Reuse of a treated red mud bauxite waste: studies on environmental compatibility

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Abstract

Red mud is the major solid waste produced in the process of alumina extraction from bauxite (Bayer process). Environmental "compatibility" of a treated red mud was studied in order to evaluate its possible recycling in environmental compartments. The leaching test requested by the Italian law on treated solid waste to be "re-introduced in the environment" was performed on this material. Moreover, in order to better evaluate the environmental compatibility, three different types of eco-toxicological tests were applied (Microtox^{TM} test, ASTM microalgae toxicity test and sea urchin embryo toxicity test). These "chemical" and eco-toxicological tests gave encouraging results. The possibility to use this material for treating contaminated waters and soils was evaluated, again with particular attention to the Italian regulatory system, through experiments on the treated red mud metal trapping ability and on the subsequent release of trapped metals, at low pH conditions. The treated red mud showed a general high metal trapping capacity and the release at low pH was generally low.
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1. Introduction

Bauxite contains aluminium hydroxides in large percentage and is therefore largely used for the production of alumina (Al_2O_3) through the Bayer chemical process, which is based on the reaction with sodium hydroxide under heat and pressure. The overall refining of bauxite to alumina through the Bayer process implies the production of a large quantity of a solid waste called "red mud" (the production of 1 t of alumina generally results in the creation of 1–1.5 t of red mud). This residue is characterized by very high alkalinity and its major constituents are *crystalline hematite* (Fe_2O_3), *boehmite* (γ-AlOOH), *quartz* (SiO_2), *sodalite* ($Na_4Al_3Si_3O_{12}Cl$) and *gypsum* ($CaSO_4 \cdot 2H_2O$), with a minor presence of *calcite* ($CaCO_3$), *whewellite* ($CaC_2O_4 \cdot H_2O$) and *gibbsite* $Al(OH)_3$. The red mud probably represents the main problem in the alumina production and its disposal constitutes an environ-

mental problem, most of all for its caustic nature. The red mud can be stored in impoundments but its reuse after adequate treatments for different purposes has been studied in several countries [1–8].

The storage solution is economically problematic due to the costs of the realization and maintenance of containment structures and implies environmental problems for the storage site (huge areas), most of all due to the mud caustic nature that could pose a risk for all living organisms. The neutralization of red mud and its adequate treatment to allow its reuse seem to be the realistically convenient steps for the disposal of this industrial residue. There are several works on red mud reuse, for example, as acidic amender or bottom sealant in disposal sites construction [1,2], as catalyst in hydrodechlorination of tetrachloroethylene [3], for iron and titanium oxides extraction [4], for the production of ceramic glazes [5–7]. The most interesting applications of red mud are however in the environmental field, after adequate neutralization, for the remediation of contaminated sites and treatment of contaminated liquid waste. With this principal aim, sev-

eral studies were carried out on the metal trapping and acid neutralisation capacities of red mud both on synthetic and on real samples [8–11]. Biological effects of red mud reuse in soil and sediment samples and in field applications were also studied [12–15].

In particular, the Virotec International Ltd. (Australia) optimised the process of red mud treatment with seawater and patented this technology and several products with the name Bauxsol[TM]. The patented treatment, as described in detail elsewhere [16–18], is based on the seawater treatment which allows the conversion of "soluble alkalinity" (above all from sodium hydroxide) into low soluble minerals (essentially Ca and Mg hydroxides, carbonates and hydrocarbonates), thus reducing the resulting red mud pH (from pH > 13 down to pH < 9). Further treatment of the material, such as acid treatment, heat treatment, addition of ferric sulphates or aluminium sulphates have been studied by Genç-Fuhrman et al. in order to evaluate the enhancement of particular properties of the final product (such as capability to trap arsenic) [17,18]. The chemical and mineralogical characterization of red mud and neutralized red mud has been carried out by Genç-Fuhrman et al. [16].

There are different possible approaches finalised to the investigation of the environmental compatibility of a waste material, in order to evaluate its possible reuse. The most general approach implies the application of standardized leaching tests, such as pH-stat test (under standardization by Working Group 6 of CEN-TC 292) [19], "Up-flow" percolation test (under standardization by Working Group 6 of CEN-TC 292 as prEN 14405) [19], Shake test (standardized by CEN as EN 12457-3) [19], Toxicity Characteristic Leaching Procedure (TCLP by EPA) [20]. These leaching procedures are commonly applied in different countries and are characterized by significant differences in parameters such as L/S ratio, pH conditions, contact time, stirring method [19,20].

