



## Research article

# Simultaneous removal of Cr(III) from high contaminated soil and recovery of lactic acid from the spent solution

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## ABSTRACT

It is proposed a closed-loop treatment cycle for Cr(III) removal from contaminated soils (2080 mg/kg). The treatment includes the use of lactic acid as washing agent, and the recovery of both Cr(II) and lactic acid from the spent solution. Results indicate that Cr(III) removal efficiency can be very high, passing 70% in all tested operative conditions. The metal forms strong complexes with lactic acid, and therefore cannot be eliminated through direct precipitation simply increasing the pH value. Therefore, lactic acid is preliminarily extracted from the solution using n-butanol at very acidic pH. The obtained extraction degree is generally high, varying between 0.5 and 1 according to the amount of used n-butanol solution. After lactic acid extraction, almost 100% of chromium can be recovered through precipitation in alkaline conditions. Lactic acid, in turns, can be purified and reused for a new washing treatment, separating it from n-butanol solution through water extraction. The extraction efficiency is once more satisfying (around 0.5), and not dependent on the operative pH.

## 1. Introduction

Soil washing is probably the most used and studied off-site technique applied to the remediation of metal contaminated soils (Gusiati and Klimiuk, 2012; Wang et al., 2016). This is due to its proved efficiency, whatever the specific condition of the site, if the washing solution and the other operative parameters are appropriately chosen (Ferraro et al., 2016a). The appropriateness of the solution depends not only on its removal capacity but also on: *i*) its cost; *ii*) its aggressiveness towards the structure and the composition of the soil; *iii*) its biocompatibility; and *iv*) its final destination (Voglar and Lestan, 2012; Von Lau et al., 2014).

While chelating agents and mineral acids have been extensively applied despite their evident limitations in terms of the over mentioned characteristics of appropriateness (Chen et al., 2018; Guo et al., 2018; Pontoni et al., 2016; Suanon et al., 2016), little is known about the possible utilization of the more environmentally friendly Low-Molecular-Weight Organic-Acids (LMWOAs). Nonetheless, these acids may represent an interesting alternative because are widely available, highly biodegradable, and have a little interference with the soil structure (Adeleke et al., 2017; Wang et al., 2014). Moreover, recent studies have shown the possibility of achieving good performances when some of these acids, such as lactic acid (LA), are used as washing agents

(Race et al., 2019; Spasiano et al., 2019). Moreover, according to Race et al. (2019), the use of LA as soil washing agent can entail good soil properties after washing and not relevant toxicological effects compared to LMWOAs.

LA is a LMWOC frequently found in natural soil as a result of biological processes, which take place in the rhizosphere (Adeleke et al., 2017). Because of its capacity of forming complexes with metals, LA is used to increase the uptake operated by plant roots (Li et al., 2010; Potysz et al., 2017). Moreover, LA biodegradation is generally completed within 5 days (Fukushima et al., 2009; Jamshidian et al., 2010). Its level of toxicity is negligible, so that LA is classified as an inert compound by the U.S. EPA (Datta and Henry, 2006). For all these characteristics, LA appears an excellent candidate to be used for soil washing processes. However, involvement of feasible treatment for the remediation of spent soil washing solution containing organic agent and extracted metals is fundamental for a safer and sustainable discharge into the environment. Further advantage of the suggested treatment is represented by the potential overcoming of thermodynamic stability of the metal-organic complexes which, instead, negatively affect the efficiency of conventional processes (such as precipitation or adsorption) for spent solution treatment (Ferraro et al., 2015).

The present paper is aimed at further investigating and optimizing

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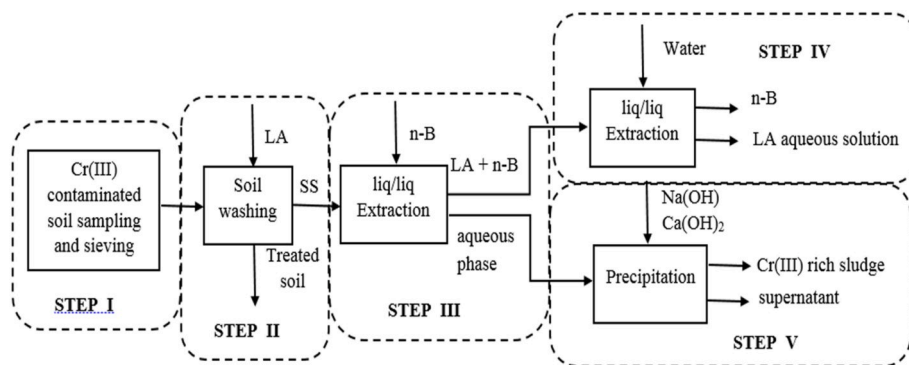


Fig. 1. Main steps of the polluted soil treatment.

the use of LA for soil washing application, analyzing the possibility of its recovery from the spent solution (SS). LA, in fact, has many industrial applications, and therefore is a valuable compound, worth to be recovered after utilization (Castro-Aguirre et al., 2016). Furthermore, the recovery allows optimizing the whole remediation process, reducing the total cost of the treatment, and avoiding any problems related to the final disposal of the SS (Ferraro et al., 2015; Trellu et al., 2017).

