

Mechanochemical immobilization of heavy metals in contaminated soils: a novel mathematical modeling of experimental outcomes

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Abstract

Mechanochemical processing to immobilize heavy metals in contaminated soils has been proposed few years ago by our research group. The corresponding experimental results have shown that, under specific operating conditions, the mechanical energy provided by suitable ball mills, can greatly reduce heavy metals mobility without the addition of any reactant. Such results, together with the extreme simplicity of the proposed technique, are still very promising in view of its industrial transposition. Along these lines, the use of suitable mathematical models might represent a valuable tool which would permit to design and control mechano-chemical reactors for field applications. In this work, a simple albeit exhaustive model is proposed for the first time to quantitatively describe the effects of the dynamics of milling process, such as impact frequency and energy, on the immobilization kinetics. Model results and experimental data obtained so far are successfully compared in terms of leached heavy metals and immobilization efficiency evolution with treatment time. Finally, the potential capability of the model to contribute to the industrial scale transposition of the proposed technique is addressed.

Keywords: mechano-chemical treatment; heavy metals immobilization; soil remediation; mathematical modelling; technology scale-up.

1. Introduction

Heavy metals represent one of the most important categories of soil pollutants resulting from anthropic activities such as, metal mining, electronic waste disposal, metallurgy, smelting and refining, pesticide usage, car shredding, gasoline processing, etc. [1–6]. As a result, there is currently the need of economically sustainable technologies to remediate heavy metals contaminated soils without affecting their relevant character. To this aim, heavy metals immobilization techniques that minimize the use of synthetic reactants or extreme operating conditions, such as high temperature, are required. Along these lines it was recently demonstrated that the mechanical treatment of different soils, within specific ball milling devices, under proper operating conditions and for suitably prolonged periods of time, is capable of reducing heavy metals mobility in soils thus minimizing their pollution potential [3,4,7–11]. Such result was achieved by using very small amounts of reactants, or even no reactants at all, and thus determining only negligible changes of the chemical and structural properties of the soil [3,4,7–11]. These aspects are very interesting if one also considers that the unit cost of soil mechano-chemical treatment was recently estimated to be of about 76 Euro m⁻³ and thus competitive with the current best available technologies for soil-remediation [1].

Typically, the mechano-chemical treatment consists of providing mechanical energy to the soil particles entrapped between milling bodies that collide or shear each other because of the motion of the device wherein they are contained. Depending on the specific soil/reactant/pollutant system considered, the energy supplied to the mixture is capable to promote very different physico-chemical transformations that in turn may result in the effective degradation or immobilization of a wide range of organic and inorganic pollutants [3,10,19,11–18]. In particular, when focusing on heavy metals, Mallampati et al. were capable to immobilize about 98-100% of As, Cd, Cr and Pb in mica/fibrolite soils by mixing it with Ca/CaO and treating the resulting mixture in a magnetic grinder for about 6h [8,20]. A very high immobilization efficiency, i.e. 98-100 %, was achieved by the same research group when treating Cs-contaminated soils with reactantssuch as Fe/Ca/Cao or NaH₂PO₄ through both planetary and tumbling ball mills for 1-2 h [3]. Recently, the possibility to use the mechano-chemical technique to reduce and immobilize Cr (VI) in soils was investigated by Yuan et al. [21]. In particular,

it was shown that the leaching concentration of Cr (VI) could be reduced from 115 mg L^{-1} to 0.51 mg L^{-1} by mixing the soil with calcium polysulfide and milling the resulting mixture in a planetary mill for about 4h [21].

However, the most promising results were obtained by Montinaro et al., who achieved immobilization efficiencies close to 100% for a wide spectrum of heavy metals in both synthetic and real contaminated soils without adding any reactant while only grinding them through Spex or Attritor mills [4,10,11,22]. These results have been recently confirmed by Yuan et al., who were capable to reduce the leachable heavy metals concentrations below the surface water regulatory thresholds of the Chinese Ministry of Ecology and Environment by treating a real contaminated soil within a planetary ball mill without adding any reactant [23]. Similar results were then obtained by Nenadović et al., who reported that Pb adsorption onto natural kaolinite, a typical component of natural soils, was increased by mechano-chemical treatment [24]. A further confirmation of these results is provided by Chen et al., who demonstrated the possibility to completely suppress heavy metal leaching from fly ashes through ball milling [25].

Despite the relevance of these results, the physico-chemical phenomena leading to the increase of heavy metal immobilization efficiency when grinding the soil are still not completely understood and only some hypothesis have been so far formulated. Among them, one of the most realistic is that one proposed by Montinaro et al. [4,10,11,22] and schematically depicted in Figure 1. Accordingly, during the initial steps of the milling process soil particles undergo breakage phenomena which lead to the opening of fresh, highly reactive, surfaces characterized by the presence of negative charges as a result of the rupture of crystalline lattice. The positive charged heavy metals can thus effectively adsorb or bound on these surfaces (cf. Figure 1a). This mechanism would be “per se” capable of reducing heavy metal leachability. However, when the process is further prolonged, broken particles tend to form aggregates due to electrostatic attraction or cold welding (cf. Figure 1b) as it may be seen from the increase of mean particle size measurement and the SEM analyses reported by Montinaro et al. [4,10,11,22]. The further mechanical processing provokes the consolidation of these aggregates wherein heavy metals remains buried and thus physically subtracted to the leaching action.

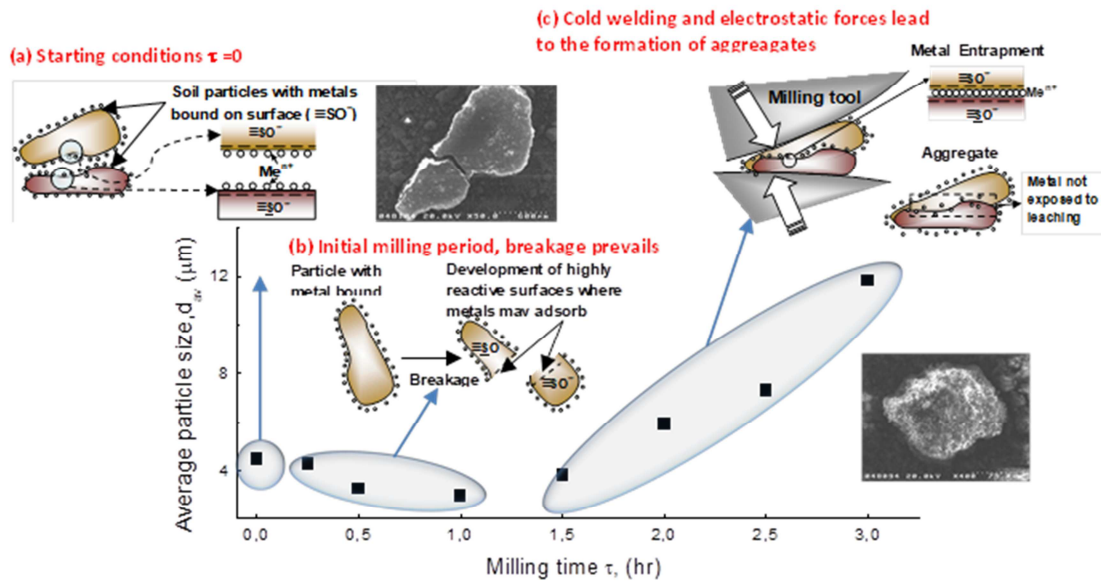


Figure 1. Evolution of mean particle size during grinding and possible phenomena leading to the entrapment of heavy metals (re-elaborated from [4,10,11,22]).