In this paper, the possibility to reuse treated red mud for treating contaminated waters and soils was evaluated; in particular, the conformity of the treated red mud to the Italian law which defines the required characteristics of treated solid waste for any kind of free reuse in the environment was checked. The Italian leaching test for waste reuse evaluation specified in the Ministerial Decree of 05/02/1998 [21] was carried out for the evaluation of metal leaching behaviour; this test applies natural pH conditions and is performed during an overall time of 16 days. Compared to the previously mentioned leaching tests, this test is much closer to the percolation and shake European leaching test (in which no pH control is foreseen) than to the other ones (where the pH is under control and maintained at a fixed value).

Moreover, in order to evaluate the environmental compatibility of this material, three different eco-toxicological tests were applied and its pH reaction grade was measured too. Finally, the possibility of application of this material in environmental pollution remediation was evaluated according to

the general approach already used in [10,13,22]. Therefore, metal trapping tests were carried out from different types of metal enriched solutions and, successively, the release of trapped metal at low pH conditions from the residue of metal trapping tests was evaluated.

2. Materials and methods

All chemicals used were of analytical reagent grade. All labware used in the experiments was soaked in diluted HNO_3 overnight and then rinsed with double deionised water.

All eco-toxicological experiments were run at least in quadruplicate and the outcomes were evaluated statistically using the Student's t-test. All the other experiments were performed in duplicate and the mean values were considered. A procedure blank was always evaluated. Analyses were performed using a Perkin Elmer ICP-MS ELAN 6100 for metals (Rh was used as internal standard) and a DIONEX DX120 Ion Chromatograph for anions.

2.1. Sample description

The treated red mud studied in this work was produced, through the technology patented by Virotec, consisting of a seawater treatment for pH neutralization, in Eurallumina plants, located in Sardinia (Italy). After arrival in the laboratory, the material has been dried at room temperature and sieved at 2 mm. A part of the material was further washed with deionised water, at a L/S ratio = 20 (v/dw) for 1 h under agitation, and then separated by centrifugation and dried at room temperature.

The elemental composition of the treated red mud considered in this work, had already been evaluated in a previous work, analysing several samples after digestion in microwave system with HNO_3, $HClO_4$ and HF [23]. The average concentration in the material of the elements considered in this paper are the following: $Cd \sim 0.7\,mg\,kg^{-1}$, $As \sim 20\,mg\,kg^{-1}$, $Ni \sim 25\,mg\,kg^{-1}$, $Zn \sim 25\,mg\,kg^{-1}$, $Pb \sim 50\,mg\,kg^{-1}$, $Cu \sim 50\,mg\,kg^{-1}$, $Cr \sim 300\,mg\,kg^{-1}$ and $V \sim 300\,mg\,kg^{-1}$.

2.2. pH reaction grade

The pH reaction grade of the treated red mud was measured following the Italian official methods for soil analyses [24]. In agreement with other international standard methods (APHA, ASTM, ISO, etc.), the Italian applied official method foresees the pH determination by potenziometry both after addition to the material of deionised water, and after addition of a 0.01 M $CaCl_2$ solution; values are more correlated to saturation grade of system in the latter case. The L/S ratio applied is 2.5 and the pH was measured after 2 h of soil–liquid contact.

2.3. Leaching test

Metal leaching behaviour was studied applying the leaching procedure indicated in the Italian Ministerial Decree of 05/02/1998, that also defines the threshold values in the leachate [21]. The test envisages the addition of deionised water to the solid sample at the L/S ratio of 5 for eight times, at a predetermined time (after 2, 8, 24, 48, 72, 102, 168 and 384 h), the supernatant is separated from the solid residue by filtration (45 μm) and a new portion of deionised water is added. All filtered leachates were separately stored at +4 °C and analysed all together at the end of the test. The results of the test are given by the sum of the values obtained in the eight separate leachates.

