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Immobilization of heavy metals in contaminated soils through ball milling with and without additives

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Abstract

In the present work, the use of ball milling for remediation of heavy metals from contaminated soils of sandy, bentonitic and kaolinitic type is investigated. Immobilization of heavy metals (Cd(II), Pb(II), Zn(II)) is achieved by mechanically treating the contaminated soil with or without additives, by taking advantage of weak transformations induced on the soil through mechanical loads occurring during collisions in the milling process. When hydroxylapatite (HA) is added to the heavy metal contaminated soil, the corresponding immobilization efficiency of the mechanochemical treatment increases. The degree of metal immobilization is evaluated by analyzing the leachable fraction of heavy metal from the treated soil as obtained through the "synthetic precipitation leaching procedure". In particular, for soils contaminated by heavy metals displaying concentration levels similar to field contaminated soils, specific ball-milling treatments without the use of hydroxylapatite were able to reduce the leachable fraction of heavy metals to levels lower than the USEPA regulatory thresholds. XRD, SEM/EDS and granulometric analyses reveal no significant alterations of the intrinsic character of sandy and bentonitic soils after milling except for a partial amorphization of the treated soil. On the other hand, the mechanical treatment causes the total amorphization of kaolinitic soil. The increase of immobilization efficiency when soils are mechanically treated is hypothesised to be due to the specific phenomena induced during ball milling such as entrapment of heavy metals into aggregates, solid diffusion into the crystalline reticulum of soil particles as well as the formation of new fresh surfaces (through particle breakage) onto which heavy metals may be irreversibly adsorbed. In addition, when HA is added to the heavy metal contaminated soils, the mechanical treatment is hypothesised to be able to provide an increase of the specific surface and reactivity of hydroxylapatite, whose metal immobilization properties are well known.

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Keywords: Ball milling; Soil remediation; Heavy metals; Immobilization; Hydroxylapatite

1. Introduction

Heavy metals are widespread in urban and industrial areas as a consequence of industrial activities, metal mining, smelting and refining, atmospheric deposition, land application of sewage sludges and industrial by-products, gasoline processing, storage, and distribution as well as production of painting materials and their use [1,2].

Inhalation and ingestion of heavy metals may cause various health diseases such as anemia, neuropsychological effects, liver diseases, gastrointestinal pathologies, terathogenic implications [3]. Moreover, it is known that the DNA-damaging effects of certain metals in humans can lead to induction of cancer and a decrease of fertility [4]. In addition, heavy metals in soils may adversely affect soil ecology, agricultural production, or product and water quality [5].

In order to avoid such hazards, strong efforts have been made to develop remediation techniques of heavy metals contaminated

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soils [6]. However, this concern is still recognized nowadays to be one of the most difficult problem to be solved by taking advantage of suitable technologies [7,8]. For this reason the development of economically feasible remediation technologies represents a very interesting technological and scientific issue.

Typical remediation techniques are constituted by extraction and immobilization processes. The aim of the first ones is to remove heavy metals from the soil matrix by transferring them to another phase. A variety of extractants have been investigated for ex situ remediation. Extractive techniques may involve inorganic acids [9,10] or organic acids and surfactants [11,12]. The ex situ extractive technologies are rarely adopted because of high risks and costs related to the use of hazardous extractants and the consequent need of treating secondary effluents. On the other hand, "in situ" extractive technologies are constituted mainly by phyto and electrokinetic extraction. The first one, which is based on the use of plants to transport and concentrate metals from the soil into the harvestable parts of roots [13], may require extremely long times, e.g. centuries, to achieve the complete remediation of soil. The electrokinetic extraction, which promotes the migration of metal ions towards the cathode through the application of electrical gradients between two electrodes inserted into the ground, may be strongly affected by soil-type and contaminant species to be removed [14].

Considering the limitations of the extractive techniques described above, immobilization processes are generally preferred as cost-effective technologies for treating heavy metals contaminated soils [1]. The aim of immobilization techniques is to prevent migration of heavy metals into the environment due to leaching, by improving soil physical characteristics, decreasing surface area across which pollutants can transfer, or by limiting the solubility or toxicity of the hazardous compounds [15]. Immobilization is typically performed by mixing contaminated soils with suitable binders which are able to reduce heavy metals leachability through pH and alkalinity control in order to minimize their solubility or by promoting adsorption, ion exchange and precipitation of pollutants [16,17]. A variety of binders have been investigated to immobilize heavy metals in soils. Very promising results were obtained by employing rock phosphate [18], zeolites, calcium hydroxide [19] and phosphates [20]. In particular good results have been obtained by using hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) for the immobilization of leachable Pb(II) in soils [21,22]. In aqueous solutions, hydroxylapatite (HA) leads to the immobilization of Al, Cd, Cu, Fe(II), Ni and Zn [23–27].

Several mechanisms, such as ion exchange, surface complexation and dissolution followed by metal phosphate precipitation and co-precipitation, have been proposed in the literature to explain the heavy metal immobilization properties of HA [28]. Although such mechanisms have not yet been well understood, HA seems to be a promising soil additive for the immobilization of heavy metals (Zn, Pb, Cu, Cd and As) in polluted soils [22].

On the other hand, although the use of HA can be effective in the remediation of heavy metal contaminated soils, Boisson et al. [22] found that at high percentages (5%), growth inhibitions of specific plant species may occur. This effect was ascribed to the fact that together with heavy metals also important nutrients may be strongly immobilized by HA, thus leading to deficiency problems for plant [22]. Moreover, at high HA percentage, mobilization of As has been detected thus determining an increase of its transport to plants and animals and the possible percolation of this element to the groundwater [22]. Therefore, to avoid phytotoxic effects, the use of HA should be limited to low concentrations. Furthermore, the use of exogenous reactants may be characterized by specific disadvantages such as the modification of original soil properties, the progressive reduction of immobilization efficiency due to reactants degradation and/or saturation and their additional costs.

Mechanical treatment processes are typically used to promote specific transformations such as combustive or gradual reactions, amorphization, activation, microstructural refinement, comminution, cold welding and alloying [29,30]. The mechanochemical reactivity of novel systems involving toxic organic was the object of several investigations [31–35]. Mechanically induced reactions have been successfully used for the degradation of organic pollutants such as exachlorobenzene [32], hexabromobenzene [34], PCBs [33,35], and more recently for the degradation of sulfonic acids [36,37]. Degradation reactions occur by a gradual conversion path or by a combustion-like reaction which may take place, after an induction period, in a very short time [32,38,39]. In the first case, the increasing amount of defects in the solid matrix permits a continuous degradation of the organic compound according to mechanisms not yet well understood [35,38,39]. In the second case, as a consequence of the high temperatures reached by the powders inside the mechanochemical reactor, the complete degradation of the organic compounds occurs through strong exothermic reactions in a relatively short time [32,40].

While several papers have been devoted in the literature to investigate degradation reactions of organic contaminants under mechanical treatment, to our best knowledge the effect of mechanical treatment on immobilization capacity of heavy metals in soils started to be studied only recently. In the present work, we analyze the efficiency of mechanical treatment of Pb(II), Cd(II) and Zn(II) contaminated soils with or without HA as additive. Specifically, for the case when HA is used, the target is to verify if mechanical treatment by ball milling allows to obtain high immobilization efficiencies using low percentages of HA in order to avoid its negative effects mentioned above. In the second part of the work the effect of ball-milling treatment on contaminated soils is tested without the use of any additive.

The characterization of possible modification of soil physical, chemical and mineralogical properties induced by the milling process is also addressed. Possible mechanisms involved during the mechanical treatment and responsible of the increase of soil immobilization capacity are discussed.

2. Materials and methods

High purity $CaCO_3$ (99%), SiO_2 (99%), bentonite (99%) kaolin (99%), Fe_2O_3 (99%), MnO_2 (99%), humic acid (99%) were mixed in order to prepare sandy soils (SS), kaolinitic soils (KS) and bentonitic soils (BS). All compounds were obtained from Sigma–Aldrich, Inc. The amount of each compound used

Table 1
Composition (wt%) of synthetic soils (cf. [41])

Compound	Sandy soil (SS)	Bentonitic soil (BS)	Kaolinitic soil (KS)
SiO_2	78%	33.5%	33.5%
Kaolin [$Al_2Si_2O_5(OH)_4$]	–	–	60%
Bentonite [$Al_2O_34SiO_2H_2O$]	20%	60%	–
$CaCO_3$	0.5%	5%	5%
Fe_2O_3	0.25%	0.25%	0.25%
MnO_2	0.25%	0.25%	0.25%
Humic acid	1%	1%	1%

for preparing synthetic soils, according to the procedure suggested by Lo and Yang [41], is reported in Table 1.

