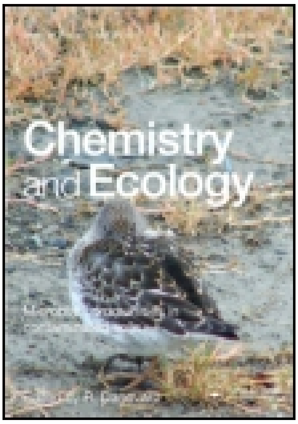

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Use of different chelating agents for heavy metal extraction from contaminated harbour sediment

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To cite this article: Luca Di Palma, Ornella Gonzini & Roberta Mecozzi (2011): Use of different chelating agents for heavy metal extraction from contaminated harbour sediment, Chemistry and Ecology, 27:S1, 97-106

To link to this article: http://dx.doi.org/10.1080/02757540.2010.534084

Chemistry and Ecology
Vol. 27, Supplement, February 2011, 97–106

Use of different chelating agents for heavy metal extraction from contaminated harbour sediment

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(*Received 1 December 2009; final version received 19 October 2010*)

This study presents the results of laboratory-scale experimental tests of contaminant extraction from marine sediment slurries. The sediment was collected in a harbour situated in a high-density industrial area, characterised by a high pollution level of heavy metals. The objective of this study was to investigate the effectiveness of selected chelating agents (rhamnolipids, EDDS, EDTA and citric acid) in heavy metal removal from contaminated sediments. To this aim, contamination of the sediment used in this experiment was artificially increased to reach final values of 1250 $\mathrm{mg \cdot kg^{-1}}$ Cu and 2026 $\mathrm{mg \cdot kg^{-1}}$ Pb. The investigated parameters during the washing tests were chelant concentration and overall washing time. To evaluate the sediment characteristics, COD and acid digestion were performed, whereas total organic carbon and heavy metal concentration were determined on the solutions extracted. The results show that the use of EDDS and EDTA gave good extraction efficiencies (up to 95%), unlike the lower removal rates achieved by using citric acid and rhamnolipids. In addition, major cations, mainly Fe and Ca, were found to be strong competitors with the target metals for metal–ligand complex formation.

Keywords: sediment remediation; heavy metal; washing; additives; rhamnolipids

1. Introduction

For centuries, heavy metals, along with other metals and minerals, have been released from their natural chemical compounds through industrial activities and processes into surface waters. As a consequence, their spread in aquatic systems and sediments has been found to increase over time. Harbour sediments are often rich in heavy metals; because heavy metals are not subjected to degradation, they can easily be suspended or dissolved by surface waters, thus becoming available to plankton, nekton and benthic filter and deposit feeders [1], finally entering the food chain [2].

The technologies used for sediment remediation are similar to those widely adopted for soil remediation, including thermal treatment, physical separation, solidification/stabilisation and washing [3,4]. In *ex situ* washing technology [5], undesirable contaminants in the sediments are removed by dissolving or suspending them in an aqueous solution of a chelating agent [6,7].

Chelating agents are ligands that form a complex with the substrate; although the bonds may be any combination of coordination or ionic bonds, chelating agents have the ability to solubilise

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ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540.2010.534084
http://www.informaworld.com

metals ions. Synthetic chelating agents, such as ethylenediaminetetraacetic acid (EDTA), have been widely investigated as efficient extracting agents to enhance performance in soil/sediments washing [8–12]. Chelating agents have the potential to perturb the natural speciation of metals and influence metal bioavailability. The largest concern, however, is that many chelating agents are only slowly biodegradable and are therefore rather persistent in the environment [13]. The main factor that should be considered when selective extracting agents are used include effectiveness, cost, public and regulatory perception, but also biodegradability and degradation products, toxicity to humans, plants and animals, and ability to recycle.

As an alternative to synthetic ligands, more biologically produced (biosurfactants) biodegradable substances have been tested in laboratory-scale applications, for example, citric acid and S,S'-ethylenediaminedisuccinic acid (EDDS), a structural isomer of EDTA containing two chiral carbon atoms resulting in the existence of three optical isomers, [S,S]-EDDS, [R,R]-EDDS and [R,S]-EDDS [14].

Biosurfactants are biologically produced by yeast or bacteria from various substrates, including wastes. They generally consist of several functional groups, such as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate compounds. A group of biosurfactants that has been studied extensively in the recent years are rhamnolipids, produced by *Pseudomonas aeruginosa* [15–17].

In this study, the use of rhamnolipids was compared with EDTA, citric acid and EDDS, for chelant-assisted washing of a sediment sample collected at an Italian harbour. The objective of this study was to evaluate the effectiveness of rhamnolipids in copper and lead removal from the sediment, based on the selectivity of rhamnolipids with respect to these metals. According to Neilson et al. [18] and Ochoa-Loza et al. [19], the relative complex stability of the metal–ligand complex for the investigated metals is in the order: for rhamnolipids, Cu > Pb > Fe(III) > Ca; for citric acid, Fe(III) > Pb Cu > Ca; and for EDDS and EDTA, Fe(III) > Cu > Pb > Ca, on the basis of the stability constants values reported in the literature [20,21].

