 3,500 rpm (3,300 g) for 15 minutes and subsequent filtration through 0.45 mm acetate cellulose filters (Millipore).

### Synthetic solutions

Synthetic solutions were prepared according to a preliminary theoretical speciation of the different leachates calculated by MINTEQA2/PRODEFA2 code (1991) by using as input concentrations the total composition reported in Table 1. Two solutions were prepared, “SA” and “SM” respectively, in order to simulate the different leachate characteristics. VFAs, alkaline and earth-alkaline metals were represented by acetate, sodium and calcium,

respectively. Salicylic acid and glycine were used to simulate phenolic and nitrogenated organic substances, respectively. Chloride, carbonate and ammonium were added at the same concentration as measured in the different leachates, whereas other components were neglected. Cd, Ni and Cu were spiked to obtain the concentrations measured in the leachates. The theoretical speciation of the selected metals (Table 2) was similar to that one calculated for the correspondent leachates.

#### Exchange on Chelex100 resin

Batch kinetic tests were performed on the three leachates, after centrifugation and 0.45 mm filtration, and on the synthetic solutions by using analytical grade Chelex100 chelating resin (Biorad Laboratory, 100–200 mesh, sodium form, exchange capacity  $0.61 \text{ meq g}^{-1}$ ), following a previously optimised procedure (Majone *et al.*, 1996). The resin was stored under vacuum in a desiccator at room temperature and was added to the leachates, and synthetic solutions, at a ratio of  $0.25 \text{ g}/25 \text{ mL}$ . Tests were performed in closed Erlenmeyer flasks at  $25^\circ\text{C}$  in a thermostated water bath under continuous stirring. Blanks without resin were also carried out to check the possible metal adsorption onto the flask walls. The pH of the suspension remained constant during the tests ( $\Delta\text{pH} < \pm 0.1$  units). The exchange based procedure made it possible to divide metals into three operational classes, namely free/labile, slowly exchangeable and inert/stable, according to their exchangeability on the resin at different contact times. The free/labile fraction was defined as the metal removed after 1 h contact time (rapidly exchangeable), the slowly exchangeable fraction as the metal removed in the interval between 1 and 24 hours contact time, and the stable/inert fraction as the metal removed after 24 hours contact time (not exchangeable).

**Table 1** Total composition of the different leachates

Parameter	Units	LA	LM1	LM2
PH		6.44	8.37	8.50
DC	$\text{mgC L}^{-1}$	3982	2017	2189
DIC	$\text{mgC L}^{-1}$	31	1544	1689
DOC	$\text{mgC L}^{-1}$	3951	473	500
COD	$\text{mgO}_2 \text{ L}^{-1}$	9155	1379	2132
$\text{N}_{\text{inorganic}}$	$\text{mg L}^{-1}$	4.3	1100	1544
$\text{N}_{\text{organic}}$	$\text{mg L}^{-1}$	1.8	96	< d.l.
phenolic substances	$\text{mg L}^{-1}$	113	201	404
Na	$\text{mg L}^{-1}$	225	576	905
K	$\text{mg L}^{-1}$	162	245	329
Ca	$\text{mg L}^{-1}$	808	16	8.0
Mg	$\text{mg L}^{-1}$	144	65	38.6
Fe	$\text{mg L}^{-1}$	5.4	1.2	2.0
Zn	$\mu\text{g L}^{-1}$	120	80	60
Pb	$\mu\text{g L}^{-1}$	15.9	30	32
Cd	$\mu\text{g L}^{-1}$	4.70	1.30	1.60
Cu	$\mu\text{g L}^{-1}$	4.8	26.5	11.5
Ni	$\mu\text{g L}^{-1}$	55	169	300
sulphate	$\text{mg L}^{-1}$	81	22	12
chloride	$\text{mg L}^{-1}$	566	1499	2873
nitrate	$\text{mg L}^{-1}$	2.2	3.2	2.9
phosphate	$\text{mg L}^{-1}$	8.2	12.0	15.4
acetate	$\text{mg L}^{-1}$	2391	< d.l.	< d.l.
propionate	$\text{mg L}^{-1}$	1302	< d.l.	< d.l.
i-butyrate	$\text{mg L}^{-1}$	104	< d.l.	< d.l.
butyrate	$\text{mg L}^{-1}$	1309	< d.l.	< d.l.
valerate	$\text{mg L}^{-1}$	1069	< d.l.	< d.l.