To further shed light on the mechanisms underlying the increase of immobilization efficiency, Montinaro et al. performed sequential extraction procedures of treated and untreated soil [11]. The goal was to verify whether the mechanical treatment had provoked a variation in the distribution of heavy metals among the different soil components. The obtained results showed that ball milling treatment led to a dramatic reduction (about 100%) of the exchangeable fraction of Pb. Even the amount of metal bound to the carbonatic and residual fraction of the soil was significantly reduced after milling. Simultaneously, a dramatic increase of the heavy metal bound to Fe/Mn oxides, ranging from +200 to +450% depending upon the soil considered, was observed. Therefore a sort of trans-speciation of Pb, which preferably bound to the Fe/Mn oxides fraction of the soil, was observed after milling. In fact, due to the presence of unpaired electrons on the newly formed surface, Fe/Mn oxides are well known to be strong physical sorbents [1] with respect to heavy metals. As a consequence, the leachability of the latter ones is strongly reduced. Moreover, according to the literature [26], the high energy milling of hematite (Fe_2O_3) might provoke the formation of magnetite small micro- and nano-particles that are capable of effectively adsorbing several heavy metals [27–29].

Finally, according to Montinaro et al., mechano-chemical treatment turned out to be able of increasing the amount of metal bound to organic matter [11] which is capable to chelate heavy metals by forming

stable organometallic complexes at functional OH groups. High energy milling of silica can trigger the formation of highly reactive radicals that, in turn, can react with organic compounds characterized by long and branched structures such as humic acids. Such reactions would lead to the formation of shorter structures and the corresponding increase of OH functional groups onto which heavy metals can bind.

While the mechanisms above might all synergistically contribute to the observed reduction of heavy metals mobility in soils after mechanical treatment, it is apparent that further research efforts are needed to quantitatively and simultaneously take into account the majority of chemical physical phenomena which are responsible of the observed heavy metal leachability decrease.

In view of better understanding the process, mathematical models could be very helpful. Moreover, the availability of a modelling tool for the quantitative interpretation of the observed experimental results would be crucial to suitably scale-up the obtained results and properly control, design and optimize ball mills operating at the field scale to remediate real contaminated soils. However, to the best of our knowledge, no mathematical models have been so far proposed in the literature to quantitatively interpret mechano-chemically promoted heavy metals immobilization in soils. For this reason, a novel theoretical tool is proposed in this work to simulate the increase of heavy metals immobilization efficiency with milling. The model is then validated by comparison with literature experimental data [4,10,11,22].

2. Materials and methods

A brief description of the experimental procedures, that is organized as shown in the scheme of Figure 2, is reported in what follows for the sake of clarity. Meaning of the symbols is better explained in the modeling section of the manuscript. For a detailed description of materials and methods adopted during the experimental trials, the interested reader should refer to the literature [4,9,10].

2.1 Synthetic soils preparation

High purity CaCO_3 , SiO_2 , bentonite, kaolin, Fe_2O_3 , MnO_2 , and humic acid were mixed in order to prepare sandy soils (SS), kaolinitic soils (SK) and bentonitic soils (SB). In sandy soil, the main components were SiO_2 (78 % wt) and bentonite (20 % wt), respectively. In kaolinitic one, the main

compounds were kaolin (60 %wt) and SiO₂ (33.5 %wt), respectively while the bentonitic soil consisted mainly of bentonite (60 %wt) and SiO₂ (33.5 %wt), respectively. The exact amount of each soil component, included the minor ones, used for preparing synthetic soils is reported elsewhere [10].

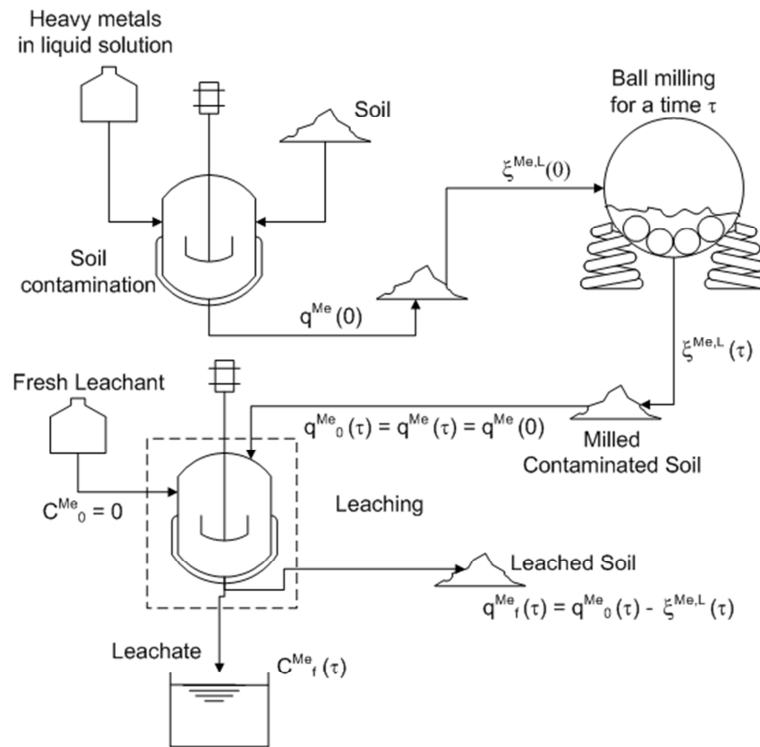


Figure 2. Schematic view of the experimental activity.

2.2 Contamination procedure

Soil contamination was carried out in suitable flasks by contacting known weights of each synthetic soil, with a solution containing known concentrations of heavy metals, i.e. Pb, Cd and Zn. The flasks were sealed and shaken for a period of time whose duration allows equilibrium conditions to be achieved, i.e. once a steady concentration of the considered heavy metal in the liquid phase. The solid concentration $q^{Me}_0(mg/kg)$ of each heavy metal (Me) transferred in the solid phase once equilibrium conditions are reached, was then determined through suitable mass balances as reported elsewhere [4]. The obtained contamination levels are summarized for each considered combination of soil and heavy metals are summarized in Table 1. It should be noted that $q^{Me}_0(mg/kg)$ represents the contamination level of the soil subsequently subjected to the mechanical treatment.

Table 1. Concentration q_{Me}^0 of heavy metals in the synthetic soils

Metal Soil	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)
SS	28'000	20'000	32'875
SB	10'000	20'000	107'181
SK	17'000	24'000	107'857

2.3 Soil mechanical treatment

The contaminated samples were then mechanically treated by ball milling using a Spex Mixer/Mill mod. 8000. In particular, 4 g of soil sample was introduced inside the vial together with two stainless steel balls of 8 g and 10 mm in diameter in order to obtain a charge ratio (C_r) equal to 4 g/g. Once sealed, the vial was fixed to the mill through a suitable vice and milling trials for different time intervals under air atmosphere were performed subsequently, according to the procedure by Montinaro et al. [4,10]

2.4 Post treatment leaching test for immobilization capacity evaluation

Unmilled and milled soils were then submitted to the “synthetic precipitation leaching procedure (SPLP)” to evaluate the degree of metal immobilization (USEPA, 1996). The test consists of contacting the soil with an acid mixture of sulphuric/nitric acid at pH equal to 4.2 ± 0.05 . A solid to liquid weight ratio equal to 1:20 and a contact time of 18 h was guaranteed. Samples were filtered and the concentration of metals in the leachate was determined by ICP-OES. It should be noted that this period of time (18 h) was observed to be sufficient for the achievement of equilibrium conditions, i.e. a steady concentration C_{Me}^{eq} (mg L⁻¹) of heavy metal in solution.