2. Materials and methods

The sediment was collected in a harbour situated in a high-density industrial area located in the south of Italy, characterised by a high level of metal pollution. The contamination of the sediment used in this experimentation was increased artificially to reach final values of $1250 \pm 50\,\mathrm{mg \cdot kg^{-1}}$ of Cu and $2026 \pm 70\,\mathrm{mg \cdot kg^{-1}}$ of Pb. Table 1 reports selected characteristics of the sediment used. Artificial contamination was carried out in order to obtain a concentration approximately twice the Italian regulation limit for copper and lead at an industrial site ($600\,\mathrm{mg\ Cu \cdot kg^{-1}}$, $1000\,\mathrm{mg\ Pb \cdot kg^{-1}}$ soil) [22]. After 60 days, the samples were subjected to laboratory-scale washing experiments using EDTA in the form of disodium salt, citric acid in the form of trisodium salt, EDDS in the form of $C_{10}H_{13}N_2Na_3O_8$ and rhamnolipids (Rh) in the form of the product BioRecOil (4% w/v solution, Jeneil Biosurfactant CO., LLC) [16]. The washing tests were performed by varying the additive concentration, at a constant 10 : 1 v/w solution-to-soil ratio (30 mL of washing solution $\cdot 3\,\mathrm{g^{-1}}$ sediments). Blank tests with distilled water were performed to evaluate the removal of contaminants only by physical mixing. Two selected surfactant concentrations were used, equal to the total molar amount of Pb and Cu, tests 1 : 1, or Pb, Cu and extractable Fe, tests 1 : 1 (Fe), respectively. In order to determine the maximum value of Fe that each additive can extract from the sediment sample (extractable Fe), a preliminary 24 h washing with a 0.1 M solution of EDTA was carried out. Extractable Al and Ca were also determined in the same test. For rhamnolipids only, a further test at a molar ratio of 2.31 : 1 with respect to the total amount of Pb and Cu was also performed, according to Mulligan [15].

Table 1. Selected sediment properties.

Properties	Value
Water content (%)	38.41
Bulk density (kg·dm^{-3})	1.58
pH	6.6
Particle size distribution (%)	
>2 mm	5.39
$0.063 < x < 2$ mm	43.43
<0.063 mm	51.18
Metals (mg·kg^{-1})	
Fe	27,481 ± 320
Fe extractable	1532.8 ± 80
Cu	50.2 ± 4.5
Pb	26.9 ± 3.0
Al	12,300 ± 210
Al extractable	20.02 ± 5.0
Ca extractable	33.07 ± 8.5

Samples were taken after 20, 40 and 60 min, and 2, 6, 24, 48 and 120 h of mixing in an orbital shaker (200 rpm) and then filtered (0.45 μm). The filtrates were then analysed to determine metal concentration by atomic absorption spectrometry, using a Philips PU 9200 instrument, after an acid digestion, using the EPA3050B method [23]. Metal removal was determined based on the initial metal content in the sediment and all results are reported as %wt metal removal. The dissolved organic carbon (DOC) was also determined using a Shimadzu TOC-5000 analyser. pH was measured after mixing 10 g of soil samples with 25 mL of a 0.01 M solution of $CaCl_2$.

To evaluate the competitive mechanisms among the cations, two parameters were introduced and calculated after 24, 48 and 120 h of mixing: the specific removal efficiency (SRE) for Pb and Cu, defined according to the equation:

$$SRE = 100\frac{\sum(\mathrm{Pb} + \mathrm{Cu})}{\sum(\mathrm{Pb} + \mathrm{Cu} + \mathrm{Fe} + \mathrm{Ca})}, \tag{1}$$

and the specific utilisation rate (SUR), defined, assuming an equimolar reaction in complex formation [24], according the equation:

$$SUR = 100\frac{\sum(\mathrm{Pb} + \mathrm{Cu})}{\mathrm{M}}, \tag{2}$$

where M is the total moles of additives added in the washing vessel.

In the definition of SRE, mainly Ca and Fe were considered as competitive metals, because negligible amounts of Al and Mg were always detected in the washing solutions.

Sequential extractions according to the Tessier procedure [25,26] to determine metal distribution among the fractions exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter and residual, were also performed.

3. Results and discussion

3.1. *Extraction kinetic*

The results of preliminary blank tests showed that no Pb and a negligible amount of Cu (0.47% wt) were extracted simply by washing the sediment with distilled water during 24 h. This extraction can attributed to the solubilisation of organic matter from the sediment; the final DOC of the extracted solution was 22 mg·L^{-1}.