2.4. Eco-toxicological tests

Three eco-toxicological tests were applied according to Microtox^{TM} test [25], American Society for Testing and Materials (ASTM) toxicity test with microalgae [26] and ASTM toxicity test with sea urchin [27], respectively. In all the three cases, the treated red mud was suspended in filtered salt water (FSW) at five different concentrations, ranging from 0.1 to 2% (dw/v). The same FSW was used as a negative control.

The Microtox^{TM} test is based on the measurement of the reduction in bioluminescence of the marine bacterium *Vibrio fischeri*; this test is widely used to characterize the acute toxicity of a pollutant. The inhibition of bacterial light emission was measured at 15 °C after 5, 15 and 30 min; the Microtox^{TM} data acquisition was used to calculate the effect percentage [25]. The ASTM toxicity test with microalgae is based on the measurement of the inhibition of growth of microalga flagellata *Dunaliella tertiolecta*; this is an approach to assess the chronic toxicity of a substance. The percentage of effect after 96 h (either stimulation or inhibition) was calculated based on the following formula: effect (%) = $((N_c - N_s)/N_c) \times 100$, where N_c and N_s are the final cell numbers in the control and in the sample [26]. The ASTM sea urchin toxicity test is based on the measurement of embryo growth inhibition in the sea urchin *Sphaeroechinus granularis*, when exposed to toxic substances; in this work, the results of embryonic development were determined on pluteus larvae after 72 h of incubation. Larvae were classified as normal pluteui (N) or retarded (R, with their dimension < 50% N) or malformed (P1) and larvae incapable of attaining the pluteus stages (P2) [27].

2.5. Metal trapping studies

Metal trapping capacity was evaluated using different mono- and multielement solutions prepared with deionised water and Ca (∼500 mg L^{-1}) and Mg (∼300 mg L^{-1}) enriched water. The concentration levels of the elements in the considered solutions were the following: As 500 μg L^{-1}, Cd 450 μg L^{-1}, Co 500 μg L^{-1}, Cu 550 μg L^{-1}, Mn 1200 μg L^{-1}, Ni 700 μg L^{-1} and Zn 4200 μg L^{-1}. These

concentration levels were chosen with the aim of reproducing a contaminated mine drainage water for As, Cd, Zn, Co and Ni (Mn and Cu concentration can be significantly higher in these kinds of contaminated waters, but in this test they were maintained at the same level of concentration as the other elements 500–1000 μg L^{-1}). Two solid/liquid ratios of treated red mud in solution were investigated: 2 g L^{-1} at a first stage and subsequently 10 g L^{-1}. The trapping kinetics was estimated measuring metals concentration in solution as a function of time.

2.6. Leaching experiments on "trapped" metals

For the leaching test at pH 5, treated red mud samples, previously used in metal trapping tests, were filtered and dried at room temperature. Then deionised water was added to the powder (L/S ratio = 8) and pH was maintained constant at a value of pH 5 by addition of diluted HNO$_3$. At the end of the predetermined contact periods (15 min and 1 h), metals concentration in the supernatant was determined.

3. Results and discussion

3.1. pH reaction grade

Almost neutral reaction grade was obtained for treated red mud: pH values around 7 were obtained both in the case of water addition (pH 7) and in the case of CaCl$_2$ 1 mol L^{-1} addition (pH 7.1). These values testify to the feasibility of using treated red mud in environmental compartments, without risk for living organisms, from a pH point of view.

3.2. Leaching test

According to Italian law, this test has to be performed on "not-hazardous" wastes before they can be recycled in the environment. Results obtained for treated red mud evidenced that some parameters were out of regulatory limits (Table 1): high anion values were mainly the consequence of the seawater treatment for the neutralization of red mud. In order to evaluate the possibility to decrease the values obtained for these parameters, an experiment was carried out also on treated red mud washed with deionised water. After 1 h of contact with a L/S ratio of 20 (v/dw), the resulting washing waters were analysed and all analytes content were found to be below the Italian regulation limits for wastewater discharge [28].