The study is carried out at lab-scale on a real contaminated soil, containing high levels of Cr(III), a metal which is difficult to remove using traditional biodegradable compounds such as Ethylenediamine-N, N'-disuccinic acid (EDDS) (Fabbicino et al., 2013). The proposed treatment, shortly summarized in the scheme of Fig. 1, includes the following main successive steps: i) soil sampling and sieving to isolate the finest fraction which contains most of the contamination; ii) soil washing with LA; iii) liquid:liquid (L:L) extraction of LA from the SS using n-butanol (n-B); iv) L:L extraction of LA from n-B using water; and v) alkaline precipitation of Cr(III) from the SS.

## 2. Materials and methods

### 2.1. Reagents and glassware

Reagents used for all analytical determinations were ACS grade or better. *dl*-lactic acid, 85 wt%, n-butanol, 99.9 wt%, calcium hydroxide (reagent grade), hydrochloric acid (reagent grade) and sodium hydroxide (reagent grade) were purchased by Sigma-Aldrich. Only Milli-Q water was used as reagent water and for all required dilutions. Before use, all glassware were soaked overnight in a nitric acid bath (2%), and rinsed several times with de-ionized water.

### 2.2. Soil sampling

Soil was sampled in the province of Naples, South of Italy (Step I, Fig. 1). The site was used, in the nineties, for the illegal disposal of industrial waste including tannery sludge, and is nowadays characterized by a diffuse contamination of Cr(III) and studied in previous researches aimed at investigating less invasive soil remediation interventions (Race et al., 2019). Sampling was effectuated manually from the top of 100 cm of soil, afterwards the samples were dried at 40 °C and screened using a 2.00 mm mesh. Only the finest fraction was used for all successive tests, and for all analytic determinations. Main characteristics of the soil are reported in Table 1.

### 2.3. Washing tests

Washing tests (Step II, Fig. 1) were conducted in triplicates, at room temperature and natural pH, in 100 mL plastic bottles, placed in a mechanical shaker. The operative parameters of the process were established according to the optimization study reported elsewhere (Race et al., 2019). In short, solid to liquid ratio was fixed at 1:10 and LA

concentration was established at 1.0 M. The total contact time was 96 h in order to reach equilibrium conditions. The SS was separated from the soil through centrifugation and successive filtration with a filter paper (0.45 μm), and then analyzed for Cr(III) determination. A chosen volume (10 mL) of the solution was treated to increase the pH up to 9.0 (using NaOH), and to verify the possibility of achieving the direct precipitation of Cr(III). The remaining volume (50 mL) was preliminarily subjected, instead, to the L:L extraction for LA recovery.

A mechanical shaker (Edmund Bühler Kombischüttler, Germany) was used for the washing tests.

### 2.4. Lactic acid extraction from spent aqueous solution using n-butanol

LA was extracted from the SS using n-B (Step III, Fig. 1) following the procedure suggested by Chawong and Rattanaphanee (2011). The extraction was performed at pH 1.0 adding HCl (1.0 M) dropwise to the SS and varying the SS/n-B volumetric ratio (R) (0.25/1; 0.5/1; 1/1; 3/1; 6/1). Samples were placed in a mechanical shaker for 1 h, and then centrifuged at 4600 rpm for 5 min. The concentrations of Cr(III) and LA were measured in the SS before and after the extraction process.

The extraction efficiency was evaluated measuring the LA extraction degree using n-B as extracting agent, and the LA partition coefficient between the organic phase (n-B) and the aqueous one (SS) (Chawong and Rattanaphanee, 2011).

The LA extraction degree ( $ED_{LA}$ ) was calculated as:

$$ED_{LA} = \frac{(V_{SS}^{in} \cdot [LA]_{SS}^{in} - V_{SS}^{out} \cdot [LA]_{SS}^{out})}{V_{SS}^{in} \cdot [LA]_{SS}^{in}} \quad (1.a)$$

The LA partition coefficient ( $P_{n-B/SS}$ ) was calculated as:

$$P_{n-B/SS} = \frac{[LA]_{n-B}^{out}}{[LA]_{SS}^{out}} \quad (1.b)$$

where:

$V_{SS}$  = volume of the spent washing solution [L];  
 $[LA]_{SS}$  = LA concentration in the spent washing solution [M];  
 $[LA]_{n-B}$  = LA concentration in the organic phase (n-B) [M];  
 $in$  = values before the extraction;  
 $out$  = values after the extraction

In addition the extracted LA purity ( $P_{LA}$ , %) was evaluated as:

$$P_{LA} = 100 \cdot \frac{[LA]_{n-B}^{out}}{[LA]_{n-B}^{out} + [Cr]_{n-B}^{out}} \quad (1.c)$$

where:

$[Cr]_{n-B}^{out}$  = Cr(III) concentration in the organic phase (n-B) after the extraction process [M]

