Full Length Research Paper

Study of potential environmental risk of trace metallic elements in mine tailings: Case of Draa Lasfar functional mine in Marrakech - Morocco

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Mining activity is one of the most important sources of heavy metals in the environment. In Marrakech region, functioning or abandoned mines represent a great hazard due to huge amounts of waste deposited in waste dumps and tailings often with high concentration of heavy metals pollution. In this study, the chemical forms of four heavy metals in mine tailings of Draa Lasfar in north-west of Marrakech city (Morocco) were studied by determining of four metals (Cd, Cu, Pb, and Zn) using standard solvent extraction and atomic absorption spectrophotometric techniques. The chemical pools of the metals indicated that the metals were distributed into six fractions with most of the metals residing in the non-residual fractions, suggesting how readily the metals are released into the environment. Results showed Cd and Cu were predominantly associated with short-term mobile fraction (F1 and F2) while Pb was largely associated with long-term mobile fraction (F3, F4 and F5) and Zn was essentially bound to Fe–Mn oxide phase (F4).

Key words: Heavy metal contamination, mining activity, sequential extraction, mine tailings, Marrakech – Morocco.

INTRODUCTION

The mining industry is an important asset for the economy of many regions across Morocco, particularly with respect to exports and employment, but also through numerous technological developments.

Active mining operations must respect governmental environmental criteria. Thus, the introduction of contaminants in the environment is limited to a level considered acceptable by the overseeing governments. Nevertheless, some abandoned / functional mine sites are not well controlled and have significant impacts on the environment (El Adnani et al., 2007).

Mining operations generate different types of
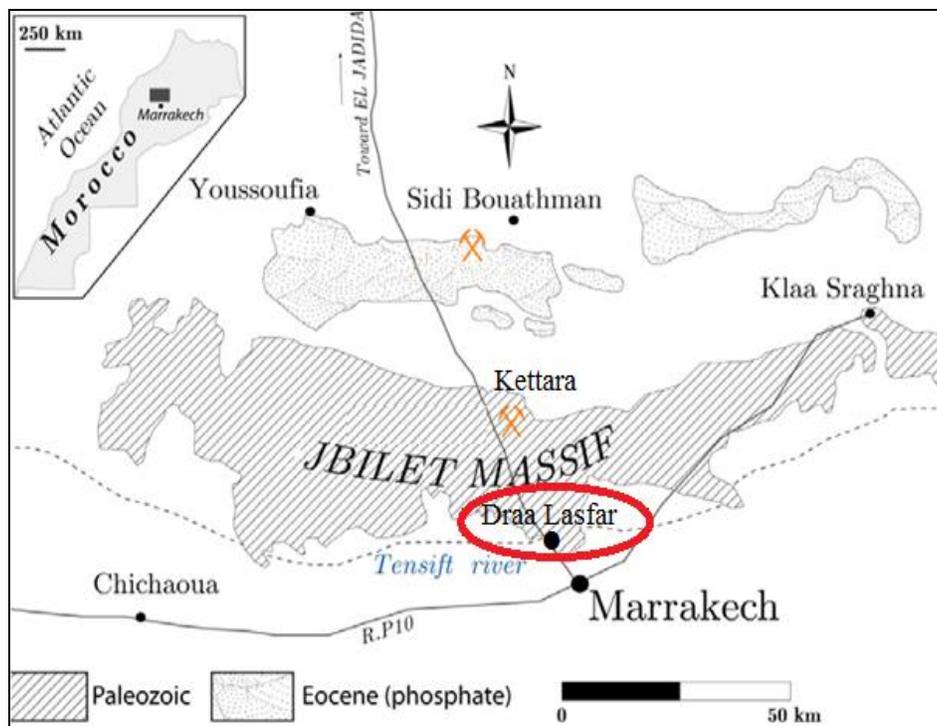
Figure 1. Location of Draa Lasfar mine.

wastes which are potentially environmentally harmful (El Gharmali et al., 2004; Aikpokpodion et al., 2013). Mining and milling/beneficiation processes (crushing, grinding, washing,) generate four major categories of waste, that is, (1) Mine waste (low-grade ore, overburden and barren rocks), (2) Tailings, (3) Dump heap leach and (4) Acid mine water (Esshaimi et al., 2012). These wastes loaded enriched in heavy metals are disposed in surrounding land and water in a more or less environmentally acceptable manner.

As a result, elevated levels of heavy metals can be found in and around disused metalliferous mines, nearby agricultural soils, food crops and stream systems, posing a potential health risk to residents in the vicinity of mining areas (Dawson and Macklin, 1998; Sahuquillo et al., 2003). The goal of this study was to determine the release of acidity and dissolved metals from the Draa Lasfar mine tailings in order to assess the impact of the functional mine residues on the biota and populations in this region.

Site description

Draa Lasfar mine, involves a pyrite deposit located 10 km northwest of Marrakech city (Figure 1) that can pose a risk for the environment due to discharge of tailings all around the mine area (Avila et al., 2012). The Draa Lasfar deposit contains 10 Mt of ore grading 5.3 wt.% Zn,

2wt.% Pb, 0.3 wt.% Cu (2007) and their orebodies consist dominantly of pyrrhotite (70 to 95 vol.% of sulphides, butcommonly up to 90 to 95 vol.% in Zn and Cu-depletedzones), with lesser sphalerite (1 to 10 vol.%), galena (0.5 to5 vol.%) and chalcopyrite (1 to 5 vol.%), and with local concentrations of deformed pyrite (2 to 3 vol.% of totalsulphides) being arsenopyrite the most common of the minor minerals (Marcoux et al., 2008).

Draa Lasfar mine is located a few hundred meters from the Tensift River, close to two