Selective removal of lead and bromide from a hazardous industrial solid waste using Limited Acid Demand and Separation Factor at ambient conditions

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The present paper is dedicated to the memory of Alexandros Th. Ioannidis.

Abstract

A detailed methodology is described for the selective removal of lead and bromide content from an industrial toxic solid waste, containing also large quantities of iron. Limited Acid Demand (LAD) was examined in order to avoid the co-dissolution of undesirable constituents. The Separation Factor (SF), which is the concentration ratio of dissolved constituents in the resulting leaching solution after the application of extraction stage, can describe the selective release of lead against iron, according to the variation of major leaching parameters (i.e. the molarity of used acid and the liquid to solid (L/S) ratio). A general equation, describing the overall leaching process was obtained, containing a specific "inhibition constant" and indicating that when the initial stoichiometry of leaching procedure and the applied L/S ratio are known, then the removal of lead can be predicted.
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1. Introduction

The use of aqueous solutions for the removal or selective extraction/separation of constituents, existing in raw materials or minerals, presents certain benefits, over other, more conventional metal recovery methods, such as pyro-metallurgical, including the minimization of hazardous air emissions during the former case. Although hydrometallurgy was previously applied for the recovery of several metals from ores or minerals, more recently its applications were extended to include also the removal and the eventual recovery of toxic metals (or other pollutants) from industrial wastes or from by-products. The extraction of lead from the respective ores or minerals by leaching was examined during several studies [1–3], although nowadays most research efforts are focused on the possibility of recovering lead from industrial wastes, such as its recycling from used batteries [4,5]. Among others, lead was also extracted and recovered from electric arc furnace dusts [6], from alloy wire

scrap [7] and from solid residues of municipal incinerators [8], as well as from contaminated soils [9,10].

The major parameters of extraction (by leaching) processes are the selection of appropriate solvent agent and the definition of optimum conditions for the efficient separation of constituents of interest from complex solid matrices, such as minerals or solid wastes. A common side effect usually observed during the relevant applications, is the parallel dissolution/leaching of other undesirable constituents from the solid matrix.

In several cases, the examination of specific hydrometallurgical procedures is based upon previously recorded experimental conditions. There are, however, numerous different types of industrial solid wastes (or of minerals), which have not been studied so far. Additionally, the total available amount (or volume) of specific waste types may not be adequate in order to apply the convenient technological options in a financially profitable way. As a result, the cumulative effect of waste disposal, mostly performed by simple dumping and without the appropriate treatment, can create several environmental pollution problems. For this reason, there is an apparent need for the examination of *in place*, low cost relevant methods, using flexible batch process units of small scale, in which the waste

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would be treated effectively, limiting in this way all the potential environmental risks.

Earlier information that can be found in previously published research papers, dealing with lead hydrometallurgy, cannot necessarily provide sufficient performance data for the treatment of other lead containing industrial wastes. Furthermore, for certain types of compounds that might exist in solid wastes, such as the hydroxy-salts of metals, the available solubility data are extremely limited, even for the respective synthetic compounds; therefore, making the selection of appropriate leaching agent and the necessary reagent concentration even more difficult. The additional problem of other constituents' simultaneous presence in real wastes (or minerals) may complicate further the problem of appropriate extraction system selection, due to their co-dissolution, which is likely to inhibit the following stages of selective hydrometallurgical process.

In this study, the appropriate physicochemical conditions, regarding the application of dilute acidic solutions at room temperature ($25\,^{\circ}$C), were determined for the treatment of a solid industrial waste, containing mainly lead, iron and bromide. A simple methodology for limiting the necessary acid demand of leaching solution was applied. Environmentally friendly (mild) conditions, i.e. ambient temperature and pressure, as well as the use of dilute acidic solutions, were applied in order to achieve the efficient separation of lead and bromide from the co-existing iron oxides, decreasing in this way the eventual environmental problems created by the application of conventional hydrometallurgical methods. Specific factors describing the separation process were also introduced, their mathematical description was discussed and the respective mechanism was suggested.

2. Materials and methods

2.1. Characterization of studied solid waste

The origin and pretreatment of examined industrial solid hazardous waste, which is the residue (ash) obtained from the incineration of tetraethyl-lead containing sludge, has been previously discussed [11]. All the samples of the homogenized waste were $<300\,\mu$m. Analytical determinations (using AAS, XRF and UV–vis spectroscopy) showed that the studied waste contain as major components: Fe 33, Pb 29.6, Br 10.1, Si 2.8, Al 1.8, Na 1.3, Ca 0.5, S 0.5, Mg 0.4, Bi 0.3, Mn 0.2, K 0.2 and Ti 0.1, expressed as % (w/w). Lead and iron were mainly found in the $<250\,\mu$m particles and bromide was found in the $<125\,\mu$m particles. Most of the lead and bromide content was found crystallized onto the surface of iron oxides, and independent needle like particles were found to contain mainly lead and bromide. The respective solid phases were characterized by the application of XRD, FT-IR and SEM-EDS spectroscopy methods and they were detected as Pb(OH)Br (34–38%, w/w) and Fe_2O_3 (44–48%, w/w, mostly as α-Fe_2O_3). The other lead-containing solid phases (such as PbO, PbO·$PbSO_4$) were estimated as 5% (w/w), whereas all the other non-lead and non-iron solid phases (mainly aluminosilicates) were estimated at 10–15% (w/w). The detailed characterization data have been previously published [12].

2.2. Experimental procedure

Pre-weighted samples of the examined solid waste were added to appropriate (stopper) glass flasks, according to the required liquid to solid (L/S) ratio (g/g). The initial quantity of waste was kept constant (5 ± 0.01 g) for all the performed experiments. The respective leaching solution was subsequently added, up to the required L/S ratio and the agitation under constant temperature ($25\,^{\circ}$C), ambient pressure and for 24 h leaching/contact time was performed in a horizontal shaking bath (at 180 rpm). The samples were subsequently left to settle for few minutes and sampling from the supernatant solution took place. These samples were directly filtered through a cellulose nitrate membrane filter ($0.45\,\mu$m) and the analytical determinations of metals' content (lead and iron) in the resulting filtrated leaching solutions were performed. The determination of solubility or availability control was examined using the appropriate methodology [13].

2.3. Methods

The determinations of lead and iron were performed using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer (AAS). Appropriate calibration with background solutions, as well as the addition of 10% (w/v) lanthanum nitrate solutions, took place in order to increase the sensitivity of measurements, according to the specifications of respective analytical methods. Bromide measurements were performed according to the ASTM D 3869–79 method [14], using the Zeiss Jena PMQ3 spectrophotometer. The Julabo SW 21 horizontal shaking bath was used for agitation purposes. All solutions were prepared using analytical grade reagents.

3. Results and siscussion

3.1. Selection of appropriate leaching solution

Several leaching solutions were examined and certain (indicative) experimental results are presented in Table 1. The use of salts, such as CH_3COONH_4, could be interesting, but only when higher temperatures would be applied. However, in this case an additional problem that can possibly arise is the increased losses of volatile constituents. The use of sulfuric acid in low temperatures was found to deteriorate the requested quantitative lead separation (release), in accordance with previously published results [15]. Conversely, sulfuric acid could be used for the selective dissolution of iron, although during the treatment of similar wastes with the examined one, significant amounts of lead would be also co-dissolved; moreover, the total removal would not be adequate (i.e. more than 90%, w/w), concerning the iron content.