**Table 1**  
– Characteristics of the contaminated soil. RSDmax <7.91

ID	Clay (%)	Silt (%)	Sand (%)	pH	Holding capacity (%)	LOI (%)	Ca (mg·kg <sup>-1</sup> )	Cr(III) (mg·kg <sup>-1</sup> )	Cr(VI) (mg·kg <sup>-1</sup> )	Cu (mg·kg <sup>-1</sup> )	Fe (mg·kg <sup>-1</sup> )	Mn (mg·kg <sup>-1</sup> )	Pb (mg·kg <sup>-1</sup> )	Cr Sequential extraction (%)			
														I fraction	II fraction	I fraction	II fraction
Soil	13	27	60	7.43	57	27	43247	2080	2	111	16978	612	101	1	32	66	1
Sample Treated Soil	7	24	69	3.3	53	27	30023	594	<1	47	8621	209	32	1	18	77	4

## 2.5. Lactic acid extraction from n-butanol using water

LA was further separated from n-B through water extraction (Step IV, Fig. 1) to recover both chemicals. At this aim the solution containing LA and n-B was poured in a plastic tube, mixed with Milli-Q water varying the volumetric ratio between the organic phase (n-B) and the aqueous one (R'), and placed in a mechanical shaker. Five different pH values, from 4.0 to 12, were tested to optimize the extraction. The separation of the two streams was simply obtained by gravimetry. After separation, LA and n-B concentrations were measured in the both phases.

The LA extraction degree ( $ED'_{LA}$ ) using Milli-Q water, and the LA partition coefficient ( $P_{w/n-B}$ ) between the aqueous phase (Milli-Q water) and the organic one (n-B), were calculated according to the following equations, formally similar to equation (1.a) and (1.b):

$$ED'_{LA} = \frac{(V_{n-B}^{in} \cdot [LA]_{n-B}^{in} - V_{n-B}^{out} \cdot [LA]_{n-B}^{out})}{V_{n-B}^{in} \cdot [LA]_{n-B}^{in}} \quad (2.a)$$

$$P_{w/n-B} = \frac{[LA]_w^{out}}{[LA]_{n-B}^{out}} \quad (2.b)$$

where:

$$V_{n-B} = \text{volume of n-B [L];}$$

$$[LA]_w = \text{LA concentration in Milli-Q water. [M]}$$

It has to be highlighted that although a small fraction of butanol might be dissolved in the recycled solution, such an event would not represent a hindrance for the solution reuse, because of the reported low bioaccumulation of butanol in the soil (Chan and Lai, 2008).

All described tests were performed in triplicates to reduce the experimental errors.

## 2.6. Cr(III) precipitation

The SS obtained before and after the organic extraction were treated using NaOH to precipitate Cr(III) as chromium hydroxide (Step V, Fig. 1). Both sodium hydroxide and calcium hydroxide were tested as alkaline reagents. The Cr(III) content in the aqueous solution was detected after the precipitation process. The percentage precipitation efficiency ( $PE_{Cr}$ , %) was calculated as:

$$PE_{Cr} = 100 \cdot \frac{[Cr]_{SS}^{in} - [Cr]_{SS}^{out}}{[Cr]_S^{in}} \quad (3)$$

where:

$[Cr]_{SS}^{in}$  = concentration of Cr(III) in the spent solution (SS) before the precipitation process [M];

$[Cr]_{SS}^{out}$  = concentration of Cr(III) in the spent solution after the precipitation process [M].

Once more tests were performed in triplicates.

## 2.7. Analytic determinations and used equipment

Tests were carried out in triplicate, unless otherwise indicated, in order to lower the experimental error related to the heterogeneity of the sample. Particle size distribution was determined according to the ASTM standard methodology (ASTM, 2003). According to the literature, only soil particles smaller than 2.0 mm were involved for further analysis (Tandy et al., 2006; Tokunaga and Hakuta, 2002). The pH of the soil was determined through a 1:2 soil-to-water ratio in accordance to the EPA Method, 9045C (EPA, 2003). Holding capacity was determined by standard methods (Klute, 1986). Soil organic matter content was evaluated through the loss-on-ignition index (LOI) at 550 °C (Schulte, 1995).

The cation exchange capacity (CEC) was determined in accordance to Chapman (1965). The element concentrations in the soil were determined using an ICP-MS (PerkinElmer Nexion 300, USA). Cr(III) concentration in the washing solution was detected using an atomic adsorption spectrometer SpectrAA-50/55 (Varian, CA, USA). Solid samples were mineralized by microwave digestion in a STRAT D oven (Milestone, CT, USA). The Cr(VI) concentration was determined according to method 3060A (EPA, 1996). The modified Community Bureau of Reference (BCR) procedure (Pueyo et al., 2008) was followed to obtain Cr(III) partition in the different soil fractions. LA and n-B were detected by high pressure liquid chromatography (Dionex pump P580, Dionex, CA, USA). Filtration was carried out using cellulose regenerated filters Whatman 0.45  $\mu\text{m}$  (Thermo Scientific, MA, USA). Extraction was performed using a IEC Centra GP8R centrifuge (Thermo Scientific, MA, USA). Finally pH was measured using HI 98190 pH/ORP pH-meter (Hanna Instruments, RI, USA).

Detailed information is presented in the Supporting Materials.

## 2.8. Mass balance and chemical speciation

Cr(III), n-B and LA mass balances were performed referring to the whole proposed treatment process, for each of the generated flows. Chemical speciation and solubility equilibrium were obtained using Visual MINTEQ ver. 3.1.