Soil contamination has been carried out in a temperature controlled shaker at 25 °C by contacting known weights of each synthetic soil, with a solution of known solute (Pb(II), Cd(II) and Zn(II)) concentration and volume in suitable flasks. $Pb(NO_3)_2$, $Cd(Cl)_2$ and $Zn(Cl)_2$ (99,99%, Alfa Aesar) were employed to obtain the solution at the desired Pb(II), Cd(II) and Zn(II) concentration, respectively. The flasks were sealed and shaken for 24 h, which was experimentally proved to be a sufficient time to reach equilibrium conditions for the three metals considered. Finally, the resulting solutions have been sampled in order to determine the solute concentration and pH. Concentration of heavy metal in the soil phase at equilibrium has been determined through the following mass balance:

$$q^{24\,\mathrm{h}} = \frac{(C^0 - C^{24\,\mathrm{h}}) \times V_{\mathrm{liq}}}{W_{\mathrm{solid}}} \tag{1}$$

where $q^{24\,\mathrm{h}}$ (mg kg^{-1}) is the heavy metal concentration in the soil solid phase after 24 h of contact, C^0 and $C^{24\,\mathrm{h}}$ (mg L^{-1}) are the initial and equilibrium concentration of heavy metal in the liquid phase, respectively, V_{liq} (L) is the volume of liquid solution and W_{solid} (kg) is the soil weight contacted with the solution. The experimental values of solute concentration, C^0 and $C^{24\,\mathrm{h}}$, respectively, were determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Vista MPX, Varian).

For the experiments conducted with additives, hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$, Sigma–Aldrich, 99% purity) was added to the polluted soil on a 3%, 4% and 5% (w/w) basis (related to the total weight of the soil–HA mixture). The HA percentage is obtained by adding the desired HA amount to a fixed weight of contaminated soil in order to assure that the amount of heavy metal in the mixture was the same for the trials with different percentages of HA.

Contaminated soils with or without additives were mechanically treated by ball milling using a Spex Mixer/Mill mod. 8000, operating at the standard milling frequency of about 870 rpm. It was equipped with a stainless steel vial, 606.75 g in weight, having the internal diameter equal to 3.8 cm and the internal height of 5.8 cm. Different soil amounts were introduced inside the vial together with two stainless steel balls of 8 g and 10 mm in diameter in order to investigate the effect of the ball to powder ratio (BPR). In particular, BPR values of 2, 4 and 6, corresponding to soil weights of 8, 4 and 2.66 g, respectively, were investigated.

Table 2
Operating conditions for milling trials

Parameter	Value	Reference
Mill type	Spex Mixer/Mill mod. 8000	–
Vial length (m)	5.8×10^{-2}	Spex Industries
Vial internal radius (m)	1.9×10^{-2}	Spex Industries
Mill arm length (m)	1.0×10^{-1}	Spex Industries
Weight of treated soil (g)	8, 4, 2.66	This work
Milling spheres weight (g)	8	This work
Ball to powder ratio	2, 4, 6	This work
Mill frequency (rpm)	870	Spex Industries
Impact velocity (m s^{-1})	4.168	[42]
Impact energy (J hit^{-1})	0.093	[42]
Impact frequency (hit s^{-1})	142	[42]
Milling time (h)	0.5–7	This work

Then, the vial was sealed under air atmosphere and fixed on the mill. Soils were mechanically treated for different time intervals. The operating conditions of ball-milling trials are summarized in Table 2.

At the end of each programmed time interval of mechanical treatment, as well as for untreated soils (i.e. milling time equal to 0), soils were suitably sampled to be analyzed. The degree of immobilization of heavy metals was evaluated using the "synthetic precipitation leaching procedure (SPLP)" reported by USEPA [43,44]. The latter one, being designed to simulate acid rain conditions, is useful to assess if a potentially contaminated material, once left "in situ", may release toxic substances when exposed to normal weathering. To perform the SPLP test, US EPA SW 846 Method 1312 [43,44] was taken into account by using an extraction fluid which consists of a 60/40 wt% sulfuric/nitric acid mixture diluted with 18.2 MΩ water to a final pH of 4.2 ± 0.05. A solid to liquid weight ratio equal to 1:20 was employed and the contact was assured for 18 h. Samples were filtered using a Whatman GF/F 0.70 μm filter. The concentration of heavy metal in the leachate was determined by ICP-OES (Vista MPX, Varian). It should be noted that at least two replicates of each experiment were taken into account. Immobilization efficiency, after each treatment interval, was calculated through the following equation:

$$\eta(t)\% = \left(1 - \frac{C(t) \times V_{\mathrm{leach}}}{q^{24\,\mathrm{h}} \times W_{\mathrm{solid}}}\right) \times 100 \tag{2}$$

where $\eta(t)\%$ is the immobilization efficiency (%) of the soil mechanically treated for a time interval equal to t(s), $C(t)$ (mg L^{-1}) is the heavy metal concentration in the leachate, V_{leach} is the leachate volume (L), $q^{24\,\mathrm{h}}$ (mg kg^{-1}) is the initial heavy metal concentration in the untreated soil (cf. Eq. (1)) and W_{solid} (kg) is the soil weight which undergoes the test. Immobilization efficiency represents an indicator of soil ability to entrap heavy metals in the solid matrix when subjected to the action of a specific leachant. In particular, if immobilization efficiency is equal to 100% no heavy metals are leached from the soil during the SPLP test. On the other hand, if immobilization efficiency is equal to 0%, all the heavy metals content is transferred to the fluid phase during the test.

Further analyses were performed in order to elucidate immobilization mechanisms and verify if soil alterations occurred during mechanical treatment. X-ray diffraction (XRD) were used to identify crystalline phases in solid samples. Analyses were carried out using a RIGAKU GEIGERFLEX diffractometer by employing Cu Kα Ni-filtered radiation ($\lambda = 15{,}418$ Å). XRD data were collected for values of 2θ between 10° and 90°. Scanning electron microscopy (SEM), and electron dispersive spectroscopy (EDS) microanalysis (HITACHI S 4000 Field emission equipped with a KEVEX SIGMA 32 probe at a resolution of 142 eV) were carried out in order to clarify heavy metal distribution within the solid matrix. Measurements of particle size distributions after each ball-milling treatment were performed by a laser granulometer CILAS 1180 in the range of length 0.04–2500 μm.

3. Results and discussion

Different contaminated soils mixtures were prepared as described in Section 2: a sandy soil, a clayey bentonitic soil and a clayey kaolinitic soil with a Pb(II) concentration in the solid phase of 39,000, 102,000 and 185,000 mg kg^{-1}, respectively. Once contaminated, the soils were mixed with HA amounts on a 5% (w/w) basis. In order to get some preliminary information about the effect of the addiction of HA on leachability of heavy metals, both the soils (unmilled) and soil–HA mixtures (unmilled) were subjected to the SPLP test.

The concentration of Pb(II) in the solution leached during the SPLP test of unmilled soils is equal to 596, 388, 1896 mg L^{-1} for the SS, BS and KS soils, respectively. For the soil–HA mixtures concentration of Pb(II) from the SPLP test is equal to 333, 228, 1783 mg L^{-1} for the SS, BS and KS, respectively.