3. Mathematical model

It was reported in the literature that mechanical treatment of contaminated soils permitted the immobilization of heavy metal in the solid phase thus reducing their potential leaching when exposed to action of liquids (cf. Figure 2a). As already discussed in the introduction, several phenomena seem to concur to such experimental evidence. However, the real occurrence of these phenomena has not so far confirmed by a dedicated experimental activity. Therefore, the only evidence so far experimentally

validated is that the ball milling treatment (*BM*), due to several phenomena taking place, is capable to trigger the transformation of soil-bound heavy metals (*Me*) from the state of “L = leachable” to the state of “I = immobilized”, according to the following schematically represented reaction:



Thus, by indicating with $\xi^{Me,L} (mg\ kg^{-1})$ the leachable mass fraction of the generic metal *Me* with respect to the total mass of soil being processed, it can be stated that the mechanical treatment leads to the progressive decrease of $\xi^{Me,L}$. Such phenomenon is more pronounced as the treatment itself is prolonged in time. Analogously, by indicating with $\xi^{Me,I}$ the immobilized fraction of the metal, it has been experimentally proven that the ball milling treatment determines its increase. It is also apparent that, by indicating with $q^{Me} (mg\ kg^{-1})$ the total mass fraction of the metal in the soil, irrespective of its leachability state, the mechanical treatment does not determine its variation since the total mass of the metal within the milling chamber must be conserved. Thereby, if we consider a generic processing time equal to τ , the following relationships hold true:

$$\xi^{Me,L}(\tau) \leq \xi^{Me,L}(0) \quad \text{and} \quad q^{Me}(\tau) = q^{Me}(0) \quad (2)$$

With that in mind, the macro-kinetic model proposed by Delogu et al. [30], can be used to simulate the generic solid state transformations occurring in the soil during milling. This model is based on the reasonable assumption that only a small fraction of the soil is effectively processed during each collision between milling bodies occurring within the ball milling device, i.e. the soli mass entrapped between the colliding milling bodies. Accordingly, each collision between milling bodies is capable to provoke a mechanical load able to trigger the considered chemical-physical transformations only in a relatively small mass m^* of the processed soil [31]. Therefore, by indicating with $K = m^*/m$ the ratio between the latter mass and the total one available within the milling device, it can be stated that the mass of soil consists of $N = 1/K$ masses whose probability to be involved in an effective collision is equal to K for each collision taking place. Thereby, the milling process could be assimilated to a series of single events (collisions) where each of them has a probability to involve or not involve the mass m^* equal to K and $(1-K)$, respectively. As a consequence the probability that a single mass element

(among the N ones constituting the total mass) is involved in a number j of effective collisions when a total of n collisions occurred in the milling device, can be assumed to follow a binomial distribution [32]:

$$P_j(n) = \binom{n}{j} K^j (1 - K)^{n-j} \quad (3)$$

Since a typical ball milling process involves a very high number of collisions, it can be reasonably imposed that $n \rightarrow \infty$. Moreover, the number of impacts occurred after a specific processing time can be evaluated as the product between the collision frequency f (h^{-1}) and the time τ , i.e. $n = f \tau$, so that Equation (3) can be re-formulated as follows:

$$P_j(n) = \lim_{n \rightarrow \infty} \binom{n}{j} K^j (1 - K)^{n-j} = \frac{(K n)^j}{j!} e^{-Kn} = \frac{(k \tau)^j}{j!} e^{-k \tau} \quad (4)$$

which represents the Poisson distribution of probability where $k = K f$. The symbol k (h^{-1}) thus refers to a phenomenological constant linked to the dynamics of milling conditions, i.e. explicitly to the impact frequency but even, implicitly, to the collision energy and the ball to powder ratio.

By definition, the probability in Eq (4) is a good estimator of the mass fraction of soil which undergoes to a number j of effective collision during a mechanical treatment prolonged for a time τ .

Thus, the mass fraction $\xi_j^{Me,L}(\tau)$ of leachable metals experiencing j effective collisions after grinding for a time τ can be evaluated as follows [32]:

$$\xi_j^{Me,L}(\tau) = \xi_j^{Me,L}(0) \frac{(k \tau)^j}{j!} e^{-k \tau} \quad (5)$$

where $\xi_j^{Me,L}(0)$ is the mass fraction of leachable metals contained in the un-milled soil that, by definition, has not experienced any effective collision. It is noteworthy that, for a matter of mass conservation, the sum of all the mass fractions involved in whatever number of effective collisions must be equal to the mass fraction of leachable metals initially contained in the un-milled soil and thus the following relationship holds true:

$$\sum_{j=0}^{\infty} \xi_j^{Me,L}(\tau) = \xi_j^{Me,L}(0) \quad (6)$$

Let us assume that at least a number J_{min} of effective collisions should be experienced by the soil for the transformation of Eq. (1) to occur. Thereby, the mass fraction of immobilized metal $\psi^{Me,I}(\tau)$ obtained after a milling time τ can be evaluated by summing up all the mass fractions having experienced at least J_{min} collisions, that is:

$$\psi^{Me,I}(\tau) = \sum_{j=J_{min}}^{\infty} \xi_j^{Me,L}(\tau) \quad (6)$$

The latter one, by exploiting the property in Eq. (6) and elaborating it by considering Eq. (5), becomes:

$$\psi^{Me,I}(\tau) = \xi^{Me,L}(0) - \sum_{j=0}^{J_{min}} \xi_j^{Me,L}(\tau) = \xi^{Me,L}(0) \left[1 - \sum_{j=0}^{J_{min}} \frac{(k \tau)^j}{j!} e^{-k \tau} \right] \quad (7)$$

which permits to evaluate the evolution of the immobilized fraction of heavy metal as a function of the processing time. On the other hand, the mass fraction of leachable heavy metals, still present after processing the soil during the time interval τ , can be evaluated as the difference between the initial content of leachable heavy metals and the amount immobilized up to that time according to:

$$\xi^{Me,L}(\tau) = \xi^{Me,L}(0) - \psi^{Me,I}(\tau) = \xi^{Me,L}(0) \left[\sum_{j=0}^{J_{min}} \frac{(k \tau)^j}{j!} \right] e^{-k \tau} \quad (8)$$

Thereby, it is possible to define a transformation degree $\chi(\tau)$ related to the reaction schematically represented in Eq. (1) that can be evaluated as follows:

$$\chi(\tau) = \frac{\xi^{Me,L}(0) - \xi^{Me,L}(\tau)}{\xi^{Me,L}(\tau)} = 1 - \sum_{j=0}^{J_{min}} \frac{(k \tau)^j}{j!} e^{-k \tau} \quad (9)$$