## 3. Results and discussion

### 3.1. Soil characterization and soil washing first step

Results from soil samples characterization indicated that investigated soil could be classified as a sandy-loam (clay 13%, silt 27%, sand 60%) (Di Stefano et al., 2010). Moreover, soil samples displayed suitable texture for proper water permeation, oxygenation, and root penetration. The CEC value was equal to 22 meq/100 g which is very high compared to the typical values reported for the sand-based soils (between 5 and 10 meq/100 g) (Donahue et al., 1983). LOI value (27%) was also higher compared to average LOI values for natural soils (5–7%) (Zeng et al., 2011). This highlighted the good potential of the investigated soil for the growth of edible cultures. According to these results, it was possible to assess that the investigated soil natural vocation was agricultural. Among all the analyzed elements, results showed that only Cr concentration exceeded the regulatory thresholds for different European Countries as well as the background values (Cicchella et al., 2008). The total Cr concentration indicated a significant contamination due to

anthropogenic activities. Cr was mainly present in Cr(III) form while the low amount of Cr(VI) was probably ascribable to equilibrium phenomena between the two species (Wu et al., 2005) and the high presence of organic matter. In fact, this latter spontaneously reduces Cr(VI) to Cr(III) for pH values around and above neutrality leading to a consequent Cr mobility decrease (Race et al., 2019).

Total Cr(III) concentration in the sieved soil was around 2100  $\text{mg kg}^{-1}$  ( $\pm 2\%$ ). The metal was mostly bound to the oxidizable fraction (66%) and to the reducible one (32%). Only 1% was bound to the exchangeable and weak acid soluble fraction, and 1% to the residual fraction.

Soil washing treatment at natural pH allowed to remove up to 70% of Cr(III) (Fig. S1), mostly from the reducible and the oxidizable fraction (73% and 93%, respectively), confirming the potentiality of LA as washing agent. The latter extraction yield values were comparable to the ones reported in a previous study focusing on soil washing technique with mineral acids as extraction agent. The amount of metal extracted versus time presented the typical trend, frequently observed in washing processes conducted with different washing agents (Fabbriano et al., 2018; Ferraro et al., 2017), characterized by an initial fast removal rate, which drastically decreased after almost 10 h. Results indicated a high removal efficiency for targeted contaminant. However, as generally reported (Ferraro et al., 2016b), the removal of essential elements also occurred (Table 1), and nutrient addition was required as a further step prior to soil reuse. In a previous work (Race et al., 2019), it has been reported a comparable low toxicity between a soil not contaminated by Cr (III) and one treated with lactic acid followed by nutrients addition. Another positive result due to the nutrient addition (for instance as carbonates and bicarbonates) is represented by the pH increase due to the improvement of the soil buffer capacity. All removed chromium was detected in the SS. The final pH, Cr(III) concentration and LA concentration of the SS after the washing process were 3.3, 145  $\text{mg L}^{-1}$  and 65  $\text{g L}^{-1}$  respectively.

### 3.2. Recovery of spent soil washing solution

In order to remove Cr(III) from the SS, a first attempt was done simply increasing the pH up to 9.0. In these conditions no chromium precipitation occurred ( $PE_{Cr} = 0$ ). Such a result was explained analyzing the distribution of chemical species reported in Fig. 2a–c, calculated considering the concentration of Cr(III) and LA detected in the SS.

According to this distribution, considering the existing species of chromium and LA (Fig. 2a and b) and the possible formation of chelates (Fig. 2c), it was supposed that metal removal from the soil was due to the

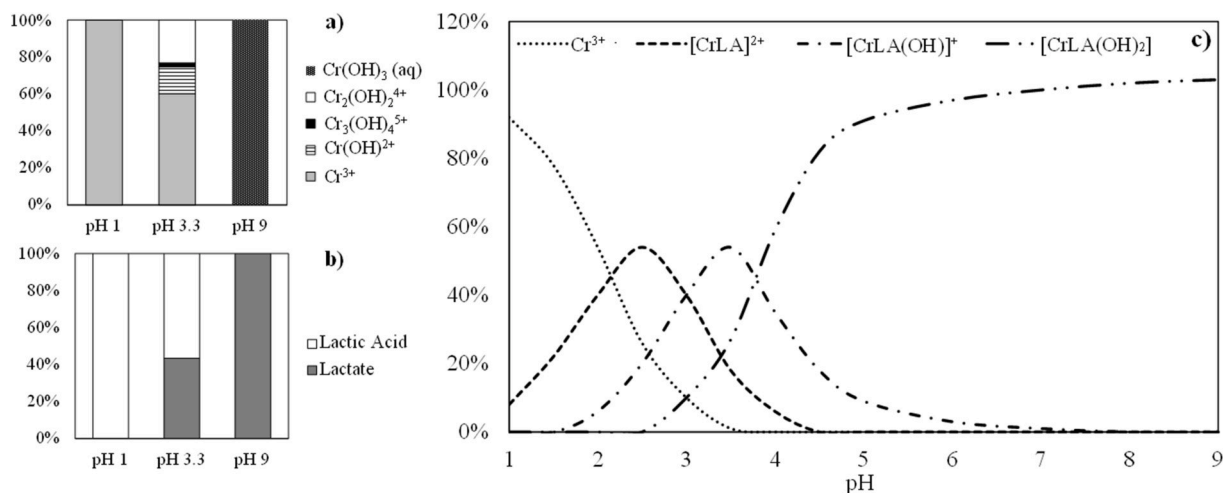


Fig. 2. Simulation of chemical speciation using Visual MINTEQ ver. 3.1: a) chromium; b) lactic acid; c) predicted metal complexes formed between Cr(III) and lactic acid. Initial chromium(III) concentration: 145  $\text{mg L}^{-1}$ ; initial lactic acid concentration: 65  $\text{g L}^{-1}$ .