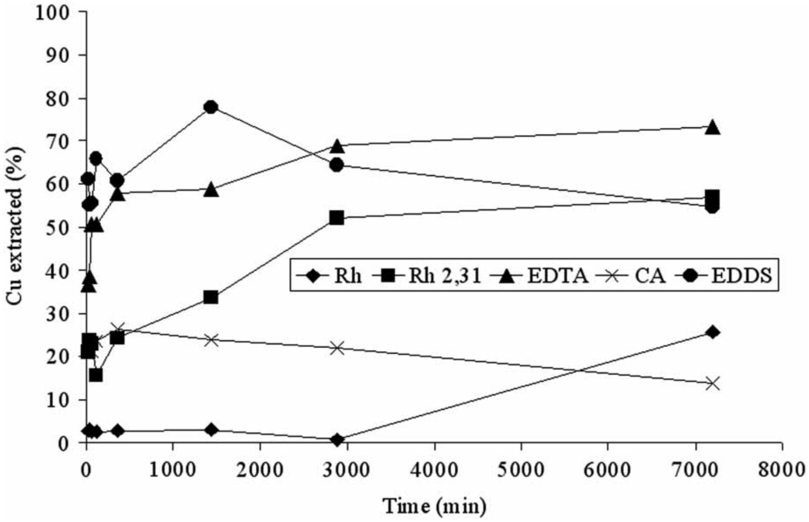

Figure 1. Cu removal for (Pb + Cu) : additive. 1 : 1 molar ratio.

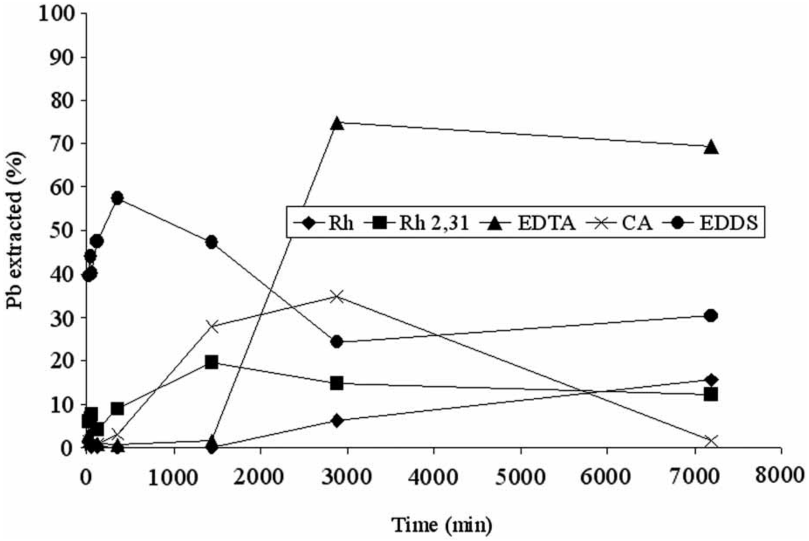

Figure 2. Pb removal for (Pb + Cu) : additive. 1 : 1 molar ratio.

This is in accordance with the results of several studies that previously assessed the stability of Cu, Pb and Fe adsorbed onto soil or sediment over a wide range of pH values [27,28].

Figures 1–4 show the results of the extraction tests. Each test was performed in triplicate and average values are reported in the figures. The average standard deviation calculated was in the range 2.2–4.5%.

As shown by the results reported in Figure 1, Cu mobilisation started immediately in the test where EDTA or EDDS were used. However, for EDTA and EDDS, different shapes were seen for the the metal concentration versus time curves; whereas EDTA showed a progressive increase in Cu mobilisation over time until the end of the test, EDDS showed a maximum after 24 h of mixing (corresponding to ~78% of Cu extraction). The particular shape of the curve for the extraction

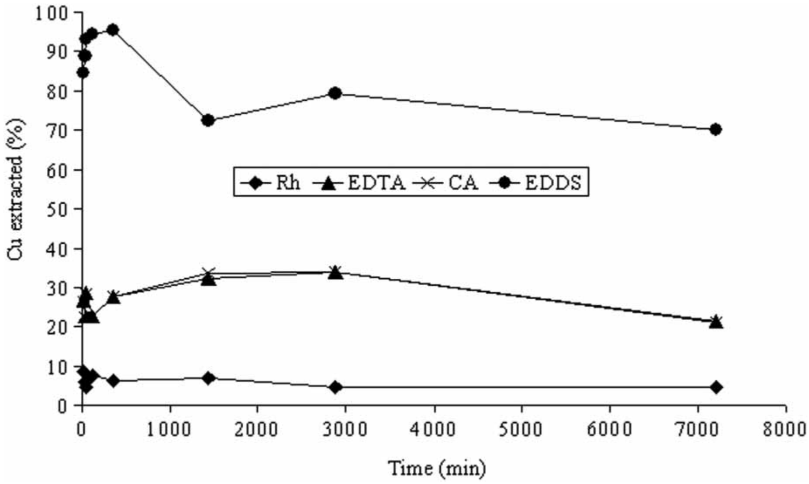

Figure 3. Cu removal for (Pb+Cu+Fe) : additive. 1 : 1 molar ratio.