The use of alkaline solutions was proved sufficient, considering the selectivity of lead dissolution, but the total removal was rather low and the filtration process problematic. As a result, emphasis has been given to the use of nitric or acetic acid, due to the expected good solubility properties of lead compounds in these reagents, which were also proved for the examined

Table 1
Results of preliminary experiments, regarding the selection of appropriate leaching solution

Leaching agent	Concentration (M)	Liquid to solid ratio (L/S)	Pb removal (%, w/w)	Fe removal (%, w/w)
HNO_3	3.3–5	10	>97	15–19
HCl	3.3–5	10	9–14	55–60
H_2SO_4	Concentrated	10	4–6	29–33
NaOH	1	10	14.9	<1
NaOH	0.5	10	9.6	<1
CH_3COOH	1–5	10	55–64	<1
CH_3COOH/CH_3COONH_4 (1:1)	1 (both)	10	51	<0.1
CH_3COONH_4	1	10	3–5	<0.1

Experimental conditions: constant temperature (25 °C), ambient pressure, 24 h leaching/contact time, using a horizontal shaking bath (at 180 rpm).

waste, indicating that the specific mineralogical form of lead (Pb(OH)Br and its derivatives) would be sufficiently soluble, as presented in Table 1. However, the used HNO_3 concentrations were rather high and as a result increased values of iron parallel co-dissolution were also recorded (around 20%, w/w). Similar problems were not encountered, when acetic acid was used, although lead removal was not quantitative, when low L/S ratios were applied.

Hematite (the main solid phase of iron in the examined waste), as well as almost all iron oxides, is practically insoluble in water (3×10^{-13} mmol/L for hematite), whereas their solubility in certain acids, such as nitric or acetic, is much lower, when compared with lead compounds [16–18]. It was therefore assumed that the use of relatively dilute acidic solutions would produce better separation results, regarding the selective dissolution of lead and the limited co-dissolution of iron. Furthermore, the dissolution of iron oxides was found to follow slower kinetics, as diffusion was mainly prevailed [18]. Additionally, the other impurities co-existing in smaller quantities in the original waste could also contain some other insoluble forms of iron (such as mixed oxides), as this waste was the residue of an incineration process.

It is worth noting that limited data are available in the literature, regarding the solubility of major solid phase of lead, which was recorded in the examined waste (Pb(OH)Br). Previous studies [19] revealed that the solubility of Pb(OH)Br in water was limited (0.106×10^{-3} mmol/L at 16.9 °C). This value, although small, is still higher by several orders of magnitude, when compared with the respective of hematite. The hydroxy salts of metals present generally low solubility values [20]. Additionally, although the solubility product (K_{sp}) values of similar lead compounds have been published in the past (e.g. K_{sp} of $PbBr_2 \cdot Pb(OH)_2$ is 2×10^{-15} [21]), the non-congruent dissolution of these phases in water has been also recorded. As a result, these values of solubility product should be rather taken as indicative.

However, when the relevant solid phases, such as Pb(OH)Cl, were detected in industrial wastes, they were characterized as easily leachable in certain solvents [6]. Moreover, as presented in Table 1, the solubility of lead compounds in HNO_3 solution (3.3 M and with L/S = 10) is almost quantitative. Therefore, the selection of HNO_3 as leaching agent, regarding the dissolution of lead was considered as adequate. It was expected that the solubility of Pb(OH)Br in dilute HNO_3 solutions would be high enough, whereas the determination of Limited Acid Demand (LAD) would diminish the co-dissolution of iron content, because the respective reactions would favor the release of more soluble lead-containing solid phases.

3.2. Determination of optimum acid concentration, using constant L/S ratio

The results of lead and iron removal/separation from the solid waste after the application of different (concerning the initial molarity) dilute HNO_3 solutions, using constant L/S ratio (equal to 10) are presented in Fig. 1. Since the applied L/S ratio was constant, the maximum theoretical concentration, assuming 100% (w/w) dissolution of major constituents (Pb and Fe), in the resulting leaching solutions is the same for all these experiments, representing the respective concentration limits. As expected, the concentrations of lead and iron in leaching solutions were increased almost linearly (Fig. 1a), whereas the removal of lead followed a non-linear behavior in relation to the increase of initial HNO_3 molarity. The partial dissolution of lead can be attributed to the co-removal of other constituents, when higher acid concentrations were applied, which can limit the release of lead. Since most of the lead content was existing in the Pb(OH)Br form, the non-congruent dissolution of this solid phase further complicates the interpretation of obtained results. As presented in Fig. 2a, the overall curve of lead removal can be split into three distinct linear parts, probably meaning the changing of employed mechanisms, according to the specific conditions. A four-fold decrease of gradient was noticed for each consecutive linear part. The rate of lead removal was decreased four times in relation to the variation of HNO_3 molarity from the 0.1–0.2 to 0.2–0.5 M ranges, whereas similar behavior was noticed for the further increase of initial HNO_3 molarity from 0.5 to 1 M range.

As the HNO_3 molarity increased up to the value of 0.5 M, the release of iron from the solid waste was also increased (Fig. 1b). The gradual increase of iron concentration, as well as of the other possibly co-dissolved impurities in the leaching solution was also observed by the increase of respective color (light yellow), firstly noticed for the addition of 0.3 M HNO_3, whose intensity was increased as the initial HNO_3 molarity increased. It can be also assumed that smaller quantities of initial iron solid phases may exist in different forms, even more soluble than hematite.
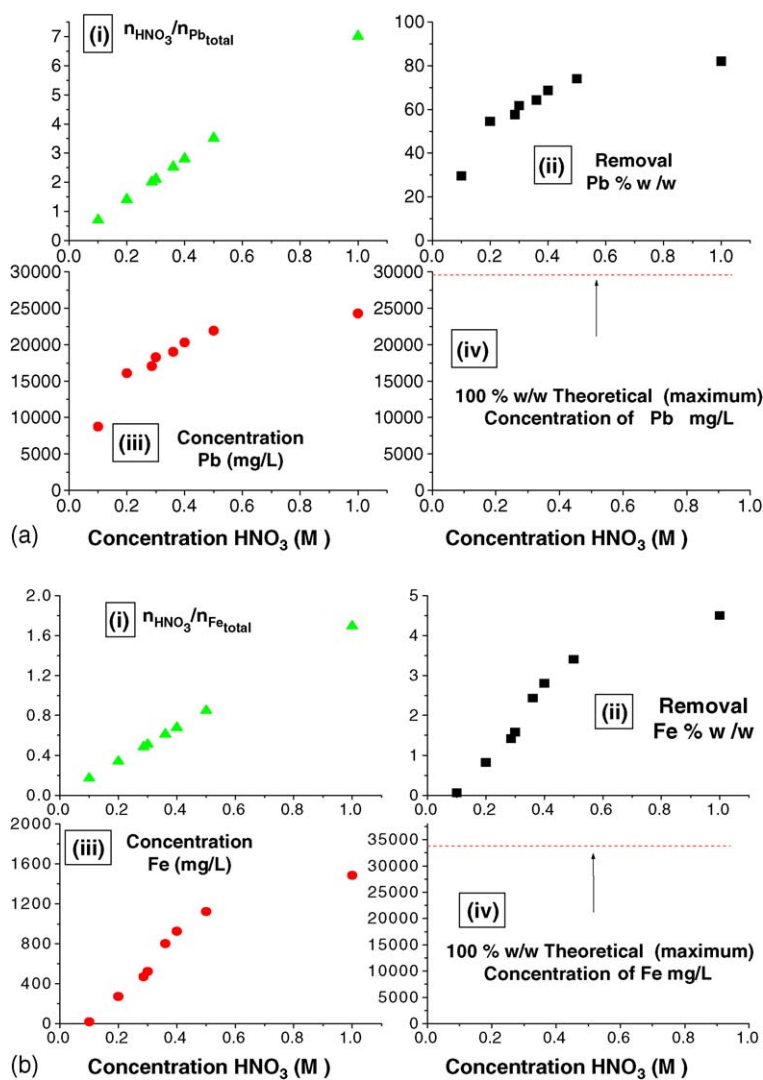
Fig. 1. (a) Lead and (b) iron selective removal from the solid waste after the application of dilute nitric acid solutions, using different molarities at constant L/S ratio (L/S = 10).