formation of Cr-LA complexes (Hamada et al., 2005; Race et al., 2019) in form of  $[\text{CrLA}]^{2+}$  and  $[\text{CrLA}(\text{OH})]^+$ , that are the prevalent species (Fig. 2c) at pH 3.3 (Lugo and Lubes, 2007). As consequence of pH increase, these species were increasingly substituted by  $[\text{CrLA}(\text{OH})_2]$ , which became prominent at pH 9.0 (Fig. 2c). Because of the negligible presence of Cr(III) ions no precipitation of  $\text{Cr}(\text{OH})_3$  could occur (Fig. 2a), and then it was impossible to remove Cr(III) from the SS.

Because of the difficulty of recovering Cr(III) through direct precipitation of the metal from the SS, it was decided to preliminarily attempt the extraction of LA from the SS with n-B and then proceed to Cr (III) precipitation, testing different values of the ratio between SS volume and n-B volume (R). Literature findings, in fact, indicate a significant effect of R on the degree of extraction and on the partition coefficient for the ternary system water/LA/n-B (Chawong and Rattanaphanee, 2011). In details, the extraction degree is reported to increase at increasing n-B/aqueous phase volume ratio. In other words, it is known that since n-B is a partially miscible solvent with water, caution is necessary when fixing the organic-to-aqueous solution volume ratio in order to prevent an incorporation of the aqueous solution phase into the organic one, which may render more difficult LA recovery. In the present case, the system was complicated since Cr(III) ions and LA-Cr(III) complexes were present in the aqueous phase. Therefore, it was necessary to assess if the data reported in the literature for the ternary system water/LA/n-B were still valid in the present case. In Table 2 the results collected during extraction runs at varying the volumetric ratio (R) are presented, from which the LA extraction degree and the LA partition coefficient were calculated. The extraction was conducted at initial pH 1.0 to have the maximum percentage of free Cr(III) ions (Fig. 2a and c).

The obtained values of  $ED_{LA}$  were quite similar to literature (Chawong and Rattanaphanee, 2011) ones (Fig. 3a) and showed a decreasing trend with R-value, characterized by an initial fast decrease for  $R < 1$ , and a much slower decrease for  $R > 1$ . On the contrary,  $P_{n-B/SS}$  values (Fig. 3b) exhibited an increasing trend with R. To explain these trends it was supposed that the transfer of LA into the organic phase was due to the incorporation of the aqueous phase into the organic one. The incorporation increased increasing the volume of used n-B. Indeed, the obtained values of  $ED_{LA}$  were limited by the extractant amount, and increased with the R value according to the following equation (Fig. 4a):

$$ED_{LA} = 0.48 \cdot (1 - e^{-5.8R}) + 1.3 \cdot (1 - e^{-0.07R}) \quad (4.a)$$

The supposed transfer mechanism excluded the solvation of LA-metal complexes into the organic phase. As a consequence, the transfer of LA did not carry any Cr(III) ions with it. Indeed  $P_{LA}$  was 100%, indicating that the metal had been completely retained into the SS. In these new conditions free Cr(III) ions dominated over chelate species in

the aqueous phase, and the successive increase of SS pH up to 9 caused the precipitation of  $\text{Cr}(\text{OH})_3$ . Total precipitation amount was very high ( $PE_{Cr} = 100\%$ ), and not dependent on the used alkaline reagent.

Table 3 reports the results of LA extraction from the n-B solution conducted with Milli-Q water at natural pH. No differences were obtained varying the pH of the water solution (Fig. S2). According to the reported values, the trend of LA extraction degree as function of the volume of the extracting agent (Fig. 4b) was very similar to the one obtained during the experiment carried out to extract LA from the washing solution, and could be modeled according to the following equation, formally similar to equation 4.a:

$$ED'_{LA} = 0.77 \cdot (1 - e^{-4.5R'}) + 29 \cdot (1 - e^{-0.0012R'}) \quad (4.b)$$

It could be therefore concluded that the extraction mechanism was the same, and therefore the process was somehow reversible.

It is worth noting that both equation 4.a and 4.b were obtained by data fitting, minimizing the modeling efficiency, as detailed in Chen et al. (2019). The reason for determining the trend of  $ED_{LA}$  and  $ED'_{LA}$  versus the corresponding volumetric ratio was to confirm that the two extraction processes were dependent on the same parameters, and that they were regulated by the same mechanism.