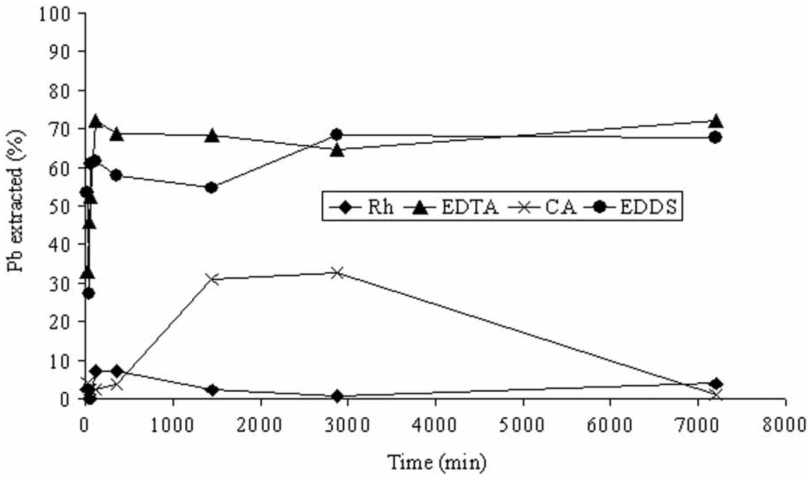

Figure 4. Pb removal for (Pb+Cu+Fe) : additive. 1 : 1 molar ratio.

with EDTA is quite similar to that found by other researchers at different ligand concentrations [5]. For both the tests performed with rhamnolipids were and citric acid, conversely, low extraction efficiencies were calculated. When rhamnolipids were used, the extraction efficiency always increased over time, up to a maximum of 26% after 120 h of mixing in the equimolar test, and 57% after 120 h in the test performed with a rhamnolipid versus metal ratio of 2.31. When citric acid was used, the Cu extraction efficiency showed a progressive decreasing behaviour until the end of the test. The affinity order observed at the end of the tests was in agreement with the order expected on the basis of the complex stability constants order for Cu: EDTA > EDDS > Rh > CA [18,20,21].

As shown in Figure 2, the initial Pb removal efficiency was generally quite low for all the additives used with respect to Cu. In addition, except for EDDS, Pb extraction started slowly, as a result of the competitive mechanisms among Pb and the other metals present in the sediment (mainly Al, Ca, Cu and Fe) that occurred during mixing [20,27,29]. Also in this case, the EDDS showed a Pb removal extraction peak of 57% after 6 h of mixing followed by a decreasing trend, whereas EDTA showed an increasing extraction until a Pb removal extraction peak of 75% after

48 h of mixing. A similar behaviour was shown by rhamnolipids at 2.31 : 1 molar ratio (the maximum Pb extraction efficiency was about 20% after 24 h of mixing), while, on the contrary, Pb extraction by EDTA, after the initial increasing phase, from 24 to 48 h of mixing, quickly rised up to 70%, and this value was about the same calculated at the end of the tests (after 120 h of mixing). For the others additives the maximum removal rate was of 20% for Rh at 2.31 molar ratio, of 15.5% for the 1 : 1 molar ratio and of 35% for citric acid, respectively. Citric acid showed a particular behaviour; during the first 48 h of mixing an increasing Pb extraction was observed, followed by a sudden reduction in the Pb concentration in the solution. This behaviour is in accordance with results obtained in another study [29], in which the desorption of pollutants by citric acid in batch tests was found to be optimal over a quite narrow pH range (6–7), and quickly decrease in alkaline conditions, as a consequence of the strong interaction of citrate with Fe- and Al-coatings of the sand surface (the average pH measured in the tests performed using citric acid was ∼7.5). The Pb initially extracted was then replaced by Fe in the complexes with citric acid, thus becoming available for precipitation as hydroxide, as observed in other studies, where Pb extraction from contaminated soils was found to be strongly pH dependent, and suddenly decreased at pH 6–8 [20] Also, in this case, the affinity order observed at the end of the tests was in agreement with the expected complex stability constants for Pb: EDTA > EDDS > Rh > CA [18,20,21].

As observed in other studies [21,27,30,31], the removal rate increased with increasing additive concentration in each test. As shown in Figure 3, in the presence of an excess of additive with respect to the target metals (Cu and Pb), all the additives, with the exception of rhamnolipids, showed a slight reduction in Cu removal efficiency starting from 2 days of mixing. This can be attributed to the development of competitive mechanisms among copper and iron ions in solution, which was not expected when rhamnolipids were used. As regards the extraction of Pb in tests with an excess of additives, EDTA and EDDS showed the higher removal rate, as shown in Figure 4, with a peak of ∼72 and 69%, respectively. A lower extraction by both citric acid and rhamnolipids was observed: they showed a maximum Pb extraction efficiency of 33% after 48 h of mixing, and of 7.4% after 6 h, respectively. Also, in this case, the order of the extraction efficiencies calculated at the end was in accordance with the the complex stability constants (EDTA > EDDS > > Rh > CA) [18,20,21].