Although the washing treatment significantly produces salt removal (chloride concentration is below the regulatory limit in case of washed treated red mud, Table 1), fluorides and sulphates are still higher than limit values even if, from the environmental point of view, the possibility of a moderate and time limited leaching of these species should not generate serious risks. In each case (both unwashed and washed treated red mud) the pH value respects the regulatory limit. It is to be

Table 1
Results for the Italian leaching test [21]

Parameters	Unwashed treated red mud	Washed treated red mud	Threshold value
Arsenic ($\mu g\,L^{-1}$)	45 ± 4	24 ± 3	50
Beryllium ($\mu g\,L^{-1}$)	<0.5	<0.5	10
Cadmium ($\mu g\,L^{-1}$)	1.0 ± 0.1	0.6 ± 0.1	5
Cobalt ($\mu g\,L^{-1}$)	<0.5	<0.5	250
Chromium ($\mu g\,L^{-1}$)	16 ± 2	6 ± 1	50
Copper ($\mu g\,L^{-1}$)	51 ± 5	2.7 ± 0.5	50
Nickel ($\mu g\,L^{-1}$)	11 ± 1	1.5 ± 0.3	10
Lead ($\mu g\,L^{-1}$)	1.7 ± 0.2	5 ± 1	50
Vanadium ($\mu g\,L^{-1}$)	555 ± 50	485 ± 70	250
Zinc ($\mu g\,L^{-1}$)	<50	<50	3000
Chloride ($mg\,L^{-1}$)	4880 ± 450	128 ± 25	200
Fluoride ($mg\,L^{-1}$)	32 ± 3	16 ± 3	1.5
Nitrates ($mg\,L^{-1}$)	2.4 ± 0.2	n.d.	50
Sulphates ($mg\,L^{-1}$)	1140 ± 100	530 ± 100	250
pH range	6.4–10.5	8.2–10.2	5.5–12.0

stressed that, both in the case of washed and unwashed treated red mud, ~60% of extracted fluorides and sulphates is already released in the first three extractions (performed after 2, 8 and 24 h, respectively) and this percentage increases up to ~90% in the case of chlorides. This suggested to experiment further treatments (double water washing) at an industrial scale, subsequent to the seawater treatment. Encouraging results were obtained decreasing the sulphates value at $310 \pm 80\,mg\,L^{-1}$, reaching the conformity to the Italian leaching test. Further efforts are still necessary to reduce fluoride leaching.

For the metals, only vanadium requires some attention: measured concentrations are, in each case, higher than leaching test threshold limit, as a consequence of the relatively high vanadium mobility at neutral-alkaline pH [29] and of the high concentration in the red mud.

The leaching behaviour of a similar material has been evaluated in Australia by other authors for its classification as an inert solid [30] by the application of the TCLP test [20]. As shown in Table 2, all considered parameters were below the limits set by the New South Wales Regulation (Australia) for the classification as an inert solid. As evidenced in Table 3, there are relevant differences in the TCLP test and in the Italian leaching test, both in relation to the procedure (pH, time, L/S ratio, etc.) and in the choice of investigated parameters. In case of same parameters even the threshold values are different, probably in function of the different procedures applied; for most elements the limit values are one order of magnitude lower in the case of Italian regulation, where deionised water instead of acid is used as leachant.

Table 2
Toxicity characteristic leaching procedure (TCLP) data for treated red mud and threshold values for classification as an inert solid in NSW, Australia [30]

Contaminant	TCLP value ($mg\,L^{-1}$)	Threshold value ($mg\,L^{-1}$)
Ag	<0.01	0.5
As	<0.01	0.5
Be	<0.01	0.1
Cd	<0.01	0.1
Cr (total)	0.046	0.5
Cu	<0.01	No limit set
Hg	<0.01	0.02
Mo	<0.01	0.5
Ni	0.018	0.2
Pb	<0.01	0.5
Se	<0.04	0.4
V	0.055	No limit set
Zn	<0.01	No limit set

3.3. Eco-toxicological tests

Eco-toxicological characterization was made using acute and chronic toxicity tests with various organisms from different levels of the trophic chain.

In general, results obtained in this study evidenced the absence of severe eco-toxicological effects. Table 4 shows the percentage of light inhibition in *Vibrio fischeri*. Experimental results do not show any significant toxic effect, in fact every value is below the Microtox^{TM} test sensitivity limit (20%) [31].