From Fig. 1 it clearly appears that the corresponding intrinsic immobilization efficiencies (without the application of ball milling) are relatively high (i.e. 61.5%, 92.4%, and 73.9% for SS, BS and KS, respectively), even when HA is not added, thus highlighting the intrinsic capability of soils to adsorb Pb(II). In fact, according to Weng [45], it is possible to assume that when soil is contaminated, Pb(II) is adsorbed onto soil particles through a surface coordination process which may be represented as a complexation reaction between soil surface sites and Pb(II) species [45]. The following equilibria may be considered to describe Pb(II) adsorption onto the soil surface [45]:

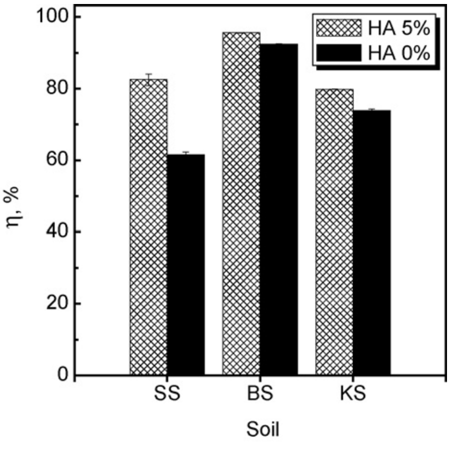


Fig. 1. Immobilization efficiency of Pb(II) for unmilled soils with and without the addiction of 5% of hydroxylapatite HA: SS—sandy soil, BS—bentonitic soil, and KS—kaolinitic soil.

$$\underline{S}O^- + Pb^{2+} \rightleftharpoons \underline{S}OPb^+ \tag{3}$$

$$\underline{S}O^- + Pb(OH)^+ \rightleftharpoons \underline{S}OPb(OH) \tag{4}$$

$$\underline{S}O^- + Pb(OH)_2^0 \rightleftharpoons \underline{S}OPb(OH)_2^- \tag{5}$$

$$\underline{S}O^- + Pb(OH)_3^- \rightleftharpoons \underline{S}OPb(OH)_3^{2-} \tag{6}$$

where $\underline{S}O^-$ refers to soil surface adsorption sites. These adsorption sites are represented mainly by the surface of silica or clay particles, but also Mn and Fe oxides (cf. Table 1), where similar adsorption mechanisms may take place [46]. Moreover, calcite present in the soil (cf. Table 1) may contribute to remove Pb(II) from the liquid phase through dissolution, followed by the precipitation of lead carbonates (i.e. cerussite) as shown in the following equilibria [47]:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{7}$$

$$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3 \downarrow \tag{8}$$

Since cerussite is characterized by a low solubility ($\log K_{sp} = -12.8$ [48]), if the content of calcite is high, such a mechanism may significantly contribute to lead immobilization.

Finally, also the humic acid may contribute to Pb(II) the immobilization capacity of soil by bounding the metal to the solid phase through the formation of specific organometallic complexes [49]. All these mechanisms may determine the high intrinsic immobilization efficiency of soils.

Although the intrinsic immobilization efficiency of soils, the concentration of Pb(II) in leachate from SPLP test is still higher than the USEPA regulatory thresholds for all the soils considered, thus indicating that a treatment or the use of an additive is needed. From Fig. 1 it is possible to observe that when 5% (w/w) of HA is added, immobilization efficiency of the resulting soil–HA mixtures further increases (81.75%, 93.3% and 79.8%, for SS, BS and KS, respectively). This fact is clearly due to the presence of HA which may promote specific mechanisms of subtraction of Pb(II) to the liquid phase.

Nowadays, these mechanisms are not yet fully understood and two theories to explain such behaviour are available. The first one attributes the immobilization capacity of HA to chemical precipitation and the second one to ion exchange [50]. In any case the result is the formation of hydroxypyromorphite ($Pb_{10}(PO_4)_6(OH)_2$) characterized by a very low solubility product ($\log K_{sp} = -76.8$ [48]).

In particular several studies [21,22,26,51–55] suggest that in an aqueous systems, Pb(II) may be removed through the breakage by dissolution of HA lattice, followed by the formation and precipitation of crystalline or amorphous lead orthophosphates (pyromorphites) according to the following reactions [22,56], respectively:

$$Ca_{10}(PO_4)_6(OH)_2(s)+14H^+ \rightarrow 10Ca^{2+}+6H_2PO_4{}^-+2H_2O \tag{9}$$

$$10Pb^{2+}+6H_2PO_4{}^-+2H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2(s)\downarrow +14H^+ \tag{10}$$

Laperche et al.[21] gave a confirmation of this mechanism through direct physical XRD patterns and SEM analysis by detecting hydroxypyromorphite particles after leaching of a soil–HA mixture with an aqueous solution.

On the other hand, it is assumed by other authors [24,56–59], that an ion-exchange mechanism may take place when a partial replacement of ions in the initial HA structure occurs without destruction of the HA lattice. In particular, according to this theory, Pb(II) would be adsorbed first on the surface of the HA particle, then, in parallel with diffusion phenomena, cation exchange would take place between apatite Ca^{2+} ions and Pb^{2+} ions in solution [60], as reported in the following reaction:

$$Ca_{10}(PO_4)_6(OH)_2(s) + x\,Pb^{2+} \rightarrow (Ca_{10-x}Pb_x)(PO_4)_6(OH)_2(s) + x\,Ca^{2+} \tag{11}$$

Although mechanisms involved in immobilization of Pb(II) using HA as additive are not yet well understood, several experimental results highlighted the effectiveness of such technique. Since large values of HA may give rise to phytotoxic effects on soil, the aim of this part of the work is to examine if the application of mechanical treatment on soil–HA mixtures may improve their immobilization efficiency, thus permitting to use less HA in order to avoid such negative effects. The objective is to verify if mechanical treatment would promote transformations on soil as well as HA particles which may improve the immobilization efficiency of the soil–HA mixtures. The effect of mechanical treatment on Pb(II) immobilization efficiency, under different milling regimes (i.e. BPR equal to 2, 4 and 6) and for different treatment times, is shown in Fig. 2a–c. The HA percentages have been fixed to 5% (w/w) for each treated soil.

From Fig. 2 it should be noted that immobilization efficiency (cf. Eq. (2)) increases when the soil–HA mixtures are mechanically treated and such effect is more evident when the milling time is augmented. The kaolinitic soil–HA mixture (cf. Fig. 2c) appears to be the most sensitive to the mechanical action since immobilization efficiency increases from 79.4% in absence of treatment to 99.9% when the soil is treated for 3 h with a BPR equal to 4. From Fig. 2a it may be seen also that the SS soil–HA mixture significantly increases its immobilization efficiency when milled. In particular, immobilization efficiency of the SS soil–HA mixture may be augmented from an intrinsic value of 82.8 to 99.98%, when mechanical treatment is prolonged up to 5 h with a BPR equal to 4. The less sensitive soil appears to be the bentonitic soil–HA mixture (cf. Fig. 2b) whose immobilization efficiency increases from 93.3% in absence of treatment to a value of 99.98% when milled for 3 h with a BPR equal to 4. However, the last result does not indicate that the BS soil is insensitive to mechanical treatment but clearly depends on the high intrinsic immobilization efficiency of the soil. On the contrary, by analyzing Fig. 2, it may be seen that immobilization efficiency is not influenced by the BPR parameter for all the soil–HA mixtures considered.

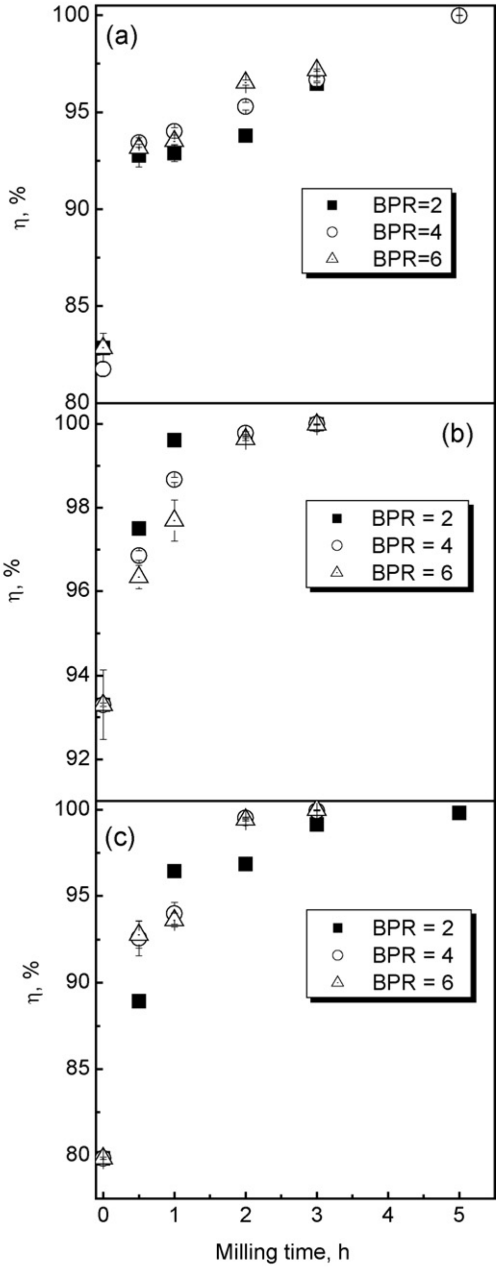


Fig. 2. Effect of mechanical treatment on immobilization efficiencies of soil–HA (5%) mixtures: (a) SS—sandy soil, (b) BS—bentonitic soil, and (c) KS—kaolinitic soil.