Iron follows slower dissolution kinetics in the presence of dilute nitric acid solution and therefore, its concentration (amount) will not remain constant even for the duration of weeks. The most important equilibrium is the one related with lead and bromide release. Lead release was found to reach constant values for the examined time periods (i.e. 24 h).

Furthermore, the bromide anions co-existing in the leaching solutions might also contribute to the increase of iron concentration. In acidic environments, the surface charge of hematite interface is expected to be positive. As a result, bromide anions can be sorbed onto these positive surface sites, causing lattice defects and enhancing in this way the overall iron release. Additionally, by applying HNO_3 (1 M) to synthetic samples of Fe_2O_3 (i.e. "blank" experiments) the measured concentrations were found lower (i.e. in the range of 300 mg/L) in comparison with the obtained results from this study. Therefore, the previous assumptions can be considered as viable. Nevertheless, the concentrations of iron in leaching solutions are considered rather small, concerning the

hydrometallurgical separation of major solid waste constituents (Pb–Fe).

The obtained results were described mathematically, when the Separation Factor of lead and iron was introduced ($SF_{Pb/Fe}$). The effect of HNO_3 molarity increase to the $SF_{Pb/Fe}$ was described by the Extended Langmuir model ($y = 1/(a + bx^{c-1})$), where a, b and c the relevant constants derived from the experimental data, Fig. 2b). The previous equation denotes that at constant L/S ratios (L/S = 10), the increase of initial HNO_3 molarity would result to the decrease of $SF_{Pb/Fe}$, because the respective release of iron would be favorably increased. However, the removal of lead from the waste, regarding the application of single-stage treatment under the specific conditions, can be considered as rather high, but not quantitative. For lower L/S ratios sequential extractions using more dilute HNO_3 solutions (0.1 M) can be possibly applied. In this case, the major advantage would be the most efficient separation, i.e. higher (overall) values for $SF_{Pb/Fe}$, whereas the major disadvantage would be the introduction of additional leaching/extraction stages.
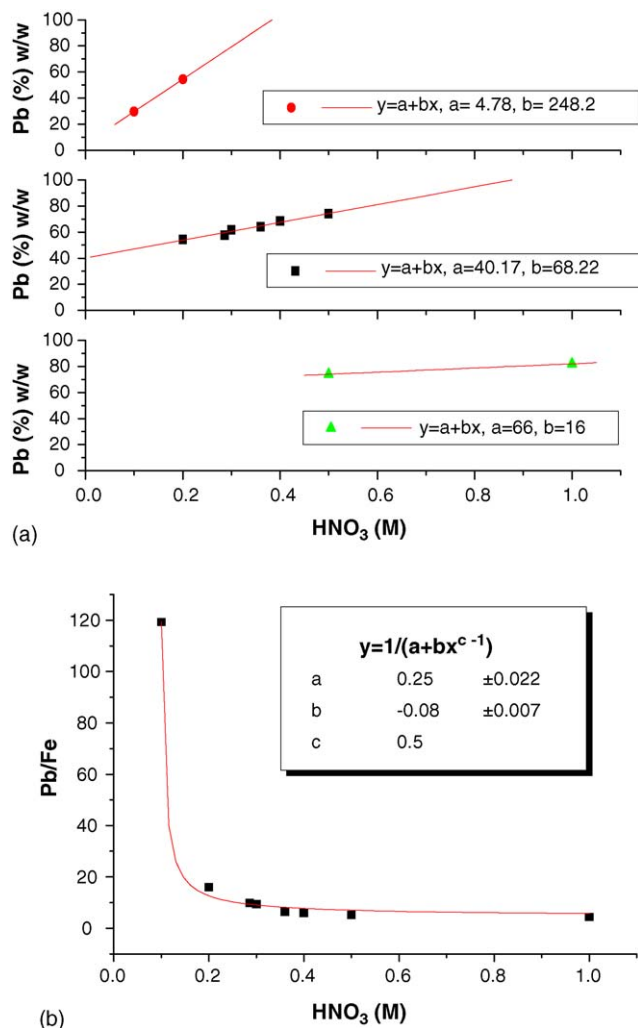
Fig. 2. (a) Split of the overall curve of lead removal into three distinct linear parts and (b) Separation Factor (Pb/Fe) measured in the leaching solutions, in relation to the HNO$_3$ molarity. The L/S ratio was kept constant (L/S = 10).

3.3. Determination of L/S ratio, using constant HNO$_3$ molarity (0.1–0.2 M)

The examination of L/S ratio variation by applying constant HNO$_3$ molarity (0.1 M) was presented in Fig. 3. The increase of L/S ratio corresponds to the simultaneous increase of HNO$_3$ molar quantity presence, as during the previous experiments (Fig. 1), although in smaller steps. Satisfactory results were obtained, concerning the effective separation (removal) of lead from the solid waste, due to selective dissolution (>90%, w/w), but without the parallel co-removal of iron (<1.5%, w/w). Furthermore, the similar concentrations of lead found in the leaching solutions, revealed that the physico-chemical "apparent" equilibrium of this system is mainly controlled by solubility (Fig. 3a), whereas the increase of lead removal (%, w/w) was linear in relation to the increase of L/S ratio up to the value of 30.

The results also showed that small amounts of lead could be incorporated into rather insoluble (under the specific experimental conditions) solid phases, therefore remaining insoluble even when excess acid concentrations would be applied and there-

fore, limiting (slightly) the removal of lead. The residual lead quantity was estimated as 2–5% (w/w) and it is likely to remain with the solid residue after the application of single step leaching/extraction treatment procedure.

The solubility at such low pH values during leaching (due to the presence of 0.1 M HNO$_3$) depends mainly from the specific chemical reagent addition and from the related dissociated ions. It is worth to note that similar pH values when applied by using other reagents, such as HCl, would not have similar effect, regarding the lead and bromide release. As a result, it is not the pH effect that is of particular importance in this case, but the applied chemical reagent, even when similar pH values were used. Additionally, when the initial concentration of applied acid is the same (i.e. 0.1 M HNO$_3$), then the variation of L/S ratio affects in a small degree the respective pH value, although slightly lower pH (i.e. more acidic) values, would be found as the L/S increases (i.e. from 10 to 50 in this study).

The comparison of Figs. 1a and 3a demonstrates that lead removal is higher in the second case, where relatively lower (molar) quantities of HNO$_3$ were applied. As a result it can be assumed that the addition of higher HNO$_3$ molarities could possibly favor the co-release of other constituents, which can limit the quantitative removal of lead, as well as of bromide from the industrial solid waste. Furthermore, this inconsistency can be attributed to the non-congruent dissolution of Pb(OH)Br, an issue that has not been previously examined at least for the applied experimental conditions.