No significant differences were observed also between control and treated red mud samples in *D. tertiolecta* growth
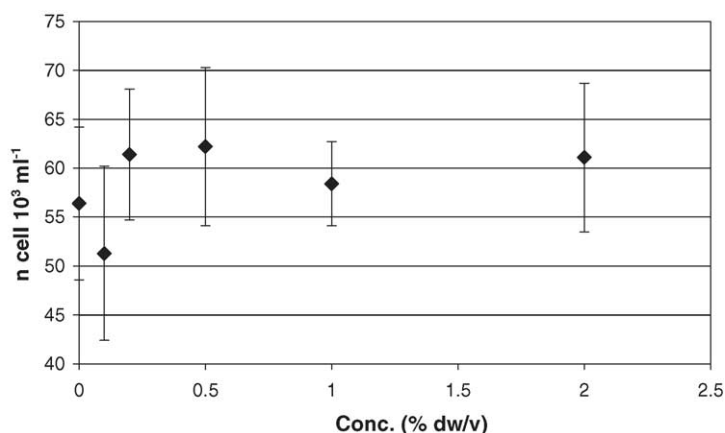
Table 3
Experimental parameters of Italian regulatory leaching test and TCLP test

	pH	Leachant	L/S ratio	Test duration	Stirring conditions	No of steps
Italian leaching test [21]	Natural − not under control	Deionised water	5	16 days (eight renewals at predetermined times)	No stirring	8
TCLP test [20]	Starting pH = 2.9 − not under control	Acetic acid solution	20	18 h	End over end rotary	1

Fig. 1. *Dunaliella tertiolecta* growth inhibition test (96 h).

Table 4
Percentage of light inhibition in *Vibrio fischeri* (±S.D.)

Concentration (%)	5′ (% effect)	15′ (% effect)	30′ (% effect)
0.1	10 ± 3	12 ± 4	8 ± 3
0.2	5 ± 1	9 ± 3	12 ± 6
0.5	13 ± 4	7 ± 2	4 ± 2
1	16 ± 2	10 ± 1	12 ± 5
2	7 ± 5	17 ± 2	9 ± 2

inhibition tests (Fig. 1). The sea urchin embryo toxicity test did not show any toxic effect (no significant differences between control and samples, see Table 5). Larval malformations were found in sea urchins in previous investigations conducted in bauxite manufacturing sludge [32] and this could testify that the seawater neutralization treatment is effective also for the reduction of red mud toxicological effects.

3.4. Metal trapping studies

Both unwashed and washed treated red mud were used for metal trapping studies. The investigated analytes were the following: As, Cd, Co, Cu, Mn, Ni, Zn. Monoelement and multielement solutions were used.

No significant differences were found between tests performed with different kinds of solutions prepared with deionised water and a Ca–Mg enriched solution. The Ca–Mg enriched solutions were also used in order to verify the level of competition between these major elements and the investigated analytes, but no significant competitive effect was observed at the considered concentration levels. No substan-

tial difference of behaviour in metal trapping was evidenced between washed and unwashed treated red mud; the removal seems to be more rapid in the case of washed treated red mud, but it reaches the same percentage value after 1 week, as can be seen for example in the case of Cu and Zn (Fig. 2a and b).

In general, a quantitative removal of several metals was already reached with 2 g L^{-1} of treated red mud: >99% for Zn and Cd; >94% for Ni, Co and Cu; about 80% of Mn. Arsenic seems to represent the exception: only 30% removed. The general trends are shown as example for Ni, Co, Cd and Mn in Fig. 3a–d, respectively.

The removal capability of treated red mud increases with the increasing of its concentration in solution: in particular, after 48 h only 35% of As (corresponding to an absolute value of 230 µg L^{-1}) was removed with 2 g L^{-1}, but the percentage significantly increased up to 70% (corresponding to an absolute value of 400 µg L^{-1}) with 10 g L^{-1} (Fig. 4). The trend of these results is in agreement with those obtained by other authors on seawater treated red mud [16] and evidence that an increase in As removal can be achieved with a higher amount of red mud in solution and, probably, waiting for a longer time to reach equilibrium. As already found in previous works [10,16], the removal of As is probably a function also of pH and As speciation in solution (As(III) or As(V)). The As is present in solution as oxyanion and therefore the surface chemical adsorption mechanism plays an important role for its removal; in particular, in recent studies, the addition of Fe and Al sulphates to treated red mud were used to lower the pH near particle surface, increasing the treated red mud capacity to remove As [17,18].