These results highlight that mechanical treatment may induce specific transformations on soil and HA particles that cause an increase of the immobilization efficiency of the corresponding soil–HA mixtures. A possible explanation of the phenomena induced by the mechanical treatment on the soil particles will be given in the final part of the paper. As far as the modifications induced on HA particles by mechanical treatment are concerned, it is reasonable to assume that a particle refining is obtained as a result of milling. This fact probably leads to an increase in the specific surface area of HA particles onto which dissolution or ion-exchange phenomena may take place (cf. Eqs. (9)–(11)). Moreover, the accumulation of crystalline defects (amorphization) on the HA lattice may determine a thermodynamic instability of HA particle surfaces which may determine an higher tendency to react or dissolve according to Eqs. (9)–(11).

Anyway, experimental results highlight that the mechanical treatment, under the operating conditions previously described, increases immobilization efficiency of soil–HA mixtures. To verify if the mechanical treatment allows to maintain high immobilization efficiencies even when using less amounts of HA, milling trials with different HA (w/w) percentages in the soil–HA mixtures were performed.

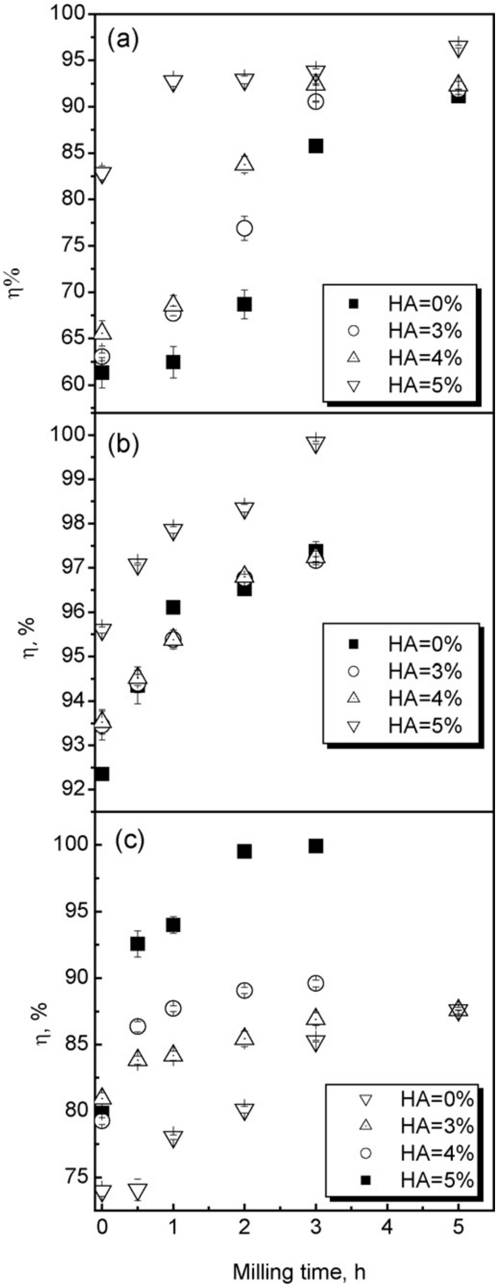


Fig. 3. Effect of mechanical treatment where the ball to powder ratio (BPR) is equal 4 on immobilization efficiencies of soil–HA mixtures obtained using different amounts of HA: (a) SS—sandy soil, (b) BS—bentonitic soil, and (c) KS—kaolinitic soil.

Fig. 3 shows the results of the milling trials on the soil–HA mixtures containing 0%, 3%, 4% and 5% (w/w) of HA, respectively. The BPR parameter was fixed to 4 for each trial.

Fig. 3 confirms that mechanical action determines an increase of immobilization efficiency for each amount of HA in the soil–HA mixture. From Fig. 3a it may be seen that by prolonging mechanical action up to 5 h, immobilization efficiency of the SS–HA mixtures reaches the same value (about 92%) when different percentages of HA (0%, 3%, 4%) are used. In particular, the sandy soil without HA (0%), when milled for 5 h, is characterized by the same immobilization efficiency of the soils–HA mixtures containing 3% and 4% of HA and milled for the same time. This fact indicates that, within the compositional range 0–4%, a suitably prolonged mechanical action may represent a valid alternative to the use of HA for immobilization of Pb(II) in sandy soils. From Fig. 3a it should be noted that SS–HA mixtures containing HA percentage equal to 5%, shows an immobilization efficiency higher than the one of the other mixtures (0%, 3%, 4%) at each milling time considered. Anyway, when mechanical action is prolonged, the immobilization efficiency of the mixtures containing less HA (0%, 3%, 4%) reaches values higher than the ones obtained for mixtures containing 5% of HA, without any mechanical treatment. This means in turn that the latter one may represent a valid alternative to the use of high percentages of HA.

Similar results have been obtained for the bentonitic soil (cf. Fig. 3b) BS. In this case no significant differences are detected when using BS containing 0%, 3% and 4% of HA, respectively. In particular, when subjected to mechanical treatment for 5 h, the three mixtures show an immobilization efficiency equal to 97.16%. For the BS–HA mixture containing 5% (w/w) of HA, higher values of immobilization efficiencies may be obtained. In particular, when milled for 5 h, the BS–HA-5% mixture shows an immobilization efficiency equal to 99.82%.

When considering the KS–HA mixtures (cf. Fig. 3c), it should be noted that an immobilization efficiency close to 99.94% may be obtained by mechanically treating the soil for 3 h with 5% HA (w/w). Similar considerations as those ones reported above can be made.

These results show that mechanical action is able to improve the immobilization efficiency of all the considered soil–HA mixtures. In particular, it may be observed that by mechanically treating the soil–HA mixtures the percentage of HA employed can be drastically reduced, thus avoiding phytotoxic effects [22] and obtaining immobilization efficiencies higher than the ones reachable with larger amounts of HA without mechanical treatment. Moreover, the soils where no HA is added, after a mechanical treatment of 5 h, reach approximately the same immobilization efficiency obtained by the soils with 3% and 4% of HA, respectively. In order to verify if high immobilization efficiencies may be achieved by mechanically treating soils without HA further experiments were performed. The absence of HA in fact may improve the economical feasibility of the technique and, at the same time, contributes to avoid negative

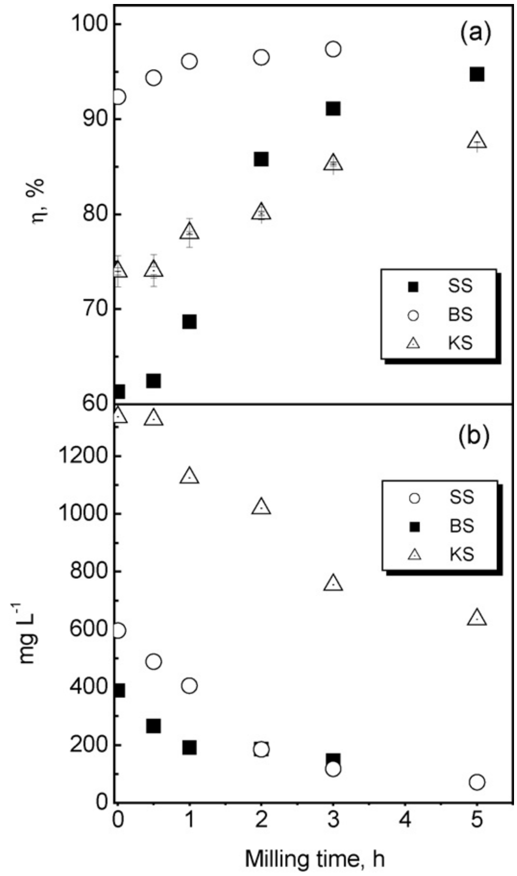


Fig. 4. Effect of mechanical treatment where the ball to powder ratio (BPR) is equal 4 on (a) immobilization efficiency of Pb(II) in soils and (b) Pb(II) concentration in leachate from SPLP (synthetic precipitation leaching procedure) test: SS—sandy soil, BS—bentonitic soil, and KS—kaolinitic soil.

effects such as phytotxitcity and chemical modification of the intrinsic properties of the soil.