It should be noted that, in order to experimentally evaluate the transformation degree above, the leachable fraction of the heavy metal content in the solid phase $\xi^{Me,L}$ should be evaluated. However, since the latter one cannot be directly measured during the experiments, the following method has been adopted to obtain model results in terms of heavy metals concentrations in the leachate which can be compared with experimental data. Let us consider the initial content of heavy metal $q^{Me}(0)$ ($mg \text{ kg}^{-1}$) in the soil irrespective of its leachability character. As mentioned above, this quantity is not affected by the mechanical treatment for a matter of mass conservation. For this reason, when submitting the soil sample to the mechanical treatment for a time τ , the total mass fraction of

heavy metal does not change (cf. Figure 1), i.e. $q^{Me} = q^{Me}(0) = q^{Me}(\tau)$. On the other hand, as discussed just above, its leachability state is changed as a result of the treatment and thus $\xi^{Me,L}(\tau) \leq \xi^{Me,L}(0)$. Now let us focus on the leaching procedure performed with a generic sample (cf. Figure 1). Since, during such procedure a specific amount of heavy metals is transferred from the soil to the liquid phase, by considering the control volume highlighted with a dotted line in Figure 2, the following macroscopic mass balance holds true:

$$[q_0^{Me}(\tau) - q_f^{Me}(\tau)]\rho_S V_S = [C_f^{Me}(\tau) - C_0^{Me}(\tau)]V_l \quad (10)$$

where the subscripts “0” and “f” refer to the beginning and the end of the leaching procedure, respectively. Therefore, $q_0^{Me}(\tau) = q^{Me}(0) = q^{Me}(\tau)$ is the total metal content of metal in the soil milled for a time τ at the beginning of the leaching test while the symbol $q_f^{Me}(\tau)$ refers to the same quantity evaluated at the end of this procedure. It should be remarked, that in this case the value of q_f^{Me} is lower than $q_0^{Me}(\tau)$ due to the transfer of a certain aliquot of metal, i.e. the leachable fraction, to the liquid phase. Accordingly, the heavy metal concentration in the liquid solution obtained by leaching the soil sample grinded for the time τ passes from the initial value $C_0^{Me}(\tau)$ to the higher value $C_f^{Me}(\tau)$ at the end of the leaching procedure. Typically, the metal concentration in the fresh leaching solution is experimentally imposed to be equal to zero and thus $C_0^{Me}(\tau) = 0$.

Moreover, the difference $[q_0^{Me}(\tau) - q_f^{Me}(\tau)]$ appearing in the left hand side of Eq. (10) represents by definition the so-called leachable fraction $\xi^{Me,L}(\tau)$ of heavy metal in the soil treated for a period of time τ . Thereby equation (10) can be re-written as:

$$\xi^{Me,L}(\tau) = \frac{V_l}{\rho_S V_S} C_f^{Me}(\tau) = \alpha C_f^{Me}(\tau) \quad (11)$$

where α is a constant conceptually similar to the inverse of the so-called partition coefficient of heavy metal. Since the concentration in the liquid phase $C_f^{Me}(\tau)$ is measured at the end of the leaching test, Eq. (11) allows one to evaluate the leachable fraction of heavy metal in the soil. Similar considerations might be done for the leachable fraction of the unmilled soil, which can be then evaluated as:

$$\xi^{Me,L}(0) = \alpha C_f^{Me}(0) \quad (12)$$

Thus, by substituting Eqs. (11) and (12) into Eq. (8), the following expression can be obtained to simulate the evolution of leached concentration $C_f^{Me}(\tau)$ as a function of the milling time τ :

$$C_f^{Me}(\tau) = C_f^{Me}(0) \left[\sum_{j=0}^{J_{min}} \frac{(k \tau)^j}{j!} \right] e^{-k \tau} = C_f^{Me}(0) \left[1 + k \tau + \frac{(k \tau)^2}{2} + \dots \right] e^{-k \tau} \quad (13)$$

Since the concentration of heavy metal at the end of the leaching procedure is experimentally evaluated, Eq. (13) permits the comparison of model and experimental results. By exploiting the same relationships, Eq. (9) can be expressed in the following form:

$$\chi(\tau) = \frac{C_f^{Me}(0) - C_f^{Me}(\tau)}{C_f^{Me}(0)} = 1 - \sum_{j=0}^{J_{min}} \frac{(k \tau)^j}{j!} e^{-k \tau} \quad (14)$$

which is useful to compare experimental and model results in terms of $\chi(\tau)$ vs τ by suitably tuning the parameter k . Finally, the quantity called immobilization efficiency introduced by Montinaro et al. [4], can be evaluated as follows:

$$\eta_{imm} = \left(1 - \frac{C_f^{Me}(\tau) V_l}{q_0^{Me}(\tau) V_S \rho_S} \right) 100 \quad (15)$$

Ultimately, once the parameters k and J_{min} are known, the model permits to simulate the experimental results as function of the milling time τ .

However, much more than the process time itself, the crucial variable affecting the phenomenology and the yield of a mechano-chemical process is the total mechanical energy provided to the unit mass of soil during a certain processing time τ . In fact, a specific transformation can take place at different times depending on the rate at which energy is provided to the soil during milling. As a consequence, modulation and control of energy parameters are crucial in view of achieving high immobilization yields within a specific processing time τ . For this reason, it can be useful to express the transformation degree χ as a function of the energy provided to the sample at a certain time τ , by considering the dependence of the parameter k from the energy ones. To this aim, the quantities called milling intensity I ($J \text{ hr}^{-1}$) and specific energy dose D ($J \text{ mg}^{-1}$) can be introduced. The first one represents the rate at which energy is provided to the soil, i.e. the kinetic energy per unit time, which according to the literature can be evaluated as follows [33]:

$$I = \frac{1}{2} f \sum_{i=1}^{n_b} m_{b,i} v_{b,i}^2 \quad (16)$$

where $n_b(/)$ is the number of milling bodies (balls) in the system, $f(hr^{-1})$ is their impact frequency, $m_{b,i}(g)$ their mass and $v_{b,i}(m s^{-1})$ their relative impact velocity.

The specific energy dose is the total amount of mechanical energy provided to the unit mass of soil after a certain time τ and according to the literature can be evaluated as follows:

$$D = \frac{I\tau}{m_p} = \frac{1}{2} \frac{f \tau}{m_p} \sum_{i=1}^{n_b} m_{b,i} v_{b,i}^2 \quad (17)$$

where $m_p(g)$ is the mass of powders (soil) being processed. If all the milling bodies have the same mass m_b and the impact velocity is assumed to reach a constant value ($v_{b,i} = v_b$) when the milling regime achieves steady state [9,34], then the milling dose can be re-written as:

$$D = \frac{1}{2} \frac{n_b m_b}{m_p} f v_b^2 \tau = \frac{1}{2} C_r f v_b^2 \tau \quad (18)$$

where the term $C_r(/)$ is the so-called charge ratio, i.e. the ratio between the mass of milling bodies and the mass of soil being processed. Therefore, by imposing:

$$k = k' \frac{1}{2} C_r f v_b^2 \quad (19)$$

and substituting in Equations (13) and (14), the following expressions can be obtained:

$$C_f^{Me}(D) = C_f^{Me}(0) \left[\sum_{j=0}^{J_{min}} \frac{(k' D)^j}{j!} \right] e^{-k' D} \quad (20)$$

$$\chi(D) = 1 - \sum_{j=0}^{J_{min}} \frac{(k' D)^j}{j!} e^{-k' D} \quad (21)$$

which represent for the first time a suitable tool to quantitatively describe the evolution of heavy metal immobilization in contaminated soil as a function of the cumulative energy dose provided during the mechanical treatment. It should be noted that all the Equations above can be used only if the quantities C_r , f and v_b are known. While the charge ratio was experimentally imposed, the values of f and v_b were evaluated through the mathematical model of the Spex Mill dynamics proposed in the literature

[9]. The corresponding values, reported in Table 2, were then used in this work to perform the simulations.

Table 2 Values of the dynamics parameters adopted to simulate the experimental results.

Parameter	Symbol	Value	Units	Reference
Charge Ratio	C_r	4	/	Experimentally set
Impact velocity	v_b	4.169	$m s^{-1}$	[34]
Impact frequency	f	142	Hz	[34]

The calculations were performed as follows. First, transformation degree vs milling time data were translated into transformation degree vs dose by inverting Eq. (18) both for experimental and model results. Subsequently, model results were fitted against the experimental ones by suitably tuning the value of the parameter k' so that to minimize the residual sum of squares (RSS) defined as

$$RSS = \sum_{i=1}^n [\chi_i^{exp}(D) - \chi_i^{mod}(D)]^2 \quad (25)$$

The results were then compared in terms of leached concentration and immobilization efficiency.