### Ultrafiltration procedure

Two different flat ultrafiltration membranes were used: Amicon YM1 (MWCO 1 kDa) and YM10 (MWCO 10 kDa). Before use the membranes were washed in 5% NaCl solution and rinsed several times with deionised water to avoid possible release of presorbed metals. Ultrafiltration tests were carried out in 50 mL stirred cell (Amicon 8050). The cell uses a magnetic rotary bar positioned close to the membrane surface to keep solution in motion and lower polarisation concentration. Operative pressure was about 60 psi and the length of each test varied from 1 to 3 hours depending on the membrane MWCO. For each test the first 5 mL of filtrate was discharged to allow membrane equilibration with the leachates. At the end of the tests the filtrates were analysed for DOC, COD, phenolic substances and heavy metals.

### Kaolinite sorption tests

Sorption tests were performed with leachates and synthetic solutions. The solid phase was commercially available pure kaolinite (Merck, no 1906). The purity of the kaolinite was checked by XRD analysis. Impurities due to quartz and illite were found to be less than 3%. The cation exchange capacity was 11.2 meq/100 g as measured by BaCl<sub>2</sub> exchange method. The specific surface area was measured by BET method and resulted 8.8 m<sup>2</sup> g<sup>-1</sup>. Before use, the kaolinite was converted in sodium form by repeated washing with 0.25 mol L<sup>-1</sup> NaNO<sub>3</sub> solutions, until the metal concentration in the liquid phase was below the detection limit of the used analytical technique. Then, the kaolinite was rinsed with deionised water and dried at 45°C. The kaolinite was then stored in a desiccator under vacuum. The sorption tests were carried out according to the following procedure: 40 mL aliquots of the leachate or synthetic solutions were transferred into 50 mL polyethylene bottles. Then, different amounts of kaolinite were added in the range 0.1–5.0 g. The equilibration of the suspensions was performed under continuous stirring at 25°C. After 48 hours the suspensions were centrifuged at 3,500 rpm (3,300 g) for 10 minutes and the supernatants were analysed for metal content. pH variation of the suspension during the sorption tests was always less than 0.1 units. Blank experiments (without kaolinite) were carried out to verify the absence of metal precipitation.

## Results

### Metal speciation by exchangeability on Chelex100 resin

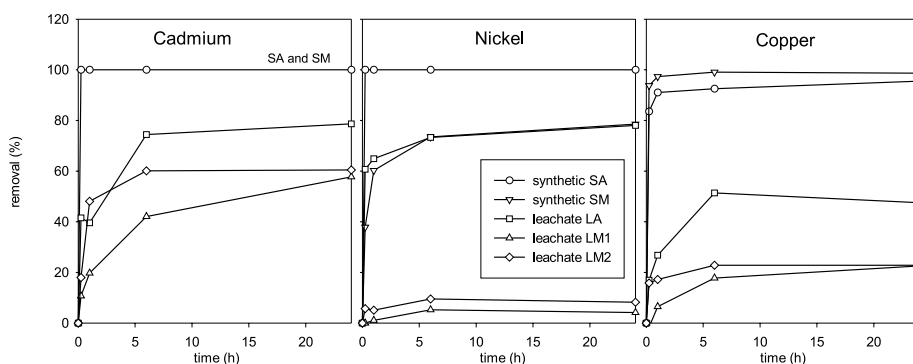
Figure 1 shows the experimental results of the Chelex100 tests in terms of metal percentage removal as function of the contact time for Cd, Ni and Cu, respectively. As for Cd, it is quantitatively removed in the shorter contact time (15 minutes) from both synthetic solutions (where Cd species, as reported in Table 2, are mainly acetate and chloride complexes for SA and carbonate complexes for SM). The experimental behaviour is clearly different in the tests with actual landfill leachates where a slower removal rate is observed. Moreover, Cd removal from LA and LM2 leachates is not quantitative at the equilibrium (24 h). LM2 shows the strongest complexing capacity (60% of total dissolved cadmium removed from LM2 versus 80% removed from LA leachate). In the case of LM1, the slower kinetics of removal does not allow to reach an equilibrium condition after 24 h of contact time, even though considering the clear decrease of the removal rate, it can be extrapolated also in this case a not quantitative removal at the equilibrium. As for Ni, a clear difference is observed among synthetic solutions (SA and SM). As a matter of fact, Ni is rapidly and quantitatively removed from SA where the prevalent species are free ion and acetate complexes (59 and 40%, respectively), whereas the removal is slower and not complete from SM (where carbonate complexes account for the total dissolved metal). Considering the leachates, about 80% of total Ni is removed after 24 h from LA, whereas LM1 and LM2

**Table 2** Main species of the metals (greater than 1%) in the synthetic solutions as calculated by MINTEQA2/PRODEFA2 speciation code (percentage of total dissolved metals)