The following synthetic soils contaminated by heavy metals (Cd(II), Pb(II), Zn(II)) were prepared: a sandy soil contaminated with Pb(II), Cd(II) and Zn(II) concentrations of 32,875, 20,000 and 28,000 mg kg^{-1}, respectively; a bentonitic soil with Pb(II), Cd(II) and Zn(II) concentration levels of 107,181, 20,000 and 10,000 mg kg^{-1}, respectively; a kaolinitic soil contaminated by Pb(II), Cd(II) and Zn(II) concentrations of 107,857, 24,000 and 17,000 mg kg^{-1}, respectively.

Pb(II) in the leachate from the SPLP test of untreated soils was equal to 596, 389 and 1330 mg L^{-1} for the SS, BS and KS soils, respectively. According to Eq. (2), these values correspond to intrinsic immobilization efficiency of 61.3%, 92.4% and 73.9%, respectively.

The effect of mechanical treatment, suitably prolonged for different milling times, on Pb(II) immobilization efficiency and on Pb(II) concentration released in the leachate from SPLP test are shown in Fig. 4a and b, respectively. It clearly appears that the immobilization efficiency increases when the soil is mechanically treated and this effect is more evident when the milling time is augmented. It should be noted that the sandy soil (SS, cf. Fig. 4a) seems to be the most sensitive to the mechanical action since immobilization efficiency increases from 61.3% in absence of treatment to 94.8% when the soil is treated for 5 h. Correspondingly, the concentration of Pb(II) released in the leachate dramatically decreases, being its concentration reduced from 596 to 70 mg L^{-1}. The effect of mechanical treatment on clayey soils (BS and KS) is less evident. However, also in this case, an increase of immobilization efficiency may be observed when the milling time is augmented. In particular, BS soil is characterized by an high intrinsic immobilization efficiency (92.4% for the untreated soil) which may be increased up to value of 97.44% by treating the soil for 3 h with BPR equal to 4. Correspondingly, Pb(II) concentration in leachate decreases from 388 to 146 mg L^{-1}. When considering the clayey KS soil (cf. Fig. 4b), a relevant increase of the immobilization efficiency (from 73.9% to 87.6% after 5 h of mechanical treatment with BPR equal to 4) may be observed. Correspondingly, Pb(II) concentration in leachate is reduced from 1336 to 635 mg L^{-1}, respectively (cf. Fig. 4b).

For the case of Cd(II) contaminated soils, the following concentrations levels have been found in the leachate when the untreated soils were subjected to the SPLP test: 17.59, 39.57 and 36.97 mg L^{-1} for the SS, BS and KS soils, respectively. The latter values correspond to intrinsic immobilization efficiencies equals to 89.37%, 79.63% and 76.93%, respectively. The increase of immobilization efficiency of the Cd(II) within

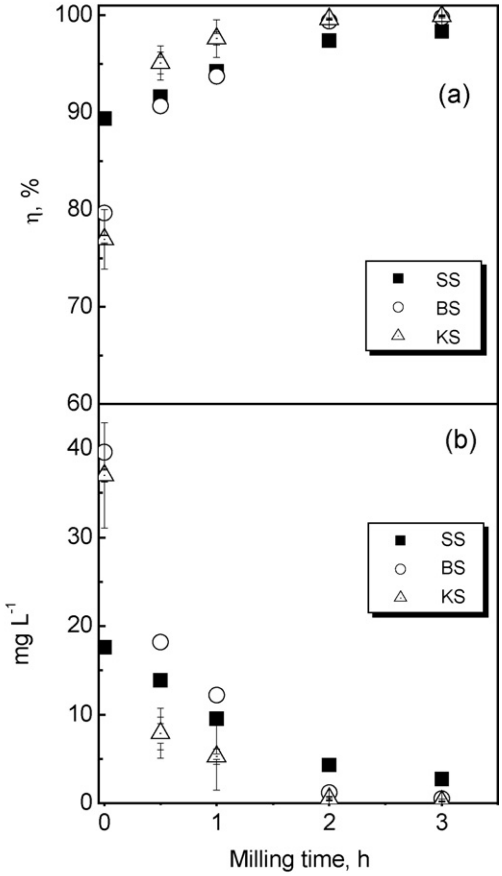


Fig. 5. Effect of mechanical treatment where the ball to powder ratio (BPR) is equal 4 on (a) immobilization efficiency of Cd(II) in soils and (b) Cd(II) concentration in leachate from SPLP (synthetic precipitation leaching procedure) test: SS—sandy soil, BS—bentonitic soil, and KS—kaolinitic soil.

the considered soils induced by ball milling is shown in Fig. 5a. The corresponding values of Cd(II) concentrations detected in the leachate, obtained when the treated soils is subjected to the SPLP test, are shown in Fig. 5b. From these figures it is possible to observe that, by prolonging the mechanical action, immobilization efficiencies of Cd(II) for all the treated soils increase. In particular, the kaolinitc soil (KS, cf. Fig. 5a) seems to be the most sensitive to the mechanical action since immobilization efficiency increases from 76.93% in absence of treatment to 99.89% when the soil is treated for 5 h. Correspondingly, Cd(II) concentrations in the leachate decreases from 36.97 to 0.2 mg L^{-1}. Bentonitic soil shows a similar behaviour since a significant increase of the immobilization efficiency of Cd(II) (from 79.63% to 99.75% after 5 h of mechanical treatment) may be observed (cf. Fig. 5a). The concentration of Cd(II) in leachate, correspondingly, decreases from 39.57 to 0.47 mg L^{-1}. Fig. 5a shows that immobilization efficiency of sandy soils is less sensitive to mechanical treatment. This behaviour may be probably ascribed to the higher intrinsic immobilization efficiency for Cd(II) (89.37% for the untreated soil). However, also in this case, immobilization efficiency may be increased up to value of 98.33% by mechanically processing the soil for 5 h being the Cd(II) concentration in leachate decreased from 17.59 to 2.75 mg L^{-1}.

Fig. 6a and b shows that also for Zn(II) mechanical treatment induced transformations on soils which result in an increased immobilization efficiency. In this case the less sensitive soil appears to be the BS one, since its immobilization efficiency increases from 90.35%, when untreated, to 95.96%

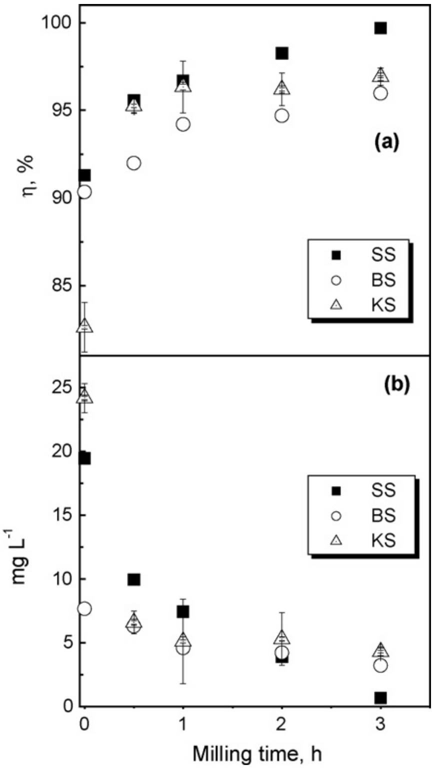


Fig. 6. Effect of mechanical treatment where the ball to powder ratio (BPR) is equal 4 on (a) immobilization efficiency of Zn(II) in soils and (b) Zn(II) concentration in leachate from SPLP (synthetic precipitation leaching procedure) test: SS—sandy soil, BS—bentonitic soil, and KS—kaolinitic soil.