The values of the SF$_{Pb/Fe}$ (Fig. 4) were similar in comparison with the previously presented data (Fig. 2), although much smaller HNO$_3$ molarity was applied, indicating that the use of dilute solutions would benefit the selective separation of lead. The respective curve of SF was found to follow the exponential decay model (first order) of the general type: $y = a + A\,e^{-x/b}$, where a, A and b are the respective constants obtained from regression analysis of this curve (Fig. 4).

The Limited Acid Demand for the almost complete removal of lead from the industrial waste, using 0.1 M HNO$_3$, would require L/S ratios higher than 30, considering that the separation/extraction would take place during single-stage treatment.

Experiments similar to those aforementioned were also performed using 0.2 M HNO$_3$ solution as leaching agent (Fig. 5). The critical values of L/S ratio in these experiments were found to be relevant with those previously defined (Fig. 3, i.e. around 30), although higher values of lead concentrations were recorded in the leaching solutions, when the application of lower L/S ratios occurred, due to the increase of applied HNO$_3$ molarity. It can be observed that the increase of L/S ratio in this case was found to affect the measured lead concentrations rather linearly (decrease), although the overall lead removal (%, w/w) was increased, according to the simultaneous decrease of maximum theoretical lead concentrations, which were obtained by assuming 100% (w/w) removal of lead (Fig. 5a(iv)).

Moreover, the release of iron was remained within the range of 200–325 mg/L, i.e. higher than that previously recorded. Substantially lower values of respective SF were recorded in these experiments (Fig. 6), when compared with the previous (Fig. 4).
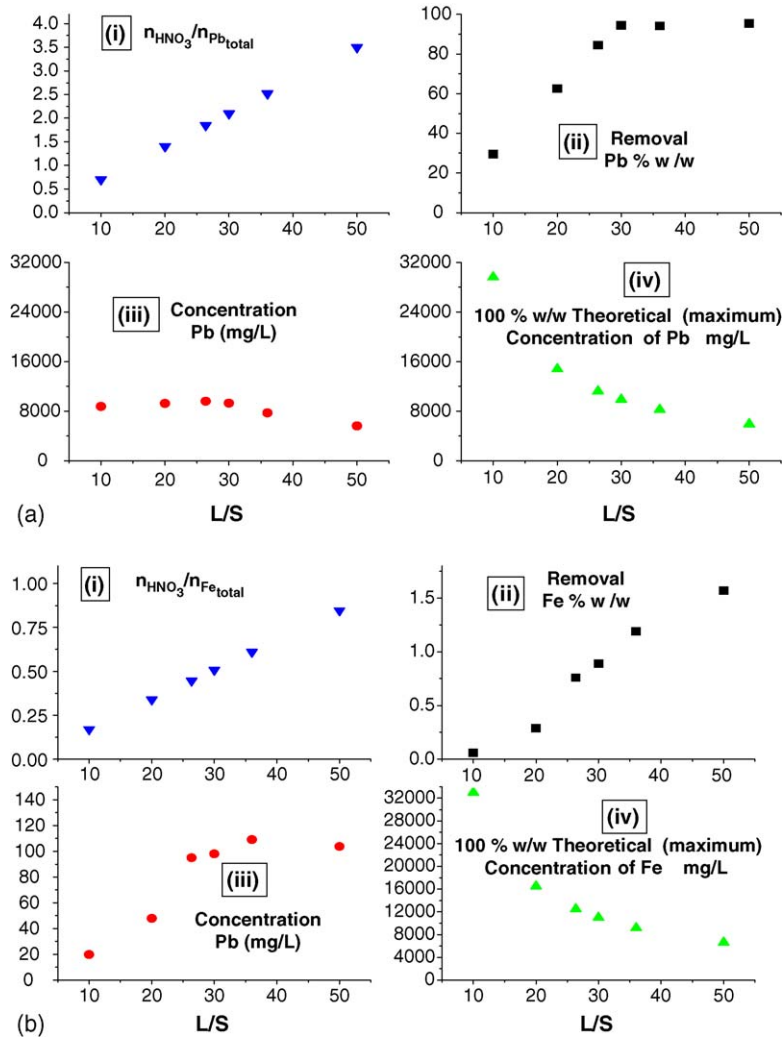
Fig. 3. (a) Lead and (b) iron selective removal from the solid waste, using 0.1 M HNO₃ as leaching agent and variable L/S ratios.

This observation can be attributed to the increase of used HNO₃ molarity. Nevertheless, these results were better, comparing with the respective values, which were obtained during the previous experiments (Fig. 2b), when using L/S = 10 and HNO₃ molarity

Fig. 4. The Separation Factor SF$_{Pb/Fe}$ in relation to the variation of L/S ratio, using constant HNO₃ molarity (0.1 M).

was up to 1 M. The higher concentrations of iron in leaching solutions (Fig. 5b), as compared with Figs. 3b and 1b, suggest that the increase of HNO₃ molarity (Fig. 1b) favors the increase of iron release and possibly that of certain other impurities.

The mathematical description of SF curve (Fig. 6) was found similar with the previous one (i.e. exponential decay model, Fig. 4), although the experimental deviation was found to be relatively higher. The respective values are presented in Fig. 6.

The Limited Acid Demand for the efficient removal of lead from the solid waste, applying one treatment stage and using 0.2 M HNO₃, would also require relatively high L/S ratio (approximately 30), although the respective SF$_{Pb/Fe}$ would be substantially decreased, when compared with the results of Fig. 4.