3.2. *Competitive effects and mass balances*

The SRE values calculated for each experimental tests after 24, 48 and 120 h of mixing are reported in Table 2.

Table 2. SRE (%) values for each test at 24, 48 and 120 h of washing.

		SRE (%)		
Test	Additive concentration	24 h	48 h	120 h
1	Rh 1:1	39.4	8.0	31.9
2	Rh 2.31:1	48.4	60.9	58.9
3	Rh 1:1 (Fe)	16.4	10.6	31.0
4	EDTA 1:1	82.5	86.1	72.6
5	EDTA 1:1 (Fe)	69.1	66.0	57.0
6	CA 1:1	59.7	56.3	29.2
7	CA 1:1 (Fe)	72.7	69.4	33.7
8	EDDS 1:1	71.7	67.3	62.9
9	EDDS 1:1 (Fe)	67.5	66.8	60.5

Notes: SRE, specific removal efficiency; Rh, rhamnolipids; EDTA, ethylenediaminetetraacetic acid; CA, citric acid; EEDS, *S*,*S*′-ethylenediaminedisuccinic acid.

The SRE is a measure of the selectivity of the additive towards the target metals: higher SRE values corresponded to higher amounts of Pb and Cu extracted from the sediment.

Results show that the calculated SRE values followed a trend dependant upon the additive used in the experiments. As regards rhamnolipids, in both the tests performed at equimolar concentration with respect to Cu and Pb or Cu, Pb and Fe, the calculated SRE showed an initial decrease over time, followed by a further increase. This indicates that at higher contact times between the solution and the sediment, equilibrium conditions were approached. As would be expected on the basis of the affinity scale for rhamnolipids, an increase in washing time corresponded to higher amounts of Cu and Pb in the contact solution, as a consequence of the cation-exchange reactions between Fe and Cu or Pb complexes [27].

As regards EDTA, the higher affinity for Fe(III) is shown by the decrease in SRE during time; nevertheless, despite the increase in Fe removal, only a slight decrease in Cu removal (Figure 1) and Pb removal (Figure 4) was observed. This indicates that equilibrium conditions were still not attained at the end of the tests. Moreover, in the case of EDTA, the strong acidic conditions observed in the batch test (the initial pH values were 4.80 in test 4 and 4.70 in test 5, respectively), induced a high initial calcium solubilisation, that was competitive with Pb and Cu extraction. In addition, according to Kim and Ong [32], under acidic conditions ($pH < 6.5$) iron in soil was found to strongly compete with Pb for EDTA ligand sites.

A decrease in SRE over time was also observed in the tests when citric acid or EDDS were used, although alkaline conditions were established in these tests: the calculated SRE values were lower with respect to the corresponding values calculated for EDTA.

All the observed removal trends were, however, in a good agreement with the order of stability constants mentioned previously.

Table 3 reports the SUR values calculated in the tests. This parameter indicates the percentage of additive actually bound to the target metals (Pb and Cu). This parameter can be used to evaluate the extent of undesired additive consumption in the remediation operations.

As shown in Table 3, when rhamnolipids were used, the calculated SUR value was generally lower than for the other additives, with the exception of citric acid, thus resulting in the need for a higher rhamnolipid dose to achieve the same metal-extraction efficiency as EDTA or EDDS. However, in view of a remediation process involving use of this additive, it can be assessed that this may not be a problem, owing to the higher biodegradability of rhamnolipids in the environment with respect to common synthetic additives such as EDTA or EDDS [15,18]. Table 3 also shows the mass balance for the additives in each test, assuming that the free additive corresponded to the difference between the total number of moles of additives added in each test and the total number of moles of Ca, Cu, Fe and Pb mobilised.

Table 3. Additives mass balance.

		SUR			Total additive combined			Free additive		
Test	Additive concentration	24 h	48 h	120 h	24 h	48 h	120 h	24 h	48 h	120 h
1	Rh 1:1	2.1	2.6	22.4	5.2	32.4	70.0	94.8	67.6	29.9
2	Rh 2.31:1	12.6	17.2	18.3	25.9	28.1	31.0	74.0	71.8	68.9
3	Rh 1:1 (Fe)	4.0	2.5	11.4	24.3	23.4	36.8	75.7	76.6	63.2
4	EDTA 1:1	39.9	70.8	72.0	48.3	82.2	99.2	51.7	17.8	0.8
5	EDTA 1:1 (Fe)	31.4	31.3	27.2	45.4	47.4	47.6	54.5	52.5	52.4
6	CA 1:1	25.2	26.3	9.7	42.2	46.7	33.2	57.8	53.3	66.8
7	CA 1:1 (Fe)	23.2	23.7	10.3	31.9	34.2	30.6	68.1	65.8	69.4
8	EDDS 1:1	67.7	51.2	46.6	97.9	76.0	84.2	2.1	23.9	15.8
9	EDDS 1:1 (Fe)	47.1	53.6	49.1	69.8	80.1	81.1	30.2	19.8	18.9

Notes: SUR, specific utilisation rate; Rh, rhamnolipids; EDTA, ethylenediaminetetraacetic acid; CA, citric acid; EEDS, *S,S′*-ethylenediaminedisuccinic acid.