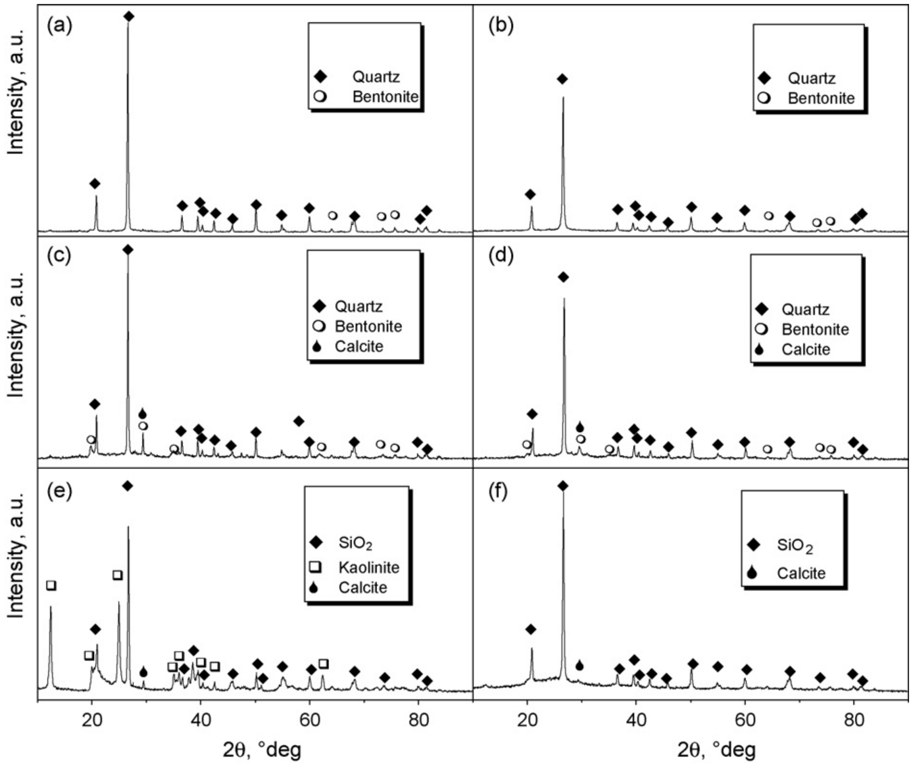


Fig. 7. XRD (X-ray diffraction) patterns for untreated soils: (a) SS—sandy soil, (c) BS—bentonitic soil, and (e) KS—kaolinitic soil and after 5 h of mechanical treatment where the ball to powder ratio (BPR) is equal 4: (b) SS—sandy soil, (d) BS—bentonitic soil, and (f) KS—kaolinitic soil.

when treated for 5 h. This fact may be explained with the higher intrinsic immobilization efficiencies of Zn(II) in the BS soil. Similar behaviour may be observed (cf. Fig. 6a) for the SS soil, although in this case an higher immobilization efficiency (99.7%) of Zn(II) can be achieved by mechanically treating the soil for 5 h. For the case of Zn(II) the most sensitive soil appears to be the kaolinitic one. In fact from Fig. 6a it is worth noting that mechanical treatment determines an increase of immobilization efficiency from the starting value of 82.63–96.91%, when prolonged for 5 h. The corresponding concentrations of Zn(II) in leachate may be extrapolated from Fig. 6b.

As a general conclusion, by considering the results reported in Figs. 4–6, it may be pointed out that mechanical action determines an important increase of immobilization capacity of the investigated soils for all the considered heavy metals.

In order to elucidate the mechanisms which determine the increase of the immobilization capacity of the contaminated soil and to verify if mechanical treatment causes drastic alterations of the original soil properties, further analyses on untreated and treated soils have been performed. Specifically, XRD analyses on untreated and mechanically treated (5 h) SS, BS, and KS soils, respectively, may be seen in Fig. 7. In particular, it is apparent from Fig. 7a and b that the same crystalline phases, i.e. quartz and bentonite are detected for SS before and after the mechanical treatment. Analogously, quartz, bentonite and calcite are found as unchanged crystalline phases for the case of BS, as it is apparent from Fig. 7c and d. This fact indicates that no reactions between soil compounds or phase transformations took place during the mechanical treatment of SS and BS soils. The only detectable effect is a partial amorphization of phases confirmed by a small decrease of XRD peak intensity. This is a typical effect induced by ball-milling treatment which determines an accumulation of structural defects, vacancies and dislocations resulting in a loss of cristallinity of soil compounds [29,30]. However, as clearly shown in Fig. 7a–d, only a weak amorphization took place for SS and BS and no significant alterations of the crystalline structure was revealed. On the contrary, mechanical treatment induced clear alteration of the crystalline structure of the kaolinitic soil (KS). As it may be seen from Fig. 7e and f, peaks related to kaolinite of the untreated KS soil (cf. Fig. 7e) disappear when the same soil was subjected to 5 h of mechanical treatment. This finding indicates that mechanical treatment causes the degradation of the crystalline structure of kaolinite. Similar results have been obtained by Frost et al. [61], which attributed the degradation of the crystal structure of kaolinite to the breakage of the O–H, Al–OH and Si–O bounds induced by dry grinding.

In Fig. 8, the effect of ball-milling treatment on particle size distribution is shown. In particular, a comparison between particle size distribution for BS, SS and KS soils, before and after 3 h of mechanical treatment (BPR = 4), is reported. It should be noted that for all soils considered the mechanical action induced an increase of particle size rather than a size refinement. This effect may be explained considering that aggregation phenomena may prevail on breakage ones. This behaviour may play a very important role, as it will be discussed in what follows, in soil immobilization efficiency induced by mechanical treatments.

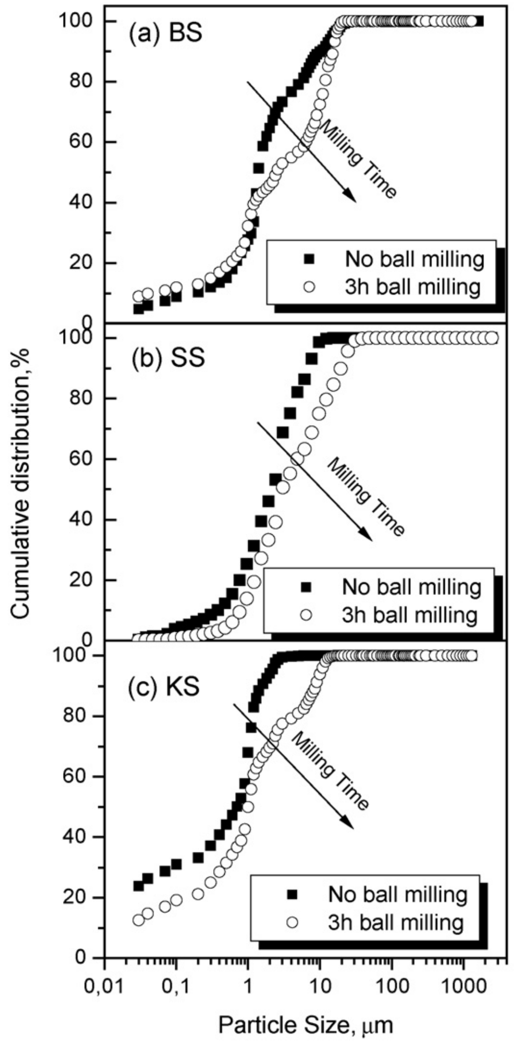
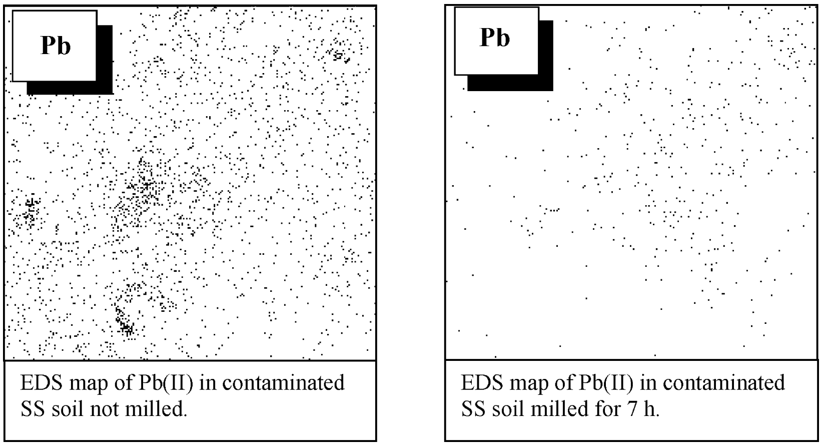


Fig. 8. Particle size distribution for untreated and treated soils after 3 h of milling: (a) BS—bentonitic soil, (b) SS—sandy soil and (c) KS—kaolinitic soil.