Based on the considerations reported above, a more detailed description of the sequence of the operations that can be planned to recover LA is presented in Fig. 5. The wastewater stream coming from soil washing treatment, is acidified at pH 1.0, and fed to a mixer (B) along with n-B. The formed suspension is allowed to separate. The two resulting phases are then separated and treated. The (organic) upper phase is mixed with water to remove LA. NaOH is added to the (aqueous) lower phase in the mixer to precipitate chromium as  $\text{Cr}(\text{OH})_3$ . Produced sludge is separated from the aqueous stream containing LA residual.

In Fig. 5 an integration of soil washing operation and recovery of LA are presented. Particular attention is devoted to consider all the possibilities to recycle water and n-B streams within the treatment process itself. Proper purging operations are thus foreseen for each recycled streams to avoid the accumulation of unwanted species. The recycled volumes need to be separately treated before their disposal.

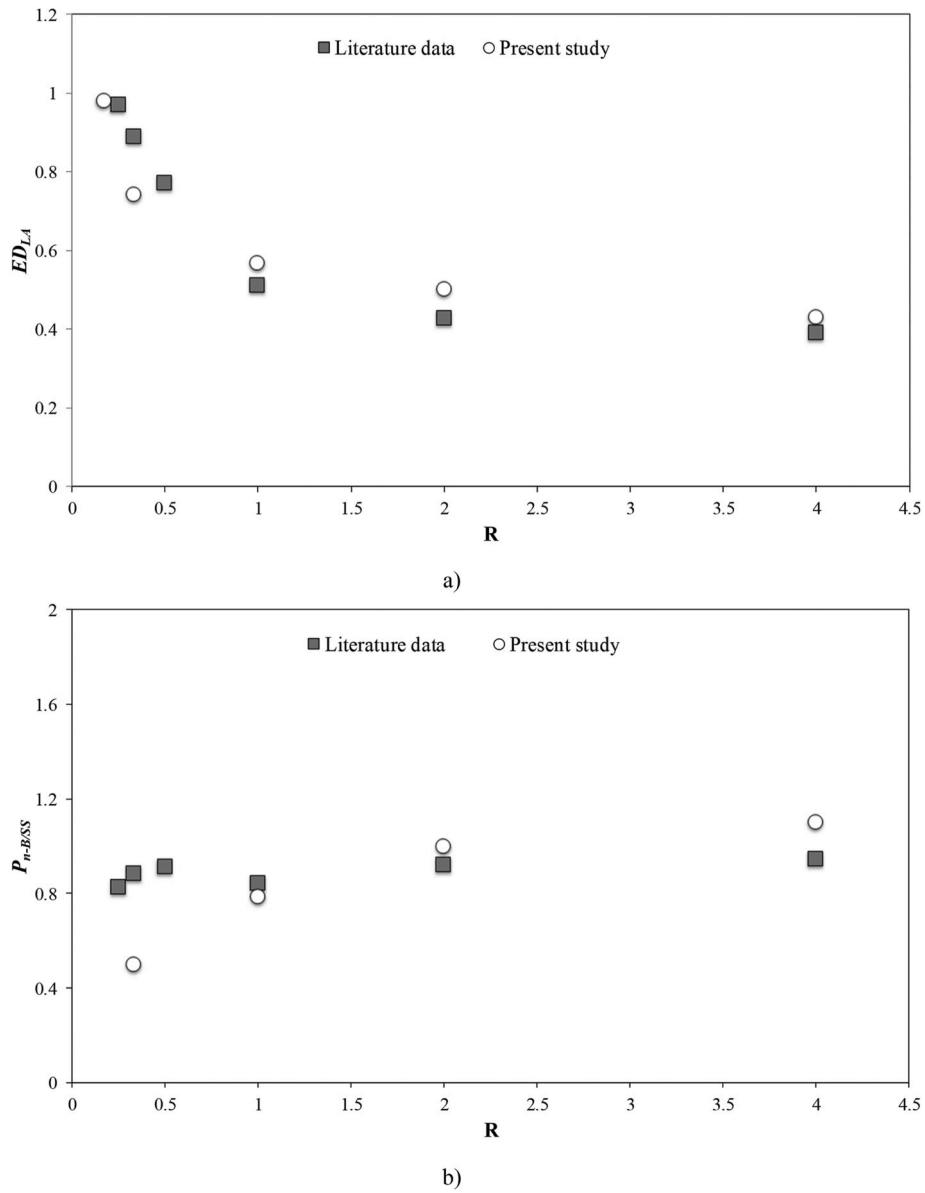
### 3.3. Technical-economic assessment

Confirmative washing tests were conducted using the recovered solutions as extracting agents. Cr removal efficiency obtained up to the third recovery step was comparable (1st cycle = 72%; 2nd cycle = 69%; 3rd cycle = 68%). These results were ascribed to the addition of a new amount of LA for each step to compensate the loss occurred in the previous one.