Component	Species	Synthetic SA (%)	Synthetic SM (%)
Cd	Cd <sup>2+</sup>	19.0	1.0
	Cd(acetate) <sup>+</sup>	41.0	–
	Cd(acetate) <sub>2</sub>	28.6	–
	CdCl <sup>+</sup>	10.6	2.4
	CdCO <sub>3</sub> (aq)	–	91.5
	CdHCO <sub>3</sub>	–	4.3
	total	99.2	99.2
Ni	Ni <sup>2+</sup>	59.0	–
	Ni(acetate) <sup>+</sup>	40.1	–
	NiCO <sub>3</sub> (aq)	–	10.2
	Ni(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	–	89.8
	total	99.1	100.0
Cu	Cu <sup>2+</sup>	9.4	–
	Cu(acetate) <sup>+</sup>	39.3	–
	Cu(acetate) <sub>2</sub>	42.5	–
	Cu(salicylate)	6.8	1.2
	CuCO <sub>3</sub> (aq)	–	12.9
	Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	–	82.3
	Cu(OH) <sub>2</sub> (aq)	–	3.5
	total	98.0	99.9

exhibit a strong complexing capacity, with less of 10% removed at the equilibrium. As for Cu, the removal from synthetic solutions is rapid and almost quantitative. The tests performed with leachates show a slower and not quantitative Cu removal. As already observed for Cd and Ni, LM1 and LM2 leachates confirm their higher complexing capacity with respect to LA.

The operational speciation obtained with the Chelex100 based-procedure is reported in Table 3, where the total dissolved metal of each leachate is divided into the three classes (free/labile, slowly exchangeable and stable/inert). As for the younger leachate, LA, all the metals are distributed among the three operational classes. Cd and Ni occur mostly in the exchangeable fractions whereas Cu is present to a relevant percentage as inert/stable one. As for old leachates, LM1 and LM2, the distribution of all the metals is shifted towards the less exchangeable fractions: Ni and Cu are mostly present in the inert/stable (80–90%), whereas Cd is still prevailing in the exchangeable ones. The results clearly show a different

**Figure 1** Cd, Ni and Cu exchange kinetics onto Chelex100 in the different matrices

behaviour between the young and the old leachates with LM1 and LM2 showing a significantly higher complexing capacity with respect to LA.

#### Ultrafiltration tests

The experimental results of the ultrafiltration tests are reported in Table 4 in terms of percentage of total dissolved metals in the different MWCO fractions. Again these results clearly show the different behaviour of the leachates depending on their age.

As for LA leachate, all metals are mostly found in the fraction with the lowest molecular weight (MWCO<1000), particularly in the case of Cd which is totally occurring in this fraction. Accordingly, most organic matter occurs in the same fraction (as expected from the high VFA concentration). The phenolic substances are also found only in the lowest MWCO fraction and thus they do not play a role in metal complexation at higher molecular weight. It is noteworthy that significant amounts of dissolved Ni and Cu (30 and 40%, respectively) are found in the intermediate MWCO fraction although they account for only a small percentage of the organic matter (5% of COD and DOC). The fraction with the larger MWCO (<10000) results negligible for all the measured parameters.

Both LM1 and LM2 leachates show a higher contribution of the fractions with MWCO>1000 for all the measured parameters. Differently from LA leachate, the dissolved organic matter is also due to substances with high molecular weight. In particular, phenolic substances are mainly found in fractions with MWs higher than 1000. Ni show a roughly homogeneous distribution in the three fractions in both leachates. Cu is mainly found in the intermediate fraction (50 and 48%) even though its percentage in the extreme fractions is quite different for LM1 and LM2. Also for Cd the intermediate fraction results similar for LM1 and LM2 (26 and 25%), while the relevance of the extreme fractions is inverted.

#### Kaolinite sorption tests

Figure 2 shows the results of the sorption tests with kaolinite in terms of the ratio between equilibrium and initial dissolved metal concentration ( $C_{eq}/C_{in}$ ) as function of quantity of kaolinite, for Cd, Ni and Cu respectively. Cd and Ni removal from both synthetic solutions show the “traditional” decreasing pattern of  $C_{eq}/C_{in}$  with the increasing quantity of solid phase. For both the metals, sorption from SA solution (weakly acidic pH and high acetate concentration) is lower with respect to SM one (alkaline pH and high carbonate content). Cu exhibits different behaviour: sorption from SA solution is always less than 20%, whereas SM solution clearly extracts Cu from kaolinite.