4. Results and discussion

The effect of high-energy mechanical treatment in Spex Mixer Mills on the immobilization of heavy metals in contaminated soils has been quantitatively simulated in this work. In order to validate model reliability, simulation results have been compared with literature experimental data [4,9,10] regarding the immobilization of Cd, Pb and Zn in sandy (SS), bentonitic (SB) and kaolinitic soils (KS), respectively.

In Figure 3 the comparison of experimental data and model results related to the immobilization of these metals in sandy soil (SS) is shown. Models results were obtained by tuning the parameter k' to the optimal fitting values shown in Table 1. As it can be seen from Figure 3a, the evolution of Cd and Zn transformation degree χ with the cumulated energy dose is well captured by setting $J_{min} = 1$. However, when considering the effect of the mechanical treatment on the immobilization of Pb, the experimental results were better interpreted when setting $J_{min} = 2$, i.e. the case where two collisions

are required to trigger all the phenomena responsible of the corresponding immobilization increase. This result explains the difference between the sigmoidal trend of model results related to Pb and the exponential one concerning Cd and Zn transformation degree. From a physico-chemical point of view, this behavior can be explained by the fact that, differently from Cd and Zn, the adsorbed Pb is subjected to phenomena triggered by the mechano-chemical processes which are characterized by a slower kinetics at the early stages of the process. Accordingly, a certain lag time is required to activate the Pb immobilization process in SS.

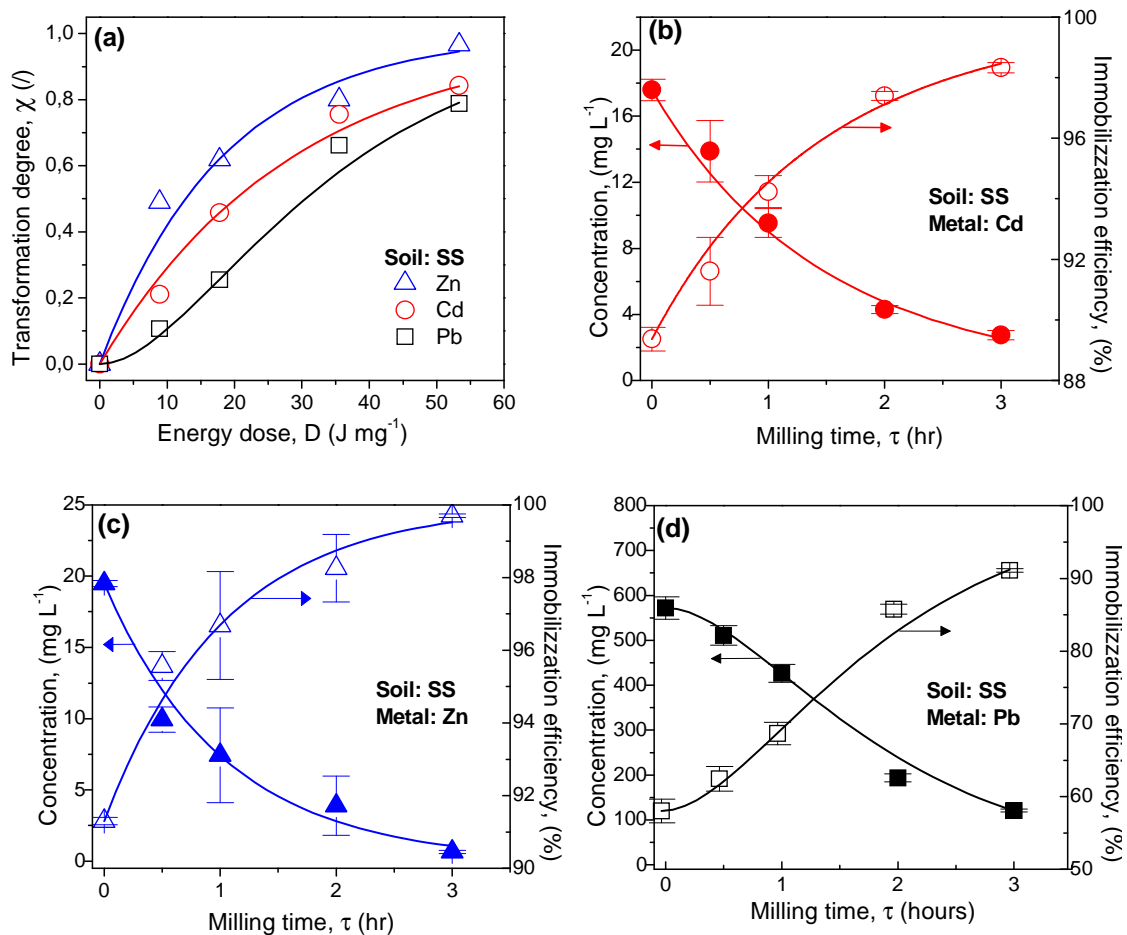


Figure 3. Comparison of experimental data (symbols) by [4,9,10] and model results (lines) obtained with the sandy soils (SS) in terms of transformation degree vs energy dose (a) and heavy metal concentration in leachate or immobilization efficiency as function of the milling time for Cd (b), Zn (c) and Pb (d).

In the Figures from 3b to 3d, the model results related to Cd, Zn and Pb are compared with the experimental ones in terms of heavy metals concentration released in the leachate and immobilization efficiency obtained after treating the SS soil for different times τ . It can be observed that the

concentration of all heavy metals leached from soils decreases as the mechanical treatment proceeds. Consequently, the related immobilization efficiency correspondingly increases. The net effect is that the contaminant potential of treated soils is drastically reduced. However, some differences among the considered heavy metals can be detected. In particular, Pb (cf. Fig.3d) seems to be the most sensitive to the mechanical action since immobilization efficiency increases from 61% in absence of treatment to 95% when the soil is treated for 5 h with a charge ratio equal to 4. On the other hand, Cd and Zn immobilization correspondingly show a less pronounced augmentation which goes from the initial value of 89.37% and 91.3 % respectively, to the final one of 98.33 and 99.7% respectively.

Table 2. Model parameters values obtained by fitting the experimental data reported in Figure 3, 4 and 5

Soil \ Metal	Cd				Pb	
	$k' (/)$	$J_{min} (/)$	$k' (/)$	$J_{min} (/)$	$k' (/)$	$J_{min} (/)$
SS	$5,45 \times 10^{-2}$	1	$3,44 \times 10^{-2}$	1	$5,50 \times 10^{-2}$	2
SB	$1,90 \times 10^{-2}$	1	$7,55 \times 10^{-2}$	1	$2,46 \times 10^{-2}$	1
SK	$5,87 \times 10^{-2}$	1	$1,30 \times 10^{-1}$	1	$2,60 \times 10^{-2}$	2

Thus, even if the mechanical treatment allowed an almost total immobilization of Cd and Zn, it could be argued that this result is somehow linked to the intrinsically high capability of the SS soil to capture these metals in the solid phase even in absence of mechanical treatment, i.e. when the milling time is zero. However, the effect of mechanical treatment is more pronounced for Pb whose leaching concentration dramatically decreases from 596 to 70 mg L⁻¹ after 5 hours of treatment. As it can be seen, such behavior, that further marks the difference of Pb with respect to the other metals investigated, is well captured by the proposed model, thus demonstrating its validity. A quantitative measure of the reliability of the model is given by the average relative errors of the fitting procedure that were equal to 6.22%, 6.38% and 6.31% for Zn, Cd and Pb respectively.