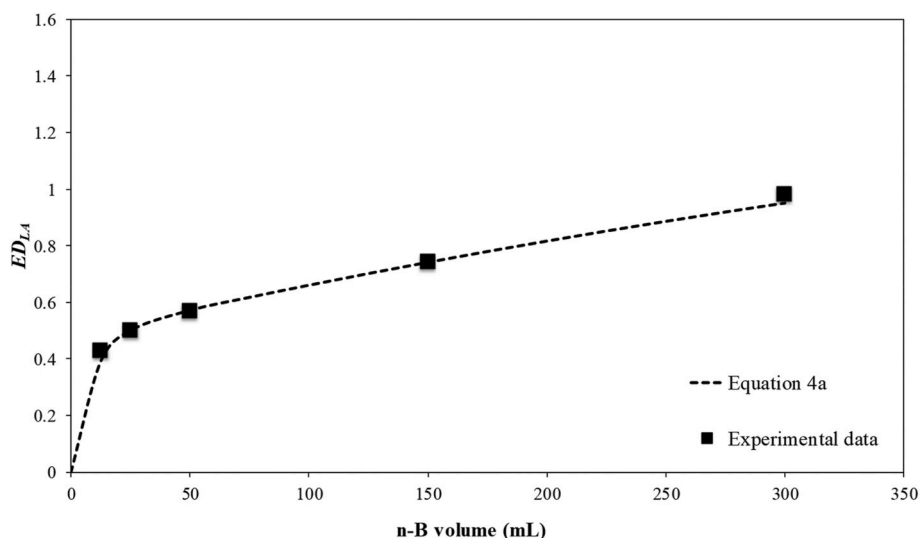
**Table 2**

- Characteristics of the organic phase and the spent solution during lactic acid extraction from the spent solution using n-butanol - (R = Ratio n-B:SS; V = volume; n-B = normal Butanol phase; SS = spent solution; LA = Lactic Acid).

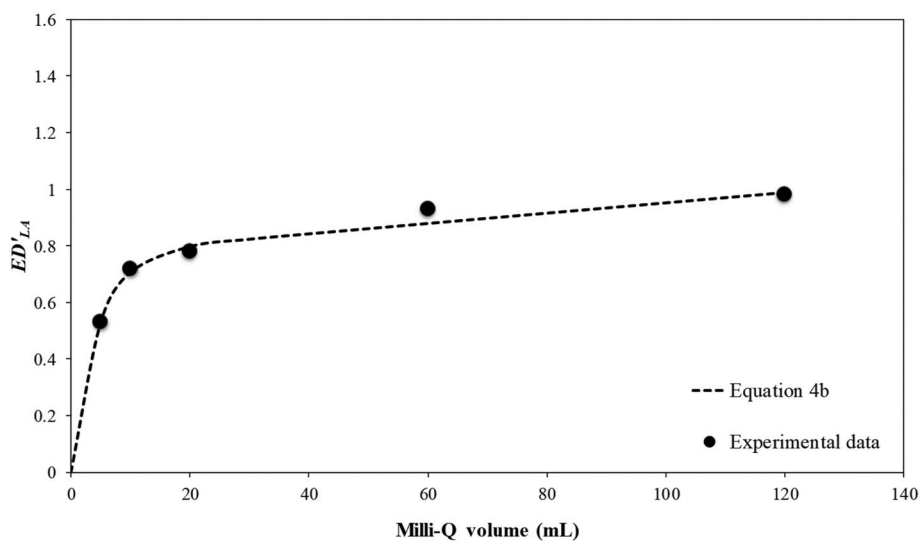
R	Initial values				Equilibrium values					
	$V_{n-B}^{in}$	$V_{SS}^{in}$	$[LA]_{n-B}^{in}$	$[LA]_{SS}^{in}$	$V_{n-B}^{out}$	$V_{SS}^{out}$	$[LA]_{n-B}^{out}$	$[LA]_{SS}^{out}$	$[Cr]_{n-B}^{out}$	$[Cr]_{SS}^{out}$
	mL	mL	$\text{g}\cdot\text{L}^{-1}$	$\text{g}\cdot\text{L}^{-1}$	mL	mL	$\text{g}\cdot\text{L}^{-1}$	$\text{g}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$
0.25:1	12.5	50	0	65	21	41	63	45	0	177
0.5:1	25	50	0	65	41	34	42	41	0	183
1:1	50	50	0	65	62	38	29	37	0	189
3:1	150	50	0	65	170	30	14	28	0	252
6:1	300	50	0	65	334	16	9	4	0	462



**Fig. 3.** Results of LA extraction vs the volumetric ratio between the LA-aqueous solution and the organic phase (n-B). Comparison between literature data and present data: a) extraction degree; b) partition coefficient.



a)



b)

Fig. 4. LA extraction degree as function of the extracting volume.: a) extraction of LA from SS using n-B; b) extraction of LA from n-B using Milli-Q water.

The proposed cycle entails a significant advantage represented by higher cheapness compared to advanced oxidation or electrochemical processes also due to the reported reagent recovery step. At this regards, scientific studies with substances comparable to lactic acid at concentrations similar to those necessary for soil remediation reported an oxidation rate higher than 70% after 5 weeks of treatment (Ali et al., 1993). Such long treatment time causes a significant increase of energy costs. This aspect and the potential occurrence of Cr (III) oxidation to Cr (VI) represent important hindrances for the feasible application of AOP processes (Gimeno et al., 2016).