Table 5
Embrional defeat in *S. granularis* (% ±S.D.)

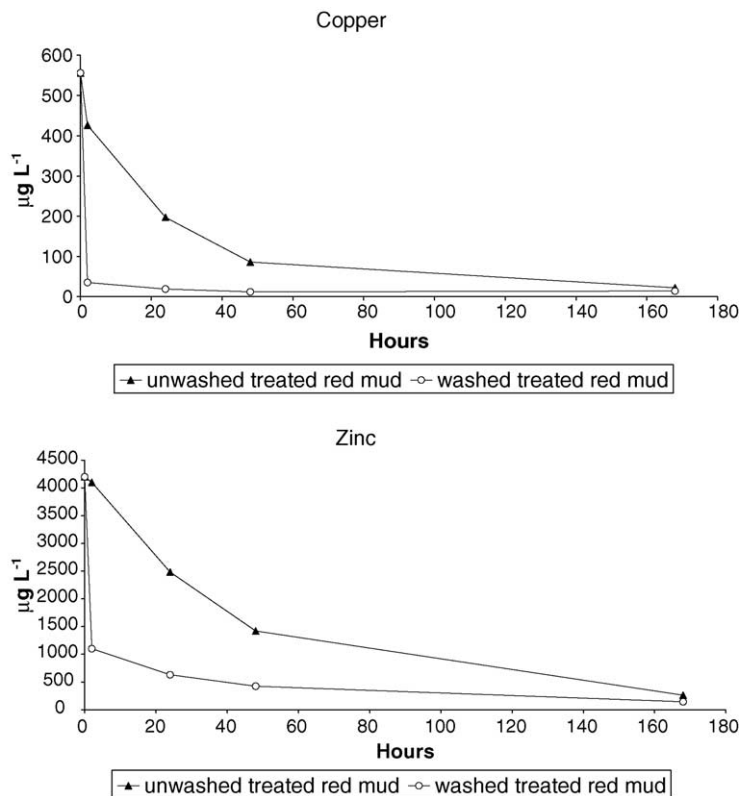| Concentration (%) (dw/v)	N = normal	R = retarded (1/2 N)	P1 = Malformed pluteui	P2 = No pluteui stage
Control	91 ± 6	3 ± 2	5 ± 1	4 ± 2
0.1	85 ± 12	7 ± 3	6 ± 2	2 ± 1
0.2	82 ± 8	3 ± 1	9 ± 3	4 ± 3
0.5	93 ± 6	2 ± 1	3 ± 2	2 ± 2
1	90 ± 9	1 ± 1	5 ± 1	2 ± 1
2	81 ± 10	2 ± 1	10 ± 2	4 ± 2

Fig. 2. (a) Metal trapping behaviour of treated red mud after 1 week (Cu); (b) metal trapping behaviour of treated red mud after 1 week (Zn).

In conclusion, high metal trapping capacity was shown by treated red mud, even if further investigations on trapping mechanism are necessary to better understand the processes that control metal removal mechanism.

3.5. Leaching experiments on "trapped" metals

As evidenced in Table 6, both in the cases of washed and unwashed treated red mud, less than 6% of trapped metal was leached in the case of As, Cd and Cu, while 10–30% was leached in the case of Mn and Zn. These results seem to confirm that for Mn and Zn removal is mainly controlled by hydroxides surface precipitation and co-precipitation, and are therefore partially reversible with pH decrease [33]; on the contrary the removal of As, Cd and Cu seems to be much more controlled by chemical adsorption phenomena, not reversible by pH modifications [34].

Table 6
Leaching test at pH 5

Metals	Leached/trapped (%)	
	Unwashed treated red mud	Washed treated red mud
As	0.5	0.2
Cd	6.2	4.1
Cu	1.4	0.6
Mn	30.9	25.6
Zn	16.3	10.8

3.6. General discussion

The studies carried out in this work seem to confirm the environmental compatibility of the studied treated red mud.