3.4. Determination of optimum leaching conditions, changing simultaneously the L/S ratio and the HNO₃ molarity

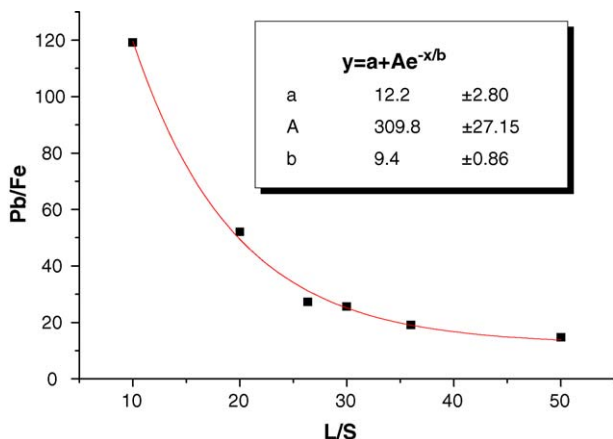During the previously presented experiments the two major leaching parameters (i.e. L/S ratio and HNO₃ molarity) were
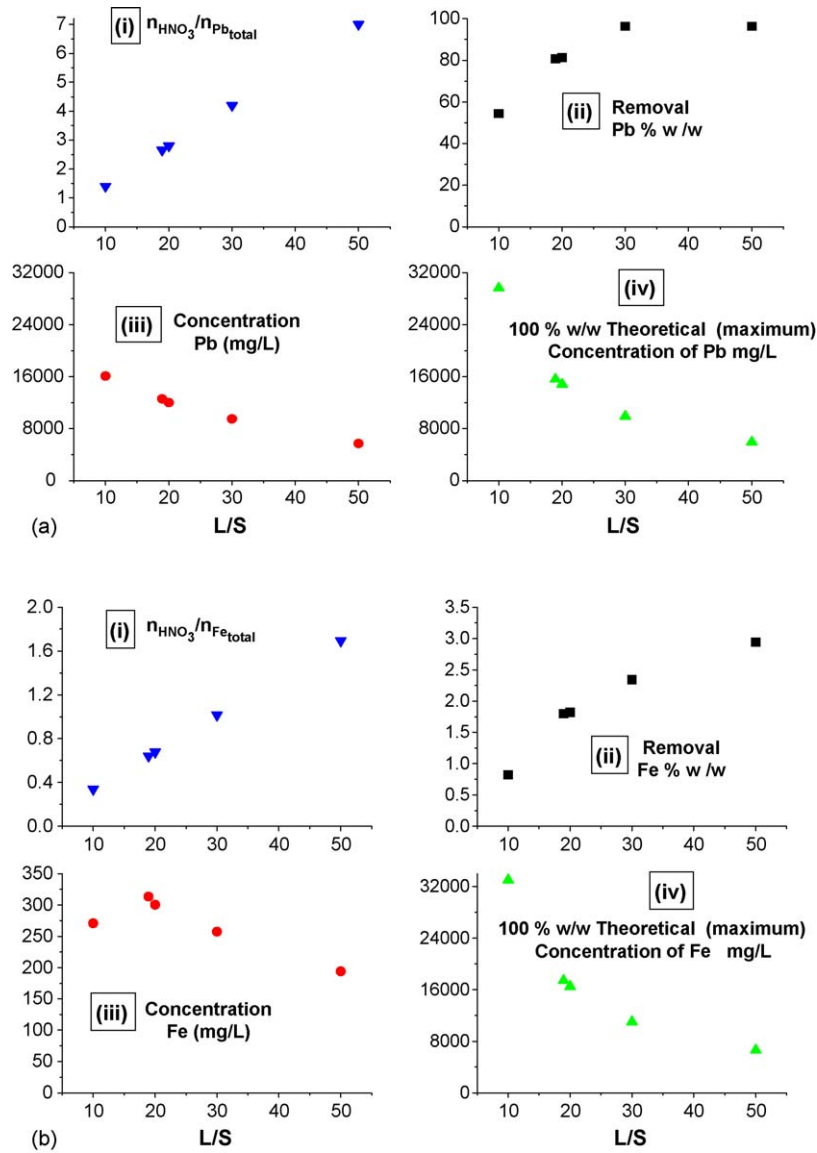
Fig. 5. (a) Lead and (b) iron selective removal from the solid waste, using 0.2 M HNO$_3$ as leaching agent and variable L/S ratios.
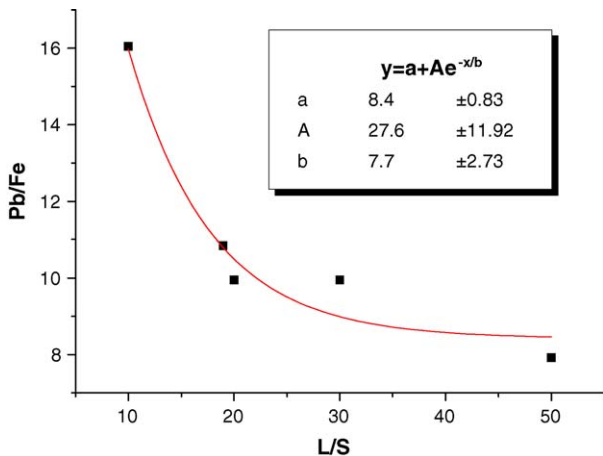

Fig. 6. The Separation Factor SF$_{Pb/Fe}$ in relation to the variation of L/S ratio, using constant HNO$_3$ molarity (0.2 M).

examined separately. In both cases, the increase of each parameter increases the addition/presence of HNO$_3$ molar quantity in the leaching solutions, although in the case of dilute solution (0.1 M) experiments the respective step of increase was smaller. By the simultaneous variation of both important parameters, appropriate leaching solutions can be prepared, which may contain similar molar quantities of HNO$_3$. In order to be able to compare the obtained results with other relevant published data, the HNO$_3$ molarities (and the respective quantities) of used acidic leaching solutions were expressed as concentrations (M). As a result, the combined effect of acid molarity and of L/S ratio can be simultaneously examined, concerning the optimization of necessary Limited Acid Demand and the effective separation conditions among lead and iron content from the solid waste can be determined, with lead removal being at the highest possible level and the iron co-removal being the lowest possible. These experiments were termed hereafter as "equimolar". In a more detailed approach, the respective calculations should
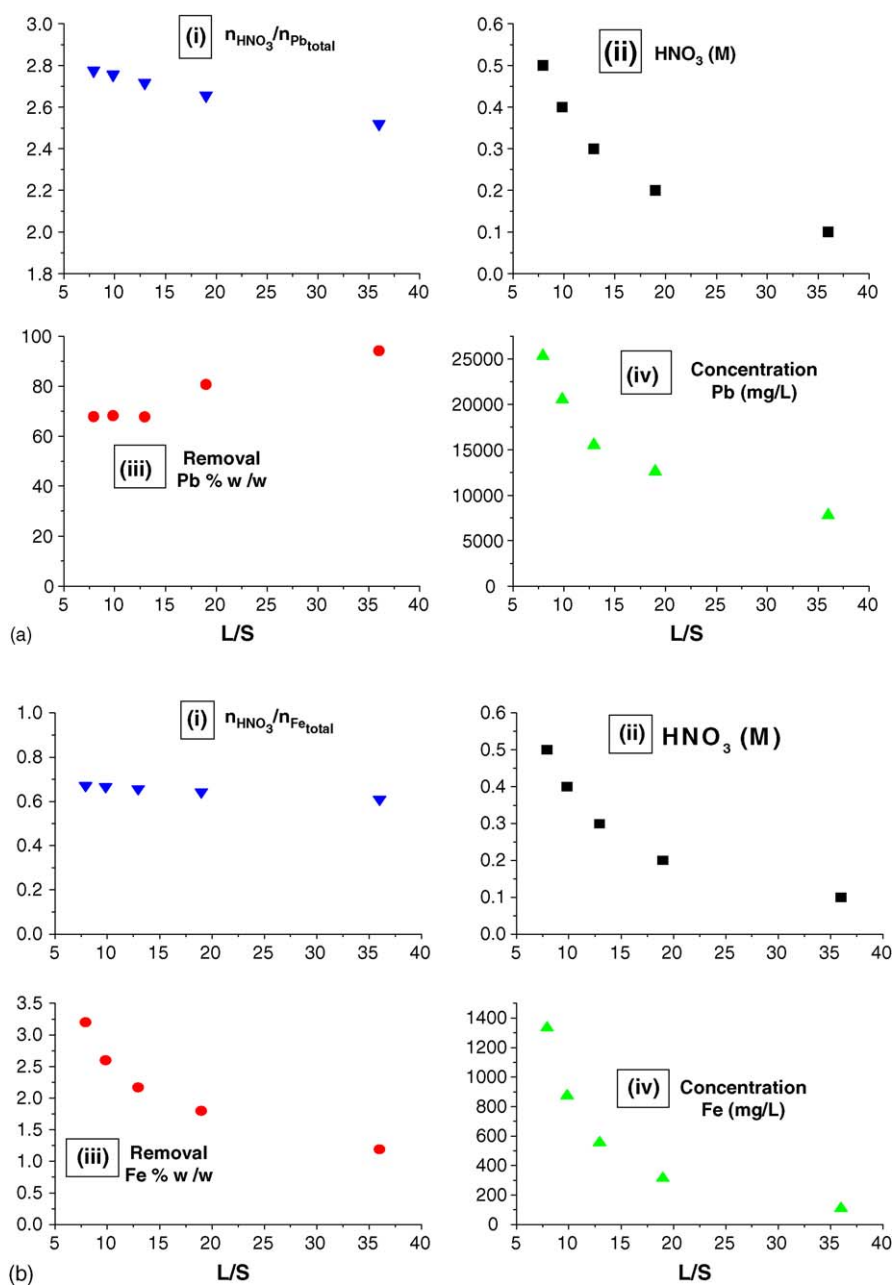
Fig. 7. (a) Lead and (b) iron selective removal from the solid waste after the application of "approximately equimolar" HNO₃ solutions, based on activity coefficients.

include also the consideration of other parameters, such as the relevant activity coefficients [17]. In the later case, the leaching solutions would contain approximately the similar molar quantities of HNO₃, but corrected with the introduction of activity coefficients and termed hereafter as "approximately equimolar" (based on molarity).