To further validate the model, the experimental results obtained by treating different soils were considered. Figure 4 shows the relevant results achieved with the bentonitic soil SB, which consisted mainly of bentonite (60% wt) and a lesser extent (33.5%) of silica (SiO₂) with respect to SS soil. As it can be seen, even in this case the mechanical treatment was capable to increase the immobilization of all concerned metals in the solid phase by reducing their leachable fraction. The best fitting values of

the empirical parameter k' for each metal are also shown in Table 2. It can be observed that, in this case the experimental data were better interpreted by setting $J_{min} = 1$ even for Pb. Since the only difference with the sandy soil SS consisted in the less amount of silica and the presence of bentonite, the difference in the immobilization kinetics might be due to a relatively faster adsorption of heavy metals onto disrupted bentonite particles rather than silica ones.

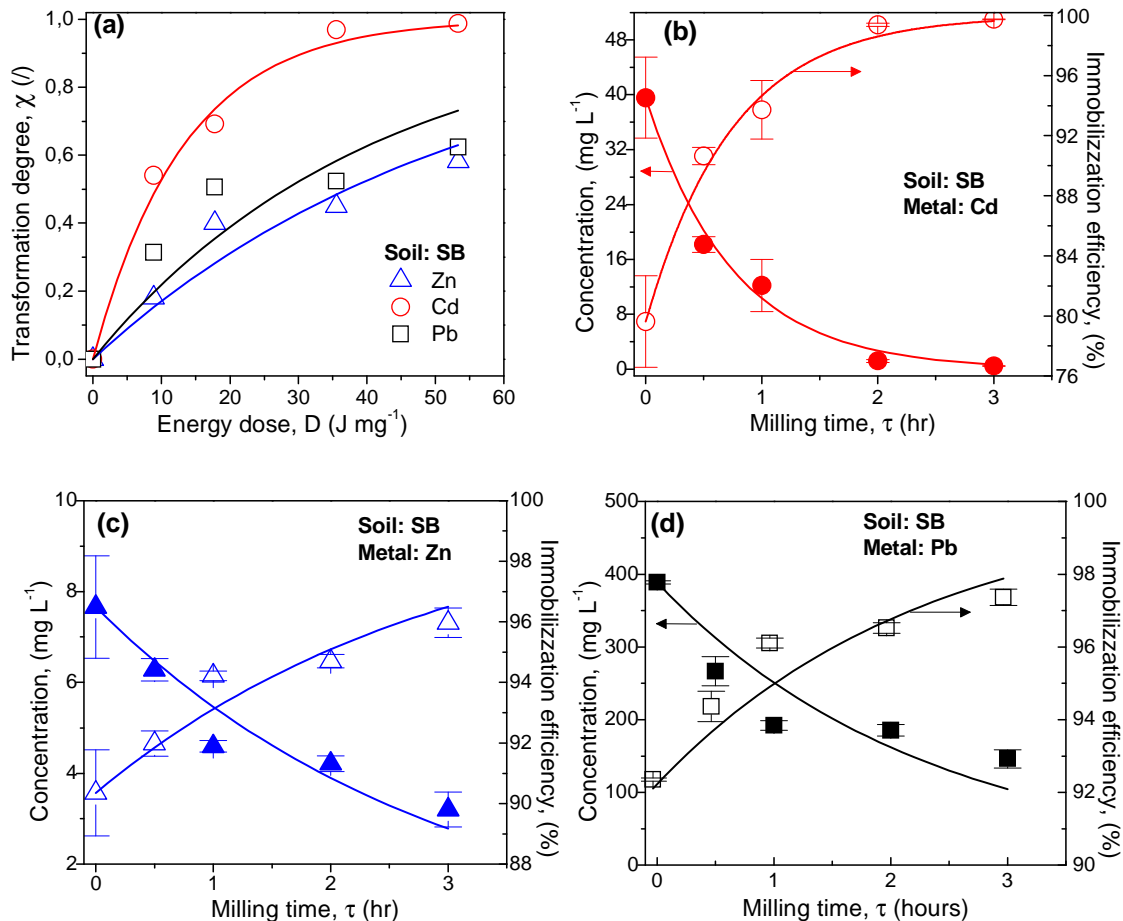


Figure 4. Comparison of literature experimental data (symbols) [4,9,10] and model results (lines) obtained with bentonitic soils (SB) in terms of transformation degree Vs energy dose (a) and metal concentration in leachate or immobilization efficiency as function of milling time for Cd (b), Zn (c) and Pb (d).

From Figure 4 it could be seen that the most sensitive metal was Cd since the supply of an energy dose of about $40\ J\ mg^{-1}$ was enough to achieve an almost complete immobilization (99.75%) in the solid phase and the corresponding abatement of the leached concentration ($0.47\ mg\ L^{-1}$). These results are much more significant if one considers that the intrinsic immobilization efficiency of SB soil was not particularly high for Cd (79.6%) and the concentration released in the leachate in absence of treatment

was about 40 mg L^{-1} . As it can be observed the experimental results are well interpreted for all heavy metals also for the case of SB soil. Only when considering Pb (cf. Figure 4d) the agreement between model and experiments was slightly worse than the one obtained for Cd and Zn. However, the experimental data are enough well captured by the proposed model. In fact the average relative errors of the fitting procedure were equal to 12%, 4% and 19% for Zn, Cd and Pb respectively.

Results obtained with the kaolintic soil SK are shown in Figure 5. Even in this case the tuned values of the empirical constant k' are shown in Table 2. By analyzing the latter one, it can be extrapolated that the evolution of Cd and Zn degree of transformation with the energy dose (cf. Figure 5a) were well captured by using $J_{min} = 1$ while the behavior of Pb was better interpreted through the sigmoidal trend obtained by setting $J_{min} = 2$.