Results show that increasing the amount of additive in the extractant solution, gave a higher amount of free additive at the end of the test. The strong decrease in Pb extractions observed in the tests performed using citric acid (tests 6 and 7) and discussed previously, resulted in a dramatic reduction in SUR from 48 and 120 h of mixing. It can be also noticed that at the end of test 4, almost all the EDTA was combined with the investigated cations.

3.3. *Evaluation of metal mobilisation through sequential extraction tests*

The final step of the study consisted of an investigation into metal mobilisation induced by each additives, in order to evaluate whether, as a consequence of the extraction, the target metals were also displaced towards more labile species. Tessier's method, based on a sequential extraction, was used to evaluate the distribution of Cu and Pb among five fractions: exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter and residual. Sequential extraction procedures offer the major advantage that, to a certain extent, they simulate various environmental conditions to which the sediment may be subjected; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment. Possible applications include evaluation of the effects of dredging operations and the prediction of trace metal behaviour in the water.

In Figures 5 and 6 the results of sequential extractions performed on the sediment samples subjected to 48 h washing treatment are shown. In particular, Figure 5 refers to Pb distribution, whereas Figure 6 refers to Cu distribution. The results show that, as a consequence of the extraction treatment, the amounts of Pb present in the exchangeable and organic fractions were lowered in all the tests performed. The remaining Pb was almost totally bound to the carbonate, oxides–hydroxides and, mainly, residual fractions. Becasuse this fin al fraction is the most stable, the Pb remaining after the extraction treatment is not expected to show significant bioavailability. Only in the tests performed using rhamnolipids was a non-negligible amount of both organic and exchangeable Pb detected in the sediment after the extraction. As regards the different behaviour shown by each additive, it can be noticed that only EDDS and, mainly, EDTA gave a strong mobilisation of Pb from the residue form to more labile species, as a consequence of the more acidic conditions established during washing with this additive [33,34].

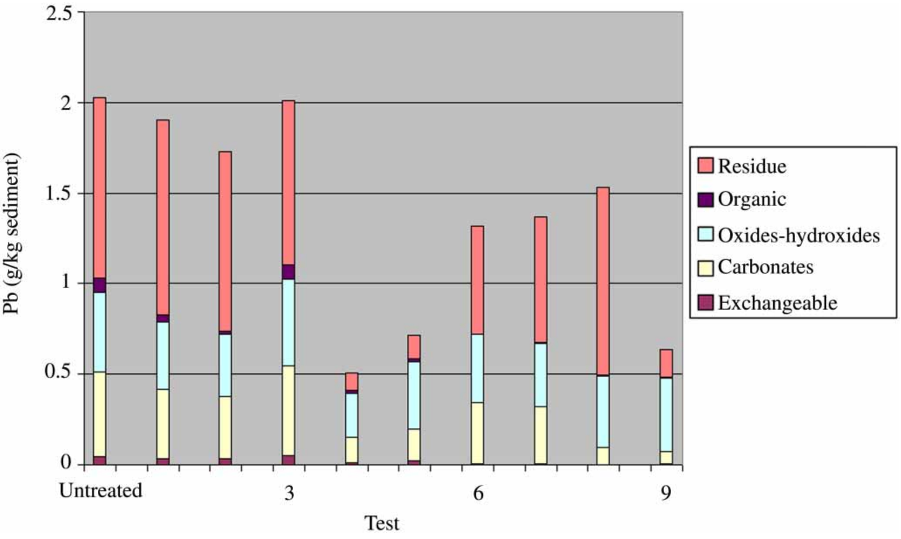

Figure 5. Sequential extraction tests for Pb.