The application of "approximately equimolar" HNO₃ solutions (Fig. 7) verified the critical importance of L/S ratio. Although in these experiments the used molar quantity of HNO₃ was similar, important differences were recorded for the separation (removal) of lead (Fig. 7a) from iron (Fig. 7b), which remained mostly with the residue of extraction process. The increase of acidity favored the respective iron release, whereas the application of higher L/S ratio produced better results,

regarding the removal of lead. In this case the parallel co-release of iron was limited to low values (i.e. less than 2%, w/w). This observation becomes more evident with the introduction of SF in relation to L/S ratio (Fig. 8), which can be interpreted by the use of a simple linear equation: $y = a + bx$, where a and b are constants derived from the experimental data. The physical meaning of this equation is that when the initial molar quantity of leaching/extraction solution is equal or similar, then the $SF_{Pb/Fe}$ (expressed in mol/L for each constituent), which can be measured in the leaching solutions, will be linearly increased in relation to the increase of L/S ratio.

Similar results were obtained by the application of even more dilute HNO₃ solutions during the "equimolar" (i.e. based on molarity) experiments (Fig. 9). These results further prove that
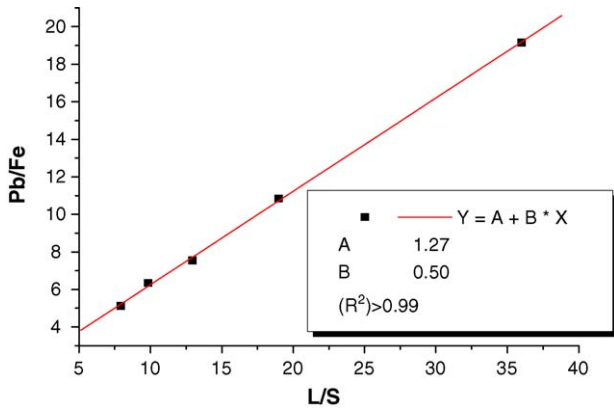
Fig. 8. The Separation Factor ($SF_{Pb/Fe}$) in relation to the L/S ratio for the "approximately equimolar" experiments.

the increase of L/S ratio led to the increase of lead release (removal) from the solid waste, although this effect was eliminated, when the SF values varied between 40 and 50. This finding can be interpreted as the main limitation of studied leaching system, concerning the release of lead and the used HNO_3 concentration.

The respective bromide measurements also verified this observation (Fig. 10). Moreover, the measured concentrations (mg/L) of lead (Fig. 9) and bromide (Fig. 10) for the L/S values 20–36 were found to be similar for each individual constituent. It can be assumed therefore, that the solubility is the major (overall) mechanism, which controls the apparent equilibrium of this leaching system and that certain limitations of this were determined.

The Separation Factors between the major constituents (Pb, Fe, Br), existing in the examined solid waste, are presented in Fig. 11. The $SF_{Pb/Fe}$ (Fig. 11a) was similar to that of "approximately equimolar" experiments (Fig. 8), indicating that even
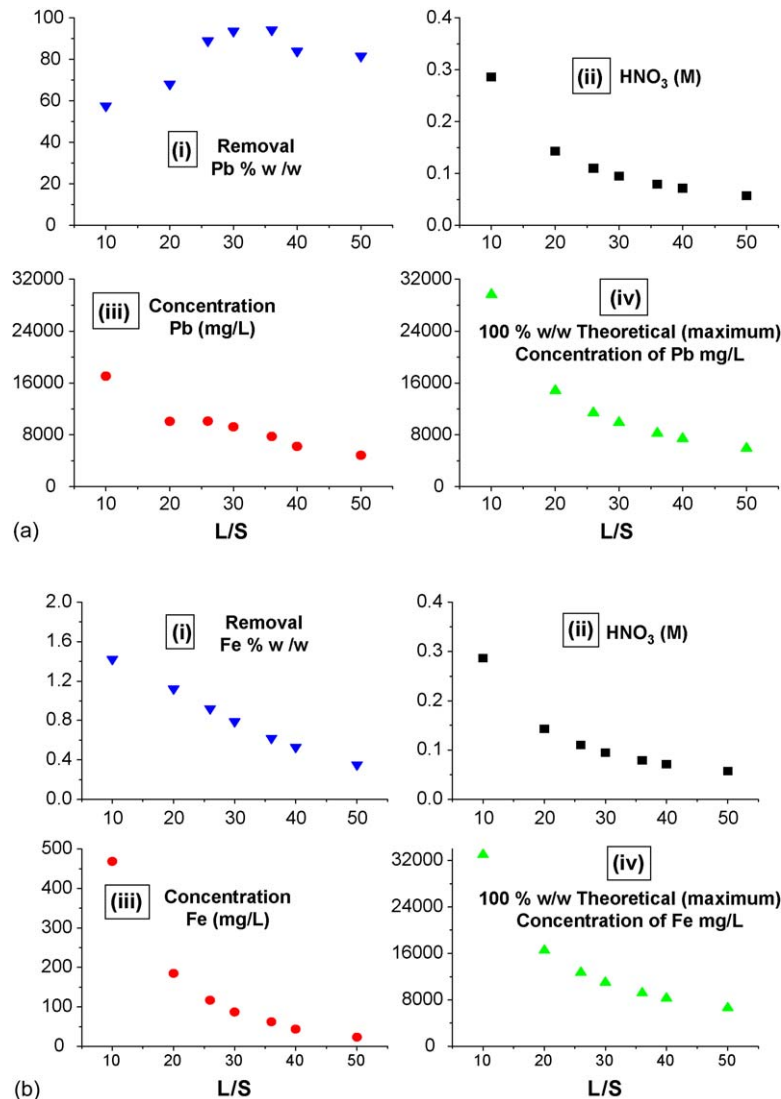

Fig. 9. (a) Lead and (b) iron selective removal from the solid waste after the application of "equimolar" HNO_3 solutions ($n_{HNO_3}/n_{Pb} = 2$ and $n_{HNO_3}/n_{Fe} = 0.48$), based on molarity concentrations.
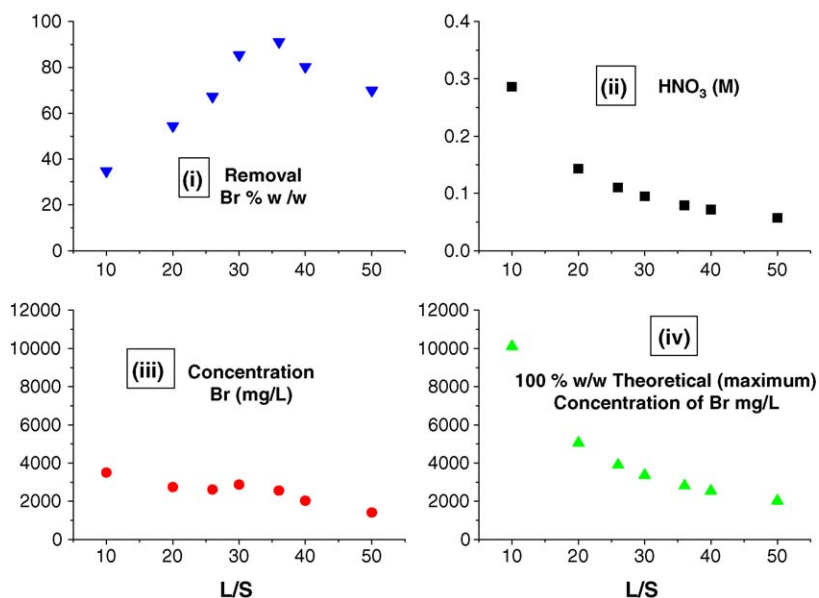
Fig. 10. Bromide removal from the solid waste after the application of "equimolar" HNO$_3$ solutions (n_{HNO_3}/n_{Br} = 2.26), based on molarity concentrations.

when small variations of HNO$_3$ concentration are applied in the leaching system, an almost linear increase of Separation Factor in relation with the increase of L/S ratio will be obtained.