Red mud seawater treatment for its neutralisation is effective and leads to the production of a material with an almost neutral pH reaction grade; the recycling of this material in the environment can reasonably be considered safe "from the pH point of view".

The conformity of treated red mud to the Italian regulation for the environment compatibility of reusable materials was investigated and all parameters resulted below the threshold limits, with the exception of vanadium and some anions (mainly derived from seawater treatment). Experiments showed that released anion concentration can be lowered by previously washing treated red mud with deionised water; the washing is however uneffective for reducing vanadium release, whose total content in the material is around $300 \, mg \, kg^{-1}$. Even if this level of concentration seems to be significantly high, however it should be evidenced that high vanadium concentration up to $460 \, mg \, kg^{-1}$ naturally occur in soils of particular origin [29]. In case of the application of the Italian leaching test, it should be stressed that the pH value in solution ranges from a value of 7 to a value of 10 and, since the vanadium mobility is higher at neutral-alkaline pH [29], the vanadium solubilization in the leaching test pH conditions is relatively higher than that of the other metals.
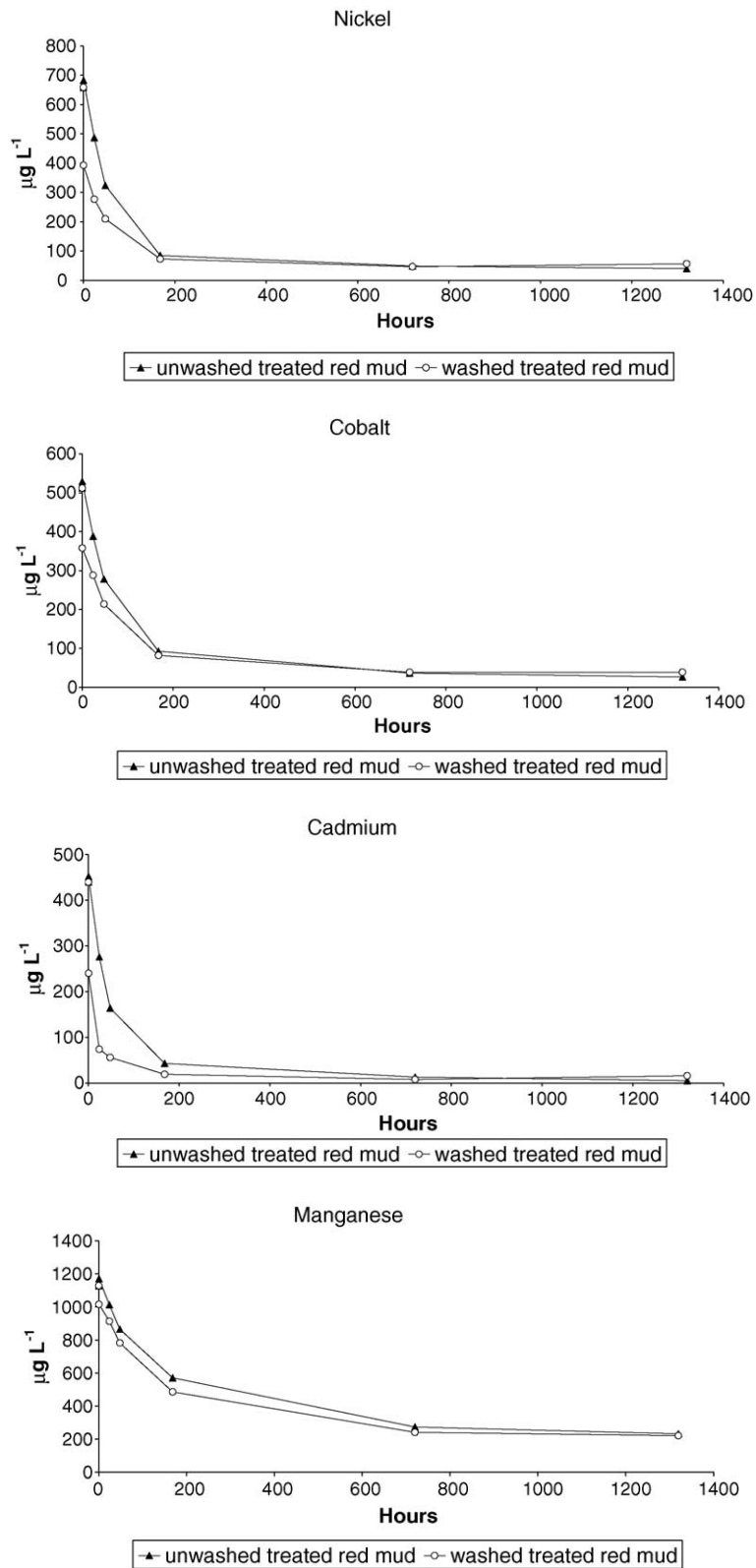
Fig. 3. (a) Metal trapping behaviour treated red mud after 2 months (Ni); (b) metal trapping behaviour treated red mud after 2 months (Co); (c) metal trapping behaviour treated red mud after 2 months (Cd); (d) metal trapping behaviour treated red mud after 2 months (Mn).
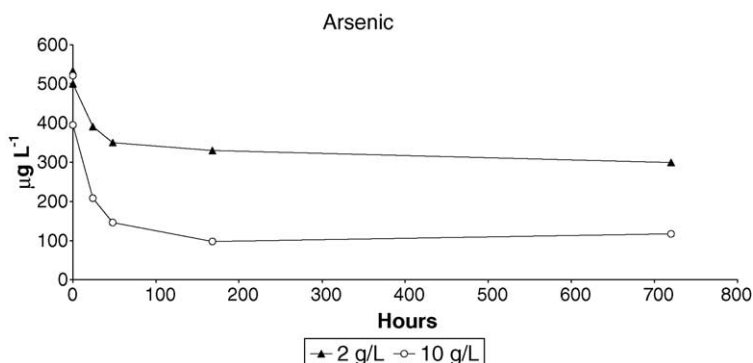
Fig. 4. Arsenic removal with 2 or $10\,\mathrm{g\,L^{-1}}$ of treated red mud.