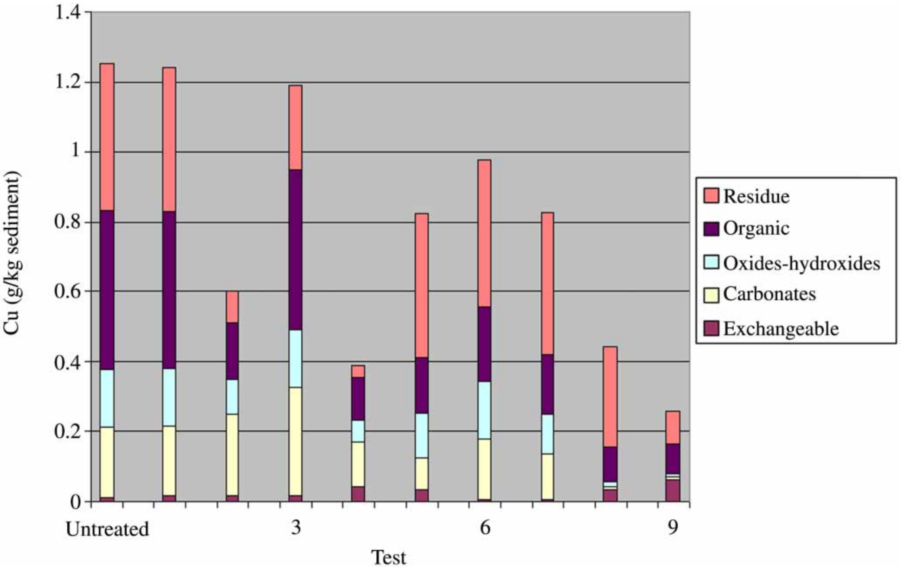

Figure 6. Sequential extraction tests for Cu.

Figure 6 shows that the initial Cu amount was present mainly in the organic and residue fractions: only the higher concentration of rhamnolipids allowed the mobilisation of Cu from the organic fraction, although lower than the mobilisation induced by the other additives. In the tests performed with EDTA and EDDS only, a substantial reduction in the Cu in the carbonate fractions of the sediment was observed. In the tests performed with citric acid the exchangeable form practically disappeared. By contrast, as a result of the treatment with EDDS, EDTA and, to a lesser extent, rhamnolipids, the total amount of Cu in the sediment was lowered, but an increase in the exchangeable fraction was observed, thus increasing Cu bioavailability [26,35].

4. Conclusions

The results of a study on 120 h of sediment washing using the four additives EDTA, EDDS, citric acid and rhamnolipids are reported and discussed. The study focused mainly on the comparing the selected additives for the removal of Pb and Cu, and the mechanisms possibly interfering with the extraction process, including competition in complex formation with sediment major cations.

On the basis of our experimental results, the efficiencies of rhamnolipids and citric acid were comparable, although rhamnolipids showed a higher calculated specific utilisation rate (SUR) and a similar calculated specific removal efficiency (SRE), due to its higher affinity for Cu and Pb with respect to competitive major cations. The use of EDDS and EDTA gave good extraction efficiencies (up to 70%) for both metals, but their action resulted in the extraction of large amounts of competitive cations, mainly Ca and Fe, and in the case of Cu, an increase in metal bioavailability.

References

[1] R.N. Jackson, D. Baird, and S. Els, *The effect of the heavy metals lead (Pb^{2+}) and zinc (Zn^{2+}) on the brood and larval development of the burrowing crustacean* Callianassa kraussi, Water SA. 31 (2005), pp. 107–116.

[2] E. His, R. Beiras, and M.N.L. Seaman, *The assessment of marine pollution- bioassays with bivalve embryos and larvae*, Adv. Mar. Biol. 38 (1999), pp. 371–378.

[3] S. McCready, G.F. Birch, and S.E. Taylor, *Extraction of heavy metals harbour sediments using 1 M HCl and 0.05 M EDTA and implications for sediments – quality guidelines*, Aust. J. Earth Sci. 50 (2003), pp. 249–255.

[4] R.W. Peters, *Chelant extraction of heavy metals from contaminated soils*, J. Hazard. Mater. B66 (1999), pp. 151–210.

[5] A. Moutsatsou, M. Gregou, D. Matsas, and V. Protonotarios, *Washing as a remediation technology applicable in soils heavily polluted by mining–metallurgical activities*, Chemosphere 63 (2006), pp. 1632–1640.

[6] R.S. Tejowulan and W.H. Hendershot, *Removal of trace metals from contaminated soils using EDTA incorporating resin trapping techniques*, Environ. Pollut. 103 (1998), pp. 135–142.

[7] B. Sun, F.J. Zhao, E. Lombi, and S.P. McGrath, *Leaching of heavy metals from contaminated soils using EDTA*, Environ. Pollut. 113 (2001), pp. 111–120.

[8] R.J. Abumaizar and E.H. Smith, *Heavy metal contaminants removal by soil washing*, J. Hazard. Mater. B70 (1999), pp. 71–85.

[9] C.N. Mulligan, R.N. Yong, and B.F. Gibbs, *Remediation technologies for metal-contaminated soils and groundwater: an evaluation*, Eng. Geol. 60 (2001), pp. 193–201.

[10] D. Fangueiro, A. Bermond, E. Santos, H. Carapuça, and A. Duarte, *Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA condition: search for optimal experimental conditions*, Anal. Chim. Acta 459 (2002), pp. 245–256.

[11] W. Zhang and I.M.C. Lo, *EDTA enhanced washing for remediation of Pb- and/or Zn-contaminated soils*, J. Environ. Eng. ASCE 132 (2006), pp. 1282–1288.