Regarding the SF$_{Pb/Br}$ (Fig. 11b), the earlier assumptions of non-congruent dissolution of major lead phase (Pb(OH)Br) were further verified. The application of lower L/S ratio values (i.e. L/S = 10) resulted to molar ratio of lead and bromide in the leaching solution around 2. When the L/S ratio was increased (i.e. L/S = 36) and the solubility limitations (concerning the maximum theoretical concentration) were met for these experimental conditions, then the respective molar ratio of lead and bromide in the leaching solution was found to be 1.13, i.e. similar to the respective value of initial solid waste; this indicates the substantial (almost quantitative) removal of lead and bromide from the solid waste under the later conditions. Furthermore, these results prove that the major limiting factor of lead and bromide release in the leaching solution is the bromide concentration, whereas the release of other constituents becomes more important for lower L/S ratios and when the applied HNO$_3$ concentration increases. In lower L/S values the expected inhibition due to the presence of other co-dissolved constituents may further diminish the overall removal of lead and bromide from the industrial solid waste. Especially, when the respective concentration limits are reached, then the co-removal of other constituents is expected to exhibit a more profound effect to the obtained results, due to the increased (overall) sensitivity of leaching system.

The SF$_{Fe/Br}$ and the respective experimentally determined constants are presented in Fig. 11c. The decrease of this factor followed the exponential decay model (first order). These data verify the synergistic role of bromides, regarding the dissolution of iron, because the application of higher HNO$_3$ molarities with lower L/S values favored the respective iron dissolution (i.e. higher values of SF$_{Fe/Br}$).

The performance of "equimolar" or "approximately equimolar" experiments revealed that when low L/S ratios will be used,

then sequential extraction (leaching) steps should be preferably applied for the effective removal of lead, whereas the increase of L/S ratio would favor the single-stage treatment procedure.

3.5. Mathematical description of the studied leaching process and the introduction of specific "inhibition constant" (k_i)

The combination of two major leaching parameters, i.e. the L/S ratio and the applied stoichiometry (molar ratio) of HNO$_3$ addition to lead, was further modeled. The most adequate relation among them was represented by the following equation:

$$f(n_{HNO_3}/n_{Pb(s)}) \times f(L/S) = k_i \times [Pb\%, w/w]$$

where $f(n_{HNO_3}/n_{Pb(s)})$ is the variation in molar ratio of reactants (stoichiometry) (expressed in mol/mol, dimensionless) (see also Appendix A); f(L/S) the ratio of volume (leaching solution) to solid waste (g/g); k_i: "inhibition constant" (dimensionless); [Pb%, w/w] is the removal/release of lead from the solid waste (expressed as %, w/w).

In Fig. 12a, the relevant values are presented, noting that few experimental data were excluded (limitation of this approach). The proposed general equation may describe the expected release (removal) of lead from the solid waste and it includes a variety of experimental conditions, concerning the molar ratio of leaching agent (HNO$_3$) to lead content of solid (i.e. acid/lead, expressed in mol/mol) and the L/S ratio (i.e. volume of leaching solution/weight of solid sample). When the experimental deviation was included ($\pm 5\%$, w/w), almost all the obtained experimental values were found within the respective area (Fig. 12b). The slope of this line is the (experimental) value of "inhibition constant" (k_i). The different values of this parameter, the respective physical meaning and the limitations of Limited Acid Demand approach (i.e. of the examined methodology), accord-
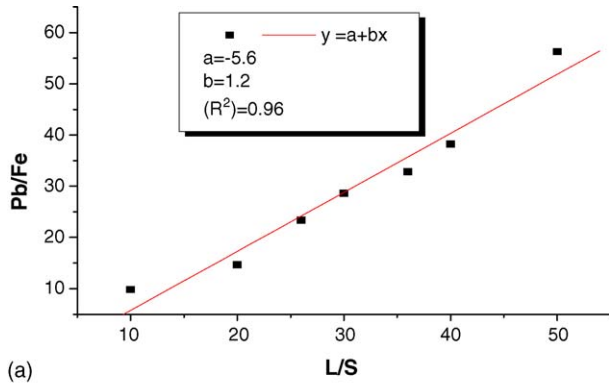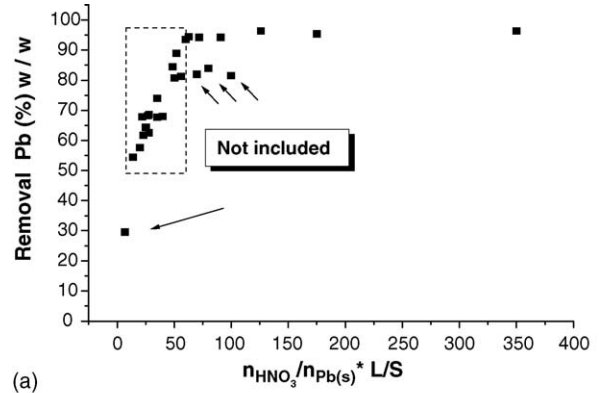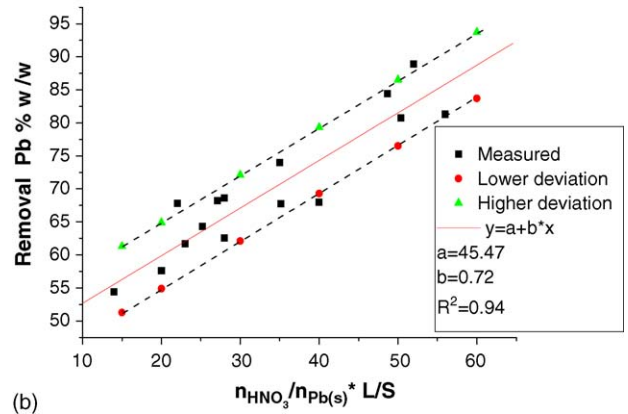
(a)
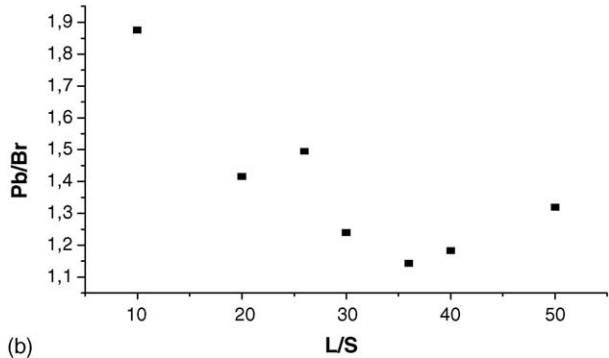
(b)
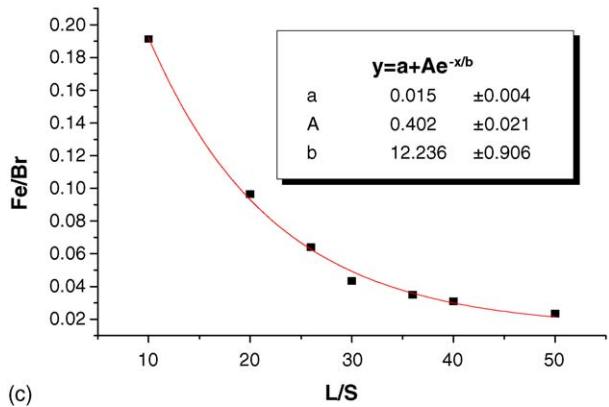
(c)

Fig. 11. (a) Separation Factor $SF_{Pb/Fe}$, (b) Separation Factor $SF_{Pb/Br}$ and (c) Separation Factor $SF_{Fe/Br}$ for the "equimolar" HNO_3 experiments.