The observed results highlight the applicability of the spent solution treatment with consequent partial reagent recovery. Indeed, the process efficiency can depend on the presence of different substances in the spent solution. In detail, organic compounds extracted from the soil during the washing step could significantly affect the LA recovery yield. However, according to the mass balance performed in the present study, from a preliminary technical-economic evaluation it was possible to observe different results according to the different ratios that can be used in the two separation phases. The reagent loss can fluctuate from

350 g to 850 g for lactic acid and 0.1 kg–5 kg for n-butanol for each kg of treated soil. In particular, under the adopted experimental conditions, the combinations n-B:SS = 0.5:1 and n-B:SS = 1:1 seem the most convenient since the resulting loss equal to 540 g of lactic acid and 230 g of n-butanol for 1 kg of treated soil. The latter result further assessed the feasibility of the suggested approach (or treatment cycle) as promising alternative solution.

#### 4. Conclusions

The paper presented an innovative treatment cycle for Cr(III) removal from contaminated soils, using lactic acid, including lactic acid recovery and Cr(III) precipitation, so to achieve a closed loop, which does not require further process for the disposal of the spent solution.

The following main conclusions may be derived from the study:

- lactic acid represents a green alternative for Cr(III) removal from contaminated soils;

**Table 3**

Characteristics of the aqueous phase and the organic phase during lactic acid extraction from the n-butanol phase using Milli-Q water (W: Milli-Q water) – (R = Ratio n-B:SS; V = volume; n-B = normal Butanol phase; SS = spent solution; LA = Lactic Acid).

R'	Initial values				Equilibrium values			
	$V_{n-B}^{in}$	$V_w^{in}$	$[LA]_{n-B}^{in}$	$[LA]_w^{in}$	$V_{n-B}^{out}$	$V_w^{out}$	$[LA]_{n-B}^{out}$	$[LA]_w^{in}$
	mL	mL	$g \cdot L^{-1}$	$g \cdot L^{-1}$	mL	mL	$g \cdot L^{-1}$	$g \cdot L^{-1}$
1:0.25	20	5	24	0	18	7	13	38
1:0.5	20	10	24	0	18	12	7	30
1:1	20	20	24	0	17	23	6	16
1:3	20	60	24	0	12	68	5	6
1:6	20	120	24	0	9	131	3	3

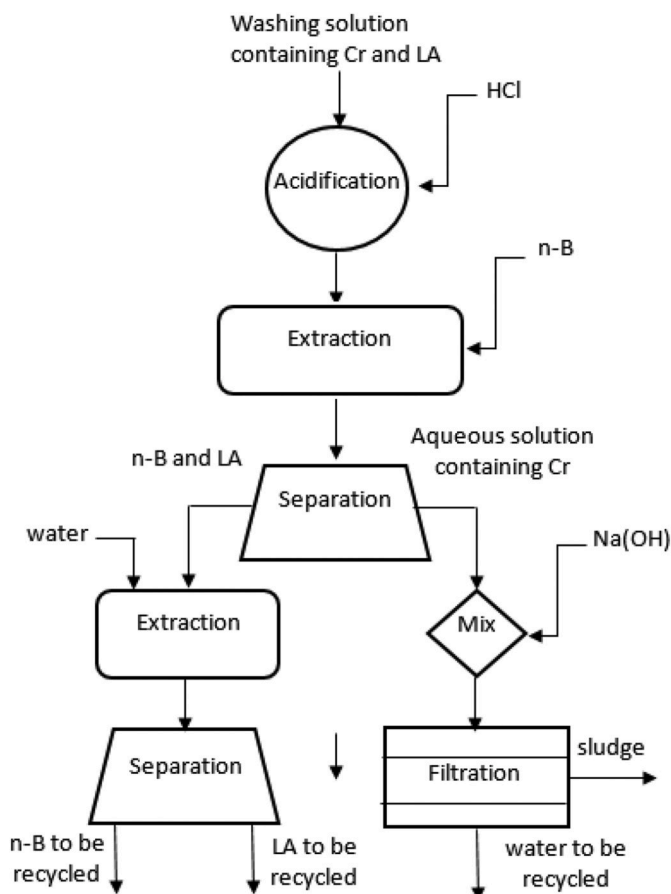


Fig. 5. Proposed sequence of operation to recover LA.

- removed chromium (III) cannot be precipitated directly from the spent solution as it forms stable complexes with lactic acid, which persist even at high pH;
- in order to precipitate chromium (III) and to regenerate the spent solution it is required the lactic acid extraction through the use of n-butanol;
- the extraction process can be optimized increasing the volume of the extracting agent, as the transfer of lactic acid into the organic phase is mainly regulated by the incorporation of the aqueous phase into the organic one;
- the extraction process is reversible, and therefore lactic acid can be further recovered from n-butanol using water as extracting agent.

Future tests could be carried out focusing on the use of lactic acid produced by biological treatments. This approach could be useful for the

significant decrease of the costs related to the soil remediation process.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

**R. Andreozzi:** Project administration, Supervision. **M. Fabbri:** Conceptualization, Writing - original draft. **A. Ferraro:** Methodology, Data curation, Validation. **S. Lerza:** Investigation. **R. Marotta:** Visualization, Writing - review & editing. **F. Pirozzi:** Funding acquisition, Supervision. **M. Race:** Writing - review & editing, Investigation, Supervision.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2020.110584>.

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