The eco-toxicological tests evidenced the absence of toxic effects for treated red mud, whereas in previous works toxic biological effects were evidenced for untreated red mud [32]. This could testify that the product obtained after seawater neutralization treatment has lower toxic effects than red mud. Metal trapping experiments evidenced good removal capability of treated red mud in general for all considered elements, with only few exceptions (As and, to a lesser extent, Mn). The leaching test at pH 5 performed on "trapped" metals showed a different behaviour for different elements; this could confirm that the trapping mechanism is controlled by various phenomena that are different for each metal in function of its characteristics and of the form in which it is present (speciation in solution, formation of complexes, formation of oxyanions, solubility of its salt). Apparently, the affinity of the treated red mud material for metals is higher for Cd, Cu, Zn and Mn than for As; however, the percentage of release of "trapped" Zn at pH 5 is around 15% and the percentage of release is even higher in the case of "trapped" Mn, while it is below 6% for all the other metals.

In any case, in general, elements seem to be trapped in treated red mud in a tight way and are not easily leached even at pH 5; this could give an indication that metals removal from enriched solutions is not simply controlled by co-precipitation phenomena due to pH increase.

4. Conclusions

In this work the environmental compatibility and metal trapping capacity of treated red mud have been investigated in order to evaluate its possible recycling and reuse in the environment for remediation actions.

The results obtained in this work by application of the Italian leaching test for waste material reuse showed a satisfactory accordance to the set limits, with the only exception of few analytes (vanadium, fluorides and sulphates). Moreover, the application of three different eco-toxicological tests evidenced no significant eco-toxicological effect for the treated red mud. Finally, the evaluation of pH grade and the metal trapping experiments evidenced that the seawater treatment

of red mud decreases the alkalinity to environmentally safe values, thus maintaining the metal trapping properties of red mud materials. In particular, results obtained in the release of "trapped" metals seem to confirm the hypothesis that entrapped metals are not easily exchangeable and removable.

The results obtained in this work are encouraging in view of the possibility to reuse treated red mud for environmental purposes in remediation activities, even if more investigation would be needed to further understand the "active" (certainly existing, but to be clearly demonstrated) metal trapping mechanisms other than simple co-precipitation as a consequence of the pH increase

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