[12] C. Chaiyaraksa and N. Sriwiriyanuphap, *Batch washing of cadmium from soil and sludge by a mixture of* $Na_2S_2O_5$ *and* Na_2*-EDTA*, Chemosphere 56 (2004), pp. 1129–1135.

[13] B. Nowack, *Environmental chemistry of aminopolycarboxylate chelating agents*, Environ. Sci. Technol. 36 (2002), pp. 4009–4016.

[14] B. Dahrazma and C. Mulligan, *Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration*, Chemosphere 69 (2007), pp. 705–711.

[15] C. Mulligan, *Environmental applications for biosurfactants*, Environ. Pollut. 133 (2005), pp. 183–198.

[16] D.C. Herman, J.F. Artiola, and R.M. Miller, *Removal of cadmium, lead, and zinc from soil by a rhamnolipid biosurfactant*, Environ. Sci. Technol. 29 (1995), pp. 2280–2285.

[17] S. Wang and C.M. Mulligan, *rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil*, Water Air Soil Pollut. 157 (2004), pp. 315–330.

[18] J.W. Neilson, J.F. Artiola, and R.M. Maier, *Characterization of lead removal from contaminated soils by nontoxic soil-washing agents*, J. Environ. Qual. 32 (2003), pp. 899–908.

[19] F.J. Ochoa-Loza, J.F. Artiola, and R.M. Maier, *Stability constants for the complexation of various metals with a rhamnolipid biosurfactant*, J. Environ. Qual. 30 (2001), pp. 479–485.

[20] C. Kim, Y. Lee, and S.K. Ong, *Factors affecting EDTA extraction of lead from lead-contaminated soils*, Chemosphere 51 (2003), pp. 845–853.

[21] A. Polettini, R. Pomi, and E. Rolle, *The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment*, Chemosphere 66 (2007), pp. 866–877.

[22] Italian Environmental Regulation, *Environmental Standards Assessment*, G.U. n. 88, 14 April 2006.

[23] C. Liu and J.B. Evett, *Soil Properties, Testing, Measurement, and Evaluation*, 5th ed., Prentice-Hall, New York, 2002.

[24] W. Maketon, C.S. Zenner, and K.L. Ogden, *Removal efficiency and binding mechanisms of copper and copper–EDTA complexes using polyethyleneimine*, Environ. Sci. Technol. 42(6) (2008), pp. 2124–2129.

[25] S. Vilar, A. Gutierrez, J. Antezana, P. Carral, and A. Alvarez, *A comparative study of three different methods for the sequential extraction of heavy metals in soil*, Toxicol. Environ. Chem. 87 (2005), pp. 1–10.

[26] C.-S. Lee and M.-M. Kao, *Effects of extracting reagents and metal speciation on the removal of heavy metal contaminated soils by chemical extraction*, J. Environ. Sci. Health A 39(5) (2004), pp. 1233–1249.

[27] L. Di Palma and P. Ferrantelli, *Copper leaching from a sandy soil: mechanisms and parameters affecting EDTA extraction*, J. Hazard. Mater. B122 (2005), pp. 85–90.

[28] A. Polettini, R. Pomi, E. Rolle, D. Cermigna, L. De Propris, M. Gabellini, and A. Tornato, *A kinetic study of chelant assisted remediation of contaminated dredged sediments*, J. Hazard. Mater. B137 (2006), pp. 1458–1465.

[29] A. Voegelin, K. Barmettler, and R. Kretzschmar, *Heavy metal release from contaminated soils: comparison of column leaching and batch extraction results*, J. Environ. Qual. 32 (2003), pp. 865–875.

[30] C. Kantar and B.D. Honeyman, *Citric acid enhanced remediation of soils contaminated with uranium by soil flushing and soil washing*, J. Environ. Eng. ASCE 132 (2006), pp. 247–255.

[31] N. Manouchehri, S. Besancon, and A. Bermond, *Major and trace metal extraction from soil by EDTA: equilibrium and kinetic studies*, Anal. Chim. Acta 559 (2006), pp. 105–112.

[32] C. Kim and S.-K. Ong, *Effects of amorphous iron on extraction of lead-contaminated soil with EDTA*, Pract Period. Hazard. Toxic Radioactive Waste Manage. 1 (2000), pp. 16–23.

[33] K. Vaxevanidou, N. Papassiopi, and I. Paspaliaris, *Removal of heavy metals and arsenic from contaminated soils using bioremediation and chelant extraction techniques*, Chemosphere 70 (2008), pp. 1329–1337.

[34] A. Barona, B. Liao, Q. Zeng, P. Qin, and S. Khan, *Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedure*, Environ. Pollut. 113 (2001), p. 79.

[35] M. Lei, B. Liao, Q. Zeng, P. Qin, and S. Khan, *Fraction distributions of lead, cadmium, copper, and zinc in metal-contaminated soil before and after extraction with disodium ethylenediaminetetraacetic acid*, Commun. Soil Sci. Plant Anal. 39 (13–14) (2008), pp. 1963–1978.