(a)

(b)

Fig. 12. (a) Correlation between the % (w/w) removal (release) of lead from the solid waste in relation to the combined expression $\{f(n_{HNO_3}/n_{Pb(s)}) \times f(L/S)\}$. (b) The mathematical description of hydrometallurgical lead extraction (separation) by selective leaching from the industrial solid waste and for a wide range of applied experimental conditions, including the deviation of data (dashed lines).

ing to the applied experimental conditions, are summarized in Table 2.

It is worth to note that although the studied leaching system can be sufficiently described in terms of lead removal, the obtained results should be also compared with the values of Separation Factors, as previously presented. The LAD approach resulting to the quantitative lead and bromide removal with the parallel limited iron co-dissolution is optimized when the previously described combined expression reaches the value of 60 (for the studied solid waste). Considering the application

Table 2
Determination of the combined expression $\{(n_{HNO_3}/n_{Pb(s)}) \times L/S\}$ values, the respective values of "inhibition constant", its physical meaning and the limitations of Limited Acid Demand (LAD) approach (methodology)

Combined expression $(n_{HNO_3}/n_{Pb(s)}) \times L/S$ values	Values of inhibition constant (k_i)	Physical meaning	Limitations of LAD approach
<10	>0.72	Immediate response to the external factor, such as increase of HNO_3 molarity	Small number of available experimental data
Between 10 and 60	0.72	Description of lead release by the linear equation: $y = 45.46 + 0.72 \cdot x$	Certain experimental data were excluded
>60	≪0.7 (almost parallel with the x-axis)	Almost quantitative lead and bromide removal from the industrial solid waste	It should be used in combination with other parameters, such as the co-release of undesirable constituents, to prevent the addition of excess leaching agent

issues of this methodology, different conditions would be possibly applied in relation with the other important factors, such as cost, technical equipment, etc. The single-stage hydrometallurgical process would require the application of higher L/S ratios (>30), whereas lower L/S ratios should be combined with the application of sequential extractions, using the same leaching agent (0.1 M HNO$_3$) and approximately the same molar quantity of this acid.

The application of optimized conditions, regarding the specific methodology, was examined by using a typical small-scale laboratory-mixing device; the obtained results proved that the removal/separation of lead and bromide from the solid waste are feasible with the application of ambient conditions (in terms of temperature and pressure). Moreover, detailed kinetic studies revealed that lead and bromide were sufficiently released within the short time of 20 min period, offering an additional advantage for the overall treatment of this specific solid waste [22]. Similar results were also obtained by the use of dilute acetic acid solutions (for the specific industrial waste), but the applied acid concentrations in that case were higher (around 1 M) [23].

4. Conclusions

The application of dilute HNO$_3$ solution (0.1 M) under ambient temperature (25 °C) and pressure was found to be adequate for the (almost) quantitative removal of lead and bromide content from a heavily polluted toxic industrial solid waste, without the parallel dissolution (practically diminished) of co-existing iron content. By applying these experimental conditions, almost the entire iron content remained in the solid residue of leaching/extraction process. Lead and iron release can be described by the respective Separation Factor (SF$_{Pb/Fe}$), which was found to increase linearly in relation to the applied L/S ratio, when similar molar quantities of HNO$_3$ were applied, whereas when the acid molarity was kept constant and the L/S ratio was varied, then this factor followed the exponential decay model (of first order). When the applied L/S ratio was kept constant, the Separation Factor was found to decrease with the increase of applied acid molarity, according to the extended Langmuir model, indicating that the increase of acid molarity will favor the relative release of iron, as well as of other impurities. The obtained experimental data can be sufficiently described by the following equation:

$$f(n_{HNO_3}/n_{Pb(s)}) \times f(L/S) = k_i \times [Pb\%, w/w],$$

where the slope of this line was the introduced "inhibition constant" (k_i). A value of 0.7 for this constant together with the value of approximately 60 for the combined expression: $\{f(n_{HNO_3}/n_{Pb(s)}) \times f(L/S)\}$ were the limiting factors of Limited Acid Demand approach, indicating that the further increase of combined expression values are not expected to result to the increase of lead removal, whereas the excess addition of acid will be spent interacting with the other solid phases of substrate (mostly with iron oxides) and therefore, it should be avoided. Furthermore, all the results proved than the use of low L/S ratio values in combination with low HNO$_3$ molarity will preferably require the application of sequential leaching/extraction stages, whereas when the application of higher L/S ratios is feasible,

then the removal of lead and bromide would be possible by the application of single treatment stage.

The applied ambient conditions ensure that numerous problems existing in similar procedures (such as specific equipment for highly corrosive environments, hazardous air emissions, use of concentrated acids, etc.) would be limited, at least for the treatment of relevant toxic industrial solid wastes.

Appendix A

Percentage removal (%, w/w): The percentage of each component measured in the leaching solution (after filtration) and expressed as % (w/w) of its initial content in the solid waste (dimensionless).

L/S ratio: Liquid/solid ratio (dimensionless). This factor can be also found in the literature as volume/solid (or phase ratio) and refers with the weight of solution (g) to the weight of solid (g). For all the performed experiments with dilute solutions the density of leaching solutions was considered approximately as 1 (g/mL).

Concentration: It refers to the measured concentration of each component in the leaching solutions (after filtration) and after the application of extraction procedure; it is expressed as mg/L.

Theoretical concentration: It refers to the expected theoretical concentration of each constituent in the leaching solution (after filtration), assuming 100% (w/w) removal from the solid matrix; it is expressed as mg/L. This parameter depends only on the applied value of L/S ratio.

SF$_{Pb/Fe,Pb/Br,Fe/Br}$: It refers to Separation Factor, i.e. the molar ratio of respective constituents in the leaching solutions (after filtration). This factor is dimensionless and it denotes e.g. the numerical value of released (dissolved) lead (expressed as molarity, M) against the (co-dissolved) iron (also as M).

$n_{HNO_3}/n_{x\,initial}$: The molar ratio of HNO$_3$ against the constituent of interest, which is contained in the industrial solid waste (dimensionless). This factor represents e.g. the respective stoichiometry of the following general dissolution reaction: $x\text{Pb}_{(s)(total)} + y\text{HNO}_3$, where $n_{HNO_3}/n_{Pb(s)} = y/x$ and $n_{Pb(s)}$ is the molar (total) quantity of lead (or of other constituent), existing in the industrial solid waste. Similar expressions may be also obtained for the other constituents (iron or bromides).

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