In Fig. 9, EDS maps related to Pb(II) in contaminated SS soil before and after 7 h of mechanical treatment are shown. Since EDS analysis qualitatively indicate the presence of heavy metals bound to the solid particle surface, from Fig. 9 it is possible to observe that the amount of Pb(II) detectable on soil particle surface decreases after milling. This fact probably indicates that a certain amount of Pb(II) has been entrapped inside new aggregates produced during the mechanical treatment. The reduction of Pb(II) amount on particle surface is a possible explanation of the increase of immobilization efficiency after milling. Similar results have been obtained for BS and KS soils. For the sake of brevity, EDS maps for these soils are not reported. Finally, it is reasonable to assume that the same mechanisms may be involved in the immobilization of the other investigated heavy metals (Cd(II) and Zn(II)).

The understanding of phenomena involved during mechanical treatment of soil and specifically those ones related to the immobilization capacity of soils is quite difficult. Solid matrix



EDS map of Pb(II) in contaminated SS soil not milled.

EDS map of Pb(II) in contaminated SS soil milled for 7 h.

Fig. 9. Electron dispersive spectroscopy (EDS) maps of Pb(II) in contaminated SS (sandy soil) before and after 7 h of milling where the ball to powder ratio (BPR) is equal 4.

of contaminated soils is a very complex system and its interactions with heavy metals is still not well understood. Moreover, the application of impulsive mechanical loads further complicates the picture. On the basis of experimental results, only some hypotheses may be formulated about mechanisms responsible of the immobilization capacity enhancement due to mechanical treatment. In what follows the case of Pb(II) contaminated soil is taken into account.

First it is possible to assume that when soil is contaminated, Pb(II) is adsorbed onto soil particles (cf. Fig. 10) through the surface coordination process previously described through reactions (3)–(6).

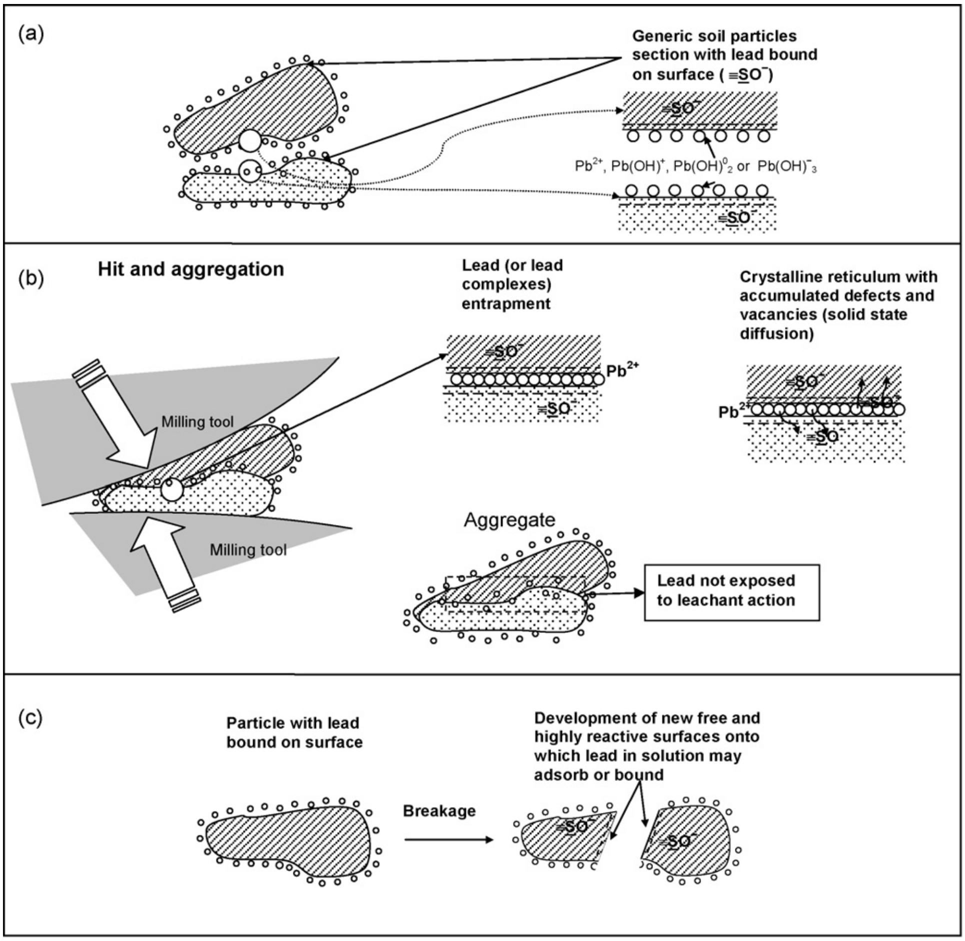


Fig. 10. Schematic representation of possible mechanisms which may determine the increase of immobilization efficiency of soils after milling: (a) Pb(II) adsorption, (b) aggregation, and (c) breakage.

When ball-milling process starts, soil particles are subjected to high energetic collisions that may promote aggregation and breakage phenomena as well as accumulation of crystalline defects and vacancies (amorphization). The occurrence of aggregation phenomena with a subsequent formation of stable aggregates results in a net increase of particle size of soils as confirmed by the data shown in Fig. 7. When aggregation occurs, the amount of Pb(II) adsorbed on the surface of two overlapping particles may be entrapped within the new formed aggregate (cf. Fig. 10b). In this way the amount of Pb(II) exposed to the leaching action is reduced thus determining an higher immobilization capacity. Moreover, since the accumulation of dislocations and vacancies in crystalline reticulum determines an increase of diffusivity within the solid matrix [62], it is possible to assume that Pb(II) complexes may diffuse within the crystalline reticulum of soil particles thus leading to a very efficient chemical entrapment of Pb(II) within the soil (cf. Fig. 10b).

On the other hand, also breakage phenomena, taking place in parallel with the aggregation ones, may determine an increase of immobilization efficiency. In fact, as shown schematically in Fig. 10c, when a contaminated soil particle breaks, it develops new "fresh" surfaces onto which Pb(II) ions may re-adsorb according to the equilibria described in reactions (3)–(6). These phenomena result in a higher adsorption capacity with respect to adsorb Pb(II), thus increasing its immobilization efficiency. The same mechanisms may be reasonably taken into account in order to explain the increase of immobilization efficiency of soils related to the other heavy metals investigated (Cd(II) and Zn(II)).

At the moment, the experimental results do not support the existence of further transformations that contribute to the increase of immobilization efficiency due to mechanical treatment of soil. In any case, although all phenomena taking place during mechanical treatment are not yet completely understood, the experimental results confirm that for the considered soils (i.e. SS, BS and KS) and for all milling regimes adopted (i.e. BPR equal to 4), the immobilization capacity increases because of the effect of mechanical action.

For this reason, further investigations have been performed in order to assess the efficiency of mechanical treatment on soils contaminated by heavy metals when considering concentration levels close to those ones of field contaminated soils, i.e. 100–1000 mg kg^{-1} for Pb(II) [63,64], 1–180 mg kg^{-1} for Cd(II) and 1000–50,000 mg kg^{-1} for Zn(II) [65]. To this, aim SS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 621.5, 88.6 and 1002 mg kg^{-1}, respectively; BS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 954.4, 98.0 and 1175 mg kg^{-1}, respectively; KS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 939.4, 76.28 and 915.0 mg kg^{-1}, respectively, were prepared and then mechanically processed for different times (BPR = 4). Zn(II), Cd(II) and Pb(II) concentrations in leachate from SPLP test after each milling trial are reported in Fig. 11a–c, respectively. It may be clearly seen that leachable heavy metals concentration significantly decrease after milling. It is worth noting that after a mechanical treatment applied for relatively short times (i.e. 7 h for Pb(II) and 3 h for Cd(II) and Zn(II), respectively) heavy metal concentration in leachate from SPLP test is lower than the regulatory limit (i.e. 0.015, 0.005 and 0.5 mg L^{-1} for Pb(II), Cd(II) and Zn(II), respectively) proposed by USEPA [43] for drinkable water.