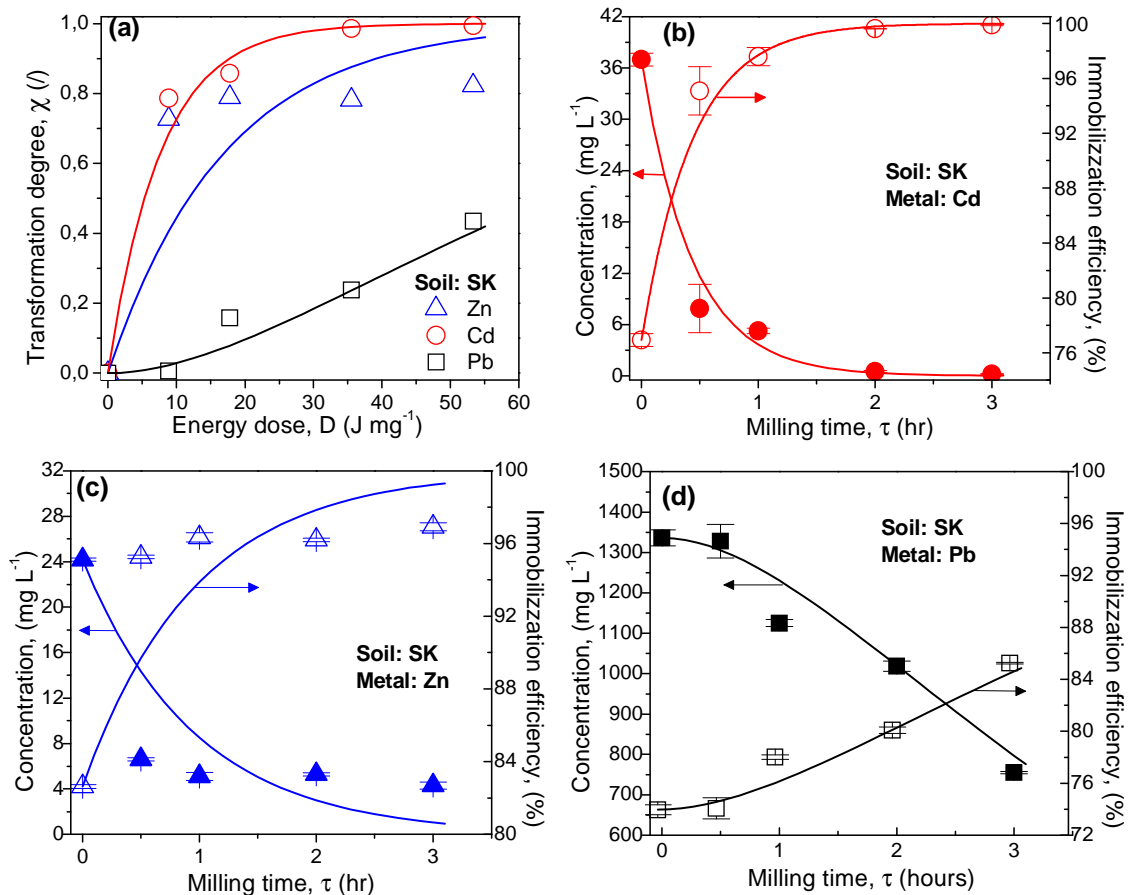


Figure 5. Comparison of literature [4,9,10] experimental data (symbols) and model results (lines) obtained with kaolintic soils (SK) in terms of degree of transformation vs energy dose (a) and metal concentration in leachate or immobilization efficiency as function of milling time for Cd (b), Zn (c) and Pb (d).

As it can be seen from Figure 5d, Pb was the metal less responsive to the mechanical treatment also for such a soil. In fact its immobilization efficiency, starting from values of about 74% after 5 hours of treatment achieves an immobilization efficiency of only 85% which results in the release of still high concentration of Pb in the leachate (about 700 mg L^{-1}). This aspect further confirms the singularity of the response of Pb to the mechanical treatment. On the contrary, Cd was the most sensitive to the mechanical treatment even for SK soil because its immobilization efficiency increased from an intrinsic value of about 75 % to about 99.9% after a 5hr prolonged treatment. Accordingly, its concentration released in the leachate was almost negligible.

As far as Zn is concerned, a good immobilization efficiency, i.e. close to 97%, was achieved after milling the SK soil for 5 hours (cf. Figure 5c). It can be observed that the experimental results are well fitted by the proposed model also for the case of SK soil. In particular, the best and the worst agreement was obtained for Cd and Zn, respectively, since the experimental data related to the latter one shows a sort of plateau at degree of transformation values of about 0.8 (cf. Figure 5a) that is difficult to interpret through the proposed model. For the case of Pb the capability of model to interpret experimental data was instead quite good. Ultimately, also in the case of SK soil the model turned out to be reliable since the average relative errors of the fitting procedure were equal to 18%, 3.7% and 14.4% for Zn, Cd and Pb, respectively.

It should be noted that the results so far discussed were obtained by suitably tuning the values of the empirical parameter k' reported in Table 2. Therefore, to evaluate the predictive capability of the proposed model further experimental data, obtained by varying different operating conditions, were interpreted by keeping fixed the values k' obtained so far, i.e. without tuning any model parameter. To this aim, the effect of prolonging milling time up to 7h on the immobilization of Pb in SS soil is shown in Figure 6.

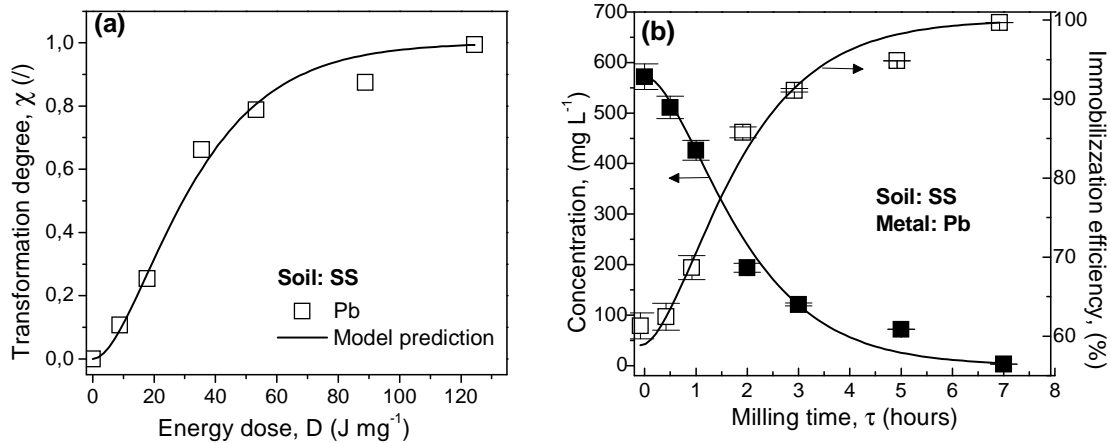


Figure 6. Effect of prolonged (up to 7h) milling time on Pb immobilization in sandy soil (SS) displayed in terms of degree of transformation vs energy dose (a) and heavy metal concentration/immobilization efficiency in leachate vs milling time (b). Model predictions are obtained without tuning model parameters.

As it can be seen, an almost total immobilization (99.7%) of Pb was achieved after 7 hours and correspondingly the leached Pb was dramatically reduced to concentration values (0.06 mg L^{-1}) that are lower than the USEPA threshold for drinkable water. From Figure 6, it can be seen that the model well predicts the experimental behavior for prolonged milling times without tuning any model parameter. This further confirms that the sigmoidal formulation, i.e. $J_{min} = 2$, instead of the exponential one, i.e. $J_{min} = 1$, is capable to quantitatively capture the experimental results for the case of Pb immobilization in SS soils.

To further test the model predictive capability the experimental results obtained by changing the milling dynamics regimes were considered. In particular, the effects of setting the chargeratio (or ball to powder weight ratio) C_r equal to 6 for the immobilization of Pb in bentonitic and sandy soil are shown in Figures 7a and 7b, respectively. For the sake of manuscript brevity, results are shown only in terms of degree of transformation vs energy dose and leachate concentration vs milling time. By comparing these results with those ones obtained using a charge ratio equal to 4 it can be observed that the increase of C_r did not result in a significant reduction of the milling time needed to achieve a released concentration of about 100 mg L^{-1} and conversion of about 0.75 for both SB and SS.

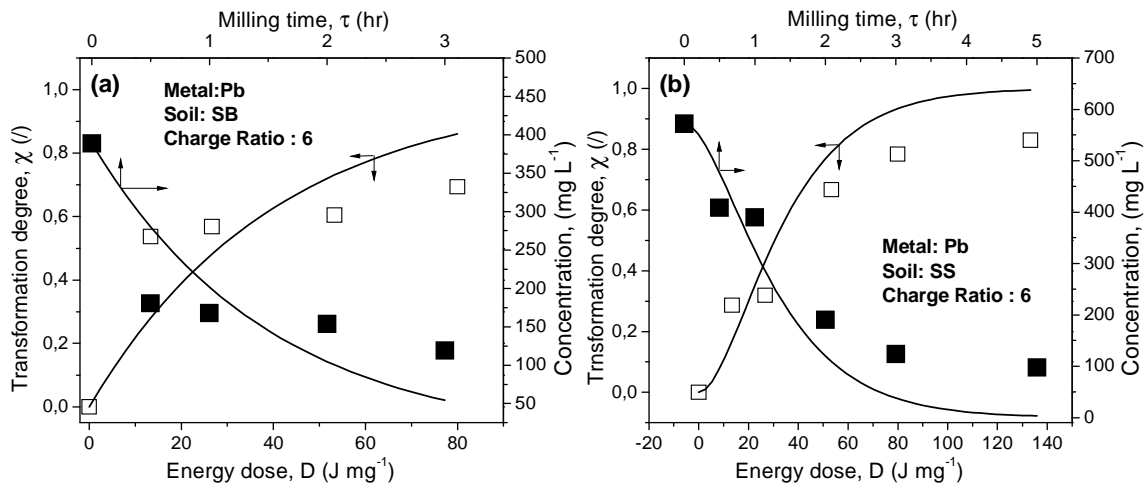


Figure 7. Comparison of model predictions and literature experimental data from [5] related to the effect of milling time on the immobilization of Pb in bentonitic (a) and sandy (b) soils when $C_r = 6$.