In the tests performed with leachates, only Ni from leachate LA is weakly sorbed onto kaolinite. In any case the sorption extent appears lower than from the correspondent

**Table 3** Metal speciation in the different leachates according to the Chelex100 based procedure. Results are in percentage respect to total dissolved metal

Fraction	Criterion	Leachate LA			Leachate LM1			Leachate LM2		
		Cd (%)	Ni (%)	Cu (%)	Cd (%)	Ni (%)	Cu (%)	Cd (%)	Ni (%)	Cu (%)
Free or labile complexed, rapidly exchangeable	removed after 1 h	40	65	27	48	5	17	20	1	6
Complexed, slowly exchangeable	removed after 24 h, excluding the previous fraction	39	13	20	12	3	6	38	3	16
Inert or stable complexed, not exchangeable	not removed after 24 h	21	22	53	40	92	77	42	96	78

synthetic solution (SA). In all other experiments, extraction is observed instead of adsorption. The release from the kaolinite is particularly significant in the case of Cu (at the highest kaolinite concentration release from the kaolinite is 1540, 1770 and 2510% of the initial dissolved metal for LA, LM2 and LM1, respectively). Even though to a lower extent, Cd is also extracted from the solid phase, particularly in LM1 tests. It has to be noted that the experimental behaviour is quite irregular for LA and LM2 tests, at the lower kaolinite concentrations. As a matter of fact, Cd is initially sorbed and then extracted as the kaolinite concentration increases. This behaviour cannot be explained in terms of repartition of only one species among the two phases.

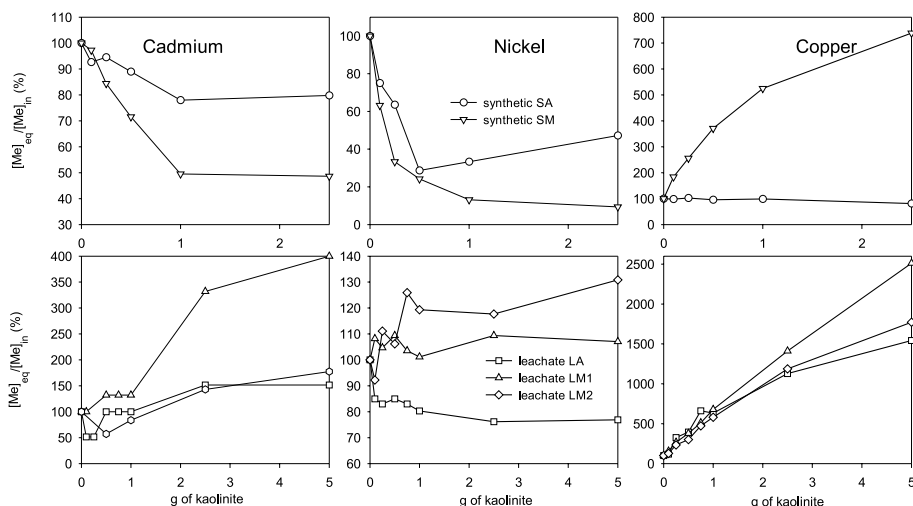
## Conclusions

Speciation in the liquid phase plays a significant role in determining the extent of the interaction between heavy metals and soil or soil constituents (such as clays). This is particularly relevant in the case of landfill leachates, where the variability and the complexity of the composition can drastically change the mobility of heavy metals during percolation through soils.

The experimental results presented in this paper have shown that the use of “broad parameters”, such as COD, DOC, pH and ionic strength, are not able to give information about the complexing capacity of actual leachates, which in turn is related to metal mobility. The exchange-based procedure has clearly indicated how leachates with significantly lower organic content bind the selected metals in complexes which are not completely removed by the strong chelating groups of the Chelex100. This behaviour seems to be related to the increase of organic compounds with molecular weight greater than 1000 Daltons. Moreover, the comparison with synthetic solutions has shown how the compounds usually adopted to model the organic fraction in leachates (such as acetate, glycine and salicylic acid) are not able to simulate the results obtained with the actual leachates. The practical implications of these results have been showed in the kaolinite batch tests. With respect to the synthetic solution, in leachate matrices the heavy metals are often extracted by the kaolinite instead of sorbed and this was particularly relevant in the case of Cu.

**Table 4** Experimental results of leachate ultrafiltration tests. Results are expressed as percentage respect to total dissolved concentration

Leachate	Parameter (%)	MWCO<1000	MWCO from 1000 to 10000	MWCO>10000
LA	Cd	100	0	0
	Ni	66	30	4
	Cu	57	43	0
	COD	91	5	4
	DOC	92	5	3
	phenolic substances	100	0	0
LM1	Cd	59	26	15
	Ni	34	41	25
	Cu	45	50	5
	COD	61	24	15
	DOC	44	42	14
	phenolic substances	25	37	38
LM2	Cd	22	25	53
	Ni	40	34	26
	Cu	24	48	28
	COD	56	29	15
	DOC	23	38	39
	phenolic substances	27	30	43



**Figure 2** Experimental results of kaolinite batch tests in the different matrices

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