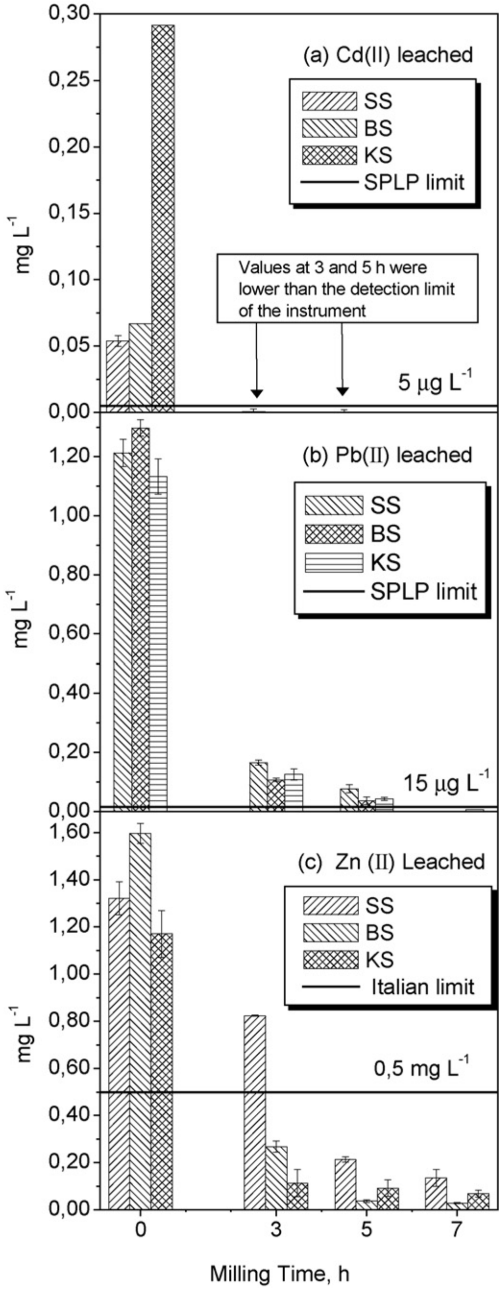


Fig. 11. Effect of mechanical treatment where the ball to powder ratio (BPR) is equal 4 on the leachable fraction of heavy metals in soils and comparison with USEPA thresholds for (a) Cd(II), (b) Pb(II) and (c) Zn(II): SS—sandy soil, BS—bentonitic soil, and KS—kaolinitic soil.

These results appear to be very promising and the ball-milling technique may be considered potentially applicable for the remediation of contaminated soil by heavy metals. A possible flow sheet for the engineering application of the investigated technique on a larger scale is shown in Fig. 12. It takes into account excavation of the contaminated soil followed by sieving in order

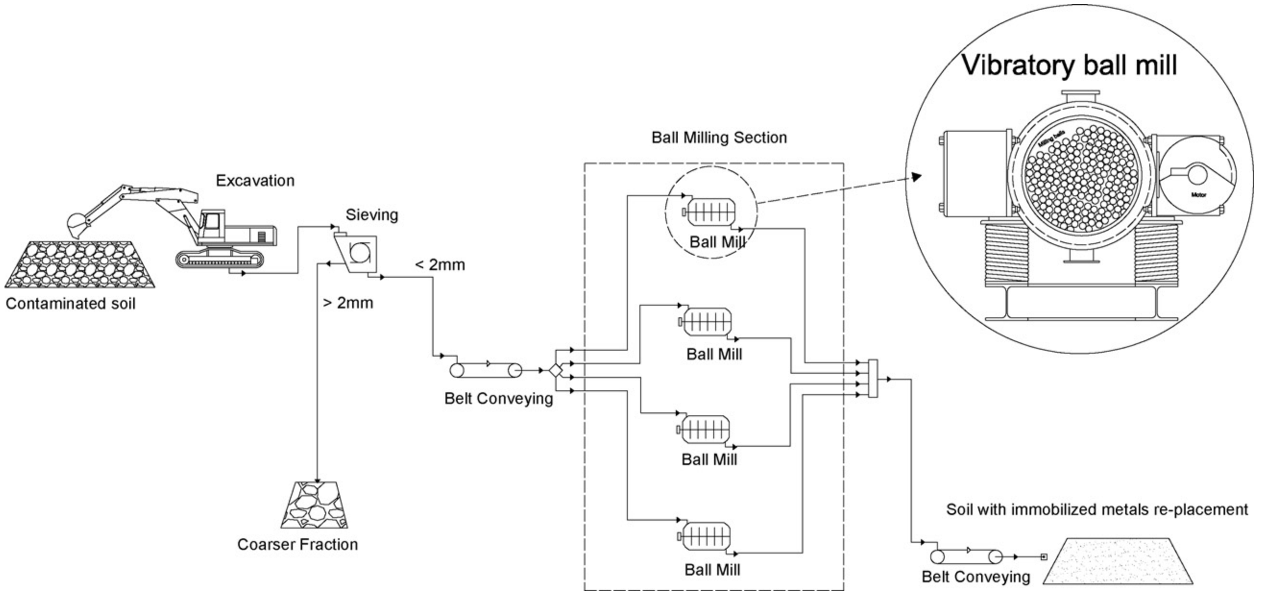


Fig. 12. Schematic flowsheet of the process proposed for the transposition of the investigated remediation technique to the real scale.

to separate the coarser (not contaminated) fraction. The soil is then transferred to the ball-milling section through suitable belt conveyors along with hydroxylapatite if necessary. In the milling section, ball-mills may assure the desired heavy metals immobilization by operating in batch mode for suitable times. A vibratory mill, already on the market (cf. [66]) may be employed to perform mechanical treatment. Once treated the soil may be discharged from mills and then placed “in situ”.

3.1. Concluding remarks

The use of HA for the immobilization of heavy metals in contaminated soils is a well known technology. The main disadvantage of this technology is that the use of high percentages of HA (>5%) may determine phytotoxic effects, high operating costs and alterations of the intrinsic properties of soils. Experimental results show that immobilization efficiency of Pb(II) in soil–HA mixtures may be strongly increased through a suitably prolonged mechanical treatment. In this way, by mechanically treating the soil–HA mixtures, high immobilization efficiencies can be obtained by using lower percentages of HA (3%), thus avoiding negative effects produced by the use of large amounts of HA. In particular, immobilization efficiencies obtained by treating the mixtures containing 3% of HA for 5 h are higher than those obtained with the unmilled mixtures containing 5% of HA. The increase of immobilization capacity with milling may be probably ascribed to phenomena such as entrapment of Pb(II) into new formed aggregates of soil particles and re-adsorption of lead on new “fresh” surfaces produced through breakage. Moreover, mechanical treatment may activate HA by increasing its specific surface and/or determining an increasing amount of defects which induces an higher HA reactivity. This fact in turn may determine an increased tendency of HA to dissolve and recombine with Pb(II), thus producing low soluble products (i.e. pyromorphyte) or to react, through ion-exchange mechanisms, with Pb(II), thus determining an high efficiency in the immobilization of Pb(II).

In order to verify if the effect of mechanical treatment may avoid the use of HA, further experiments were performed on the contaminated soils without the use of any exogenous reactant. In this case also Cd(II) and Zn(II) contaminated soils were considered. Experimental results show that also in this case immobilization of heavy metals can be achieved through mechanical treatment. In particular, immobilization efficiency may be strongly increased for all the considered heavy metals, i.e. Cd(II), Pb(II) and Zn(II), as milling time is augmented. In addition, under the operating conditions investigated in this work, no significant alterations of the original characteristics of the SS and BS soils are detected except for a weak amorphization and a relative increase of particle size. Only for the KS soil, instead, mechanical treatment determined the total amorphization of kaolinite.

Finally, when mechanical treatment is applied to soils which simulate real contaminated ones, very promising results were obtained. In fact, after relatively short milling times, leachable fraction of heavy metals from each soils was reduced under the EPA regulatory limits for drinkable water. These results demonstrate the potential applicability of this technique for the remediation of field situations. Moreover, it is important to remark that, contrarily to what happens for classical immobilization technologies, these last results have been obtained without any reactant addition and taking advantage of very simple apparatus. These aspects are particularly encouraging in view of a possible technological transposition of the proposed technique.

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