The increase of C_r from 4 to 6 was likely not sufficient to produce relevant effects on the immobilization efficiency. The experimental behavior is enough well predicted by the model without tuning any model parameter up to 3 hours. On the other hand, the effect mechanical treatment with $C_r = 6$ is slightly overestimated by the model for milling times of about 5 hours. However, the general trend of immobilization evolution is quite well captured, thus demonstrating the proposed model reliability.

It should be noted that the results so far discussed have been obtained by treating soils contaminated by heavy metal concentrations (cf. Table 1) that are much higher than those ones typically found in real contaminated soils. For this reason, further experiments were performed by Montinaro et al. using soils contaminated by heavy metals concentration levels close to the typical ones of field contaminated soils [4,9,10]. The comparison between model results and experimental data obtained under these conditions is shown in Figure 8.

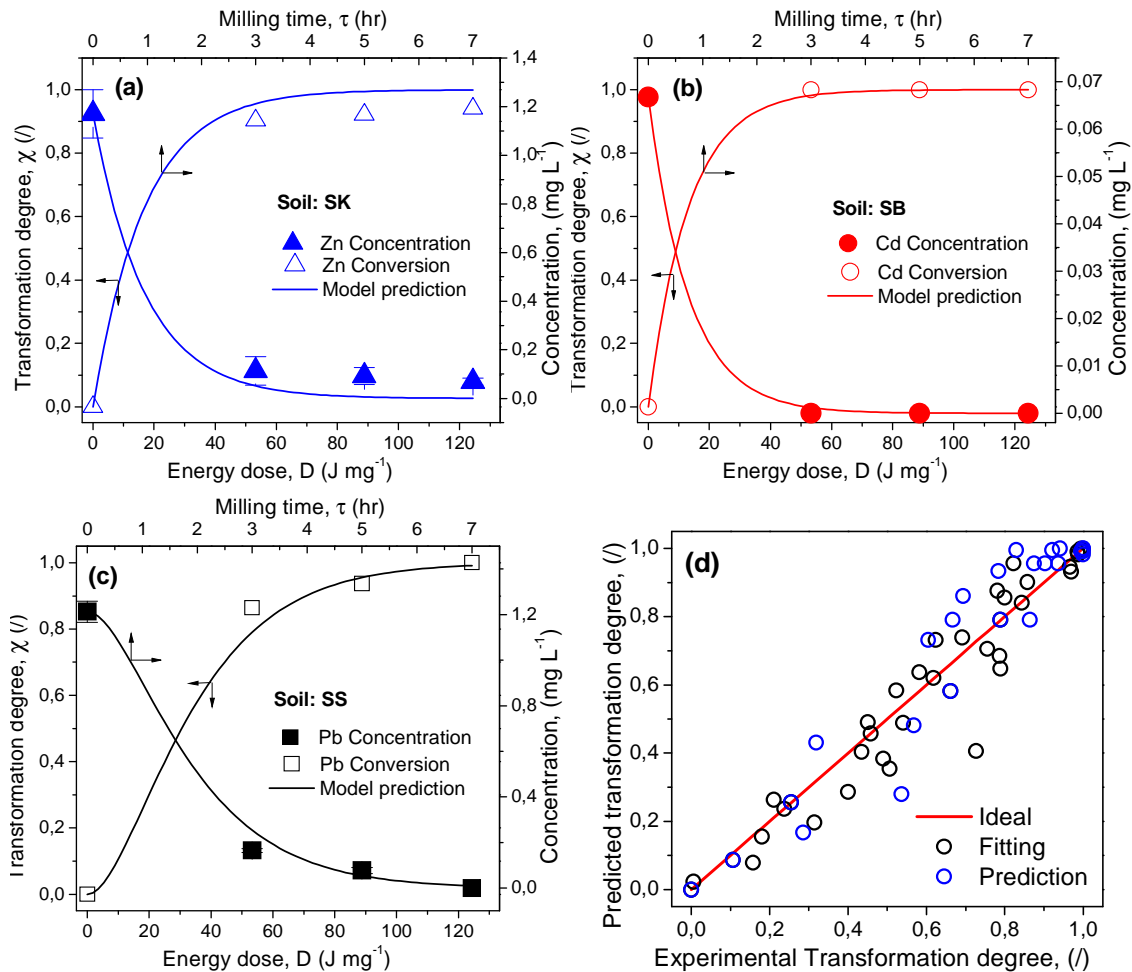


Figure 8. Comparison of model predictions and literature experimental data [4,9,10] related to the immobilization of Zn in kaolinitic soil (a) Cd in bentonitic soil (b) and Pb in sandy soil, respectively, contaminated by concentration levels of heavy metals typical of real polluted soils. Parity plot is reported in Figure 8d.

In particular, the experimental results obtained by mechanically treating for 7 hours a kaolinitic soil SK contaminated by 76.3 mg kg^{-1} of Cd are depicted in Figure 8a. Figure 8b shows the results achieved by performing the same treatment on bentonitic soil SB contaminated by 1175 mg kg^{-1} of Zn. Finally, in Figure 8c the case of sandy soil SS contaminated by 621.5 mg kg^{-1} of Pb is taken into account. As it can be seen the results show that leached concentration is dramatically reduced for each considered combination of soil and metal. In particular, after a prolonged treatment of 7 hours, the concentrations of heavy metals in the leaching solutions were in agreement with the regulatory threshold proposed by USEPA (USEPA, 1996) for drinkable water. On the other hand, it can be observed that 3 hours are sufficient to achieve a drastic abatement of heavy metal mobility even in this case. These results

demonstrate the possibility of applying the proposed mechano-chemical technique even at the real scale. Moreover, Figures from 8a-c also demonstrate the capability of the model to well predict the experimental data without tuning any model parameter even when considering contamination levels similar to those ones observed in the field. Finally, Figure 8d shows a graphic summary of the model performance in predicting experimental data obtained under the very different operating conditions considered above and for the three metals taken into account with or without tuning its parameters. As it can be observed, the proposed model is characterized by a high degree of reliability.

Since the model parameter k' is strongly linked to the milling device dynamics it is apparent how the proposed model could be used to establish operating conditions such as ball to powder ratio, mill frequency and milling time that allows to achieve the desired immobilization efficiency for the specific soil/pollutant system considered.

5. Concluding remarks

A semi-empirical mathematical model for the simulation of the effect of mechanical treatment on heavy metal immobilization in contaminated soil has been proposed for the first time in the literature. The model is capable to provide a clear relationship between heavy metals concentration in the leachate and milling dynamics. By comparing model results with literature experimental data obtained under different operating conditions a good matching is achieved for different combinations of heavy metals and soil typologies. The model might thus represent the first step towards the development of a software tool useful to optimize the implementation of the mechano-chemical treatment at the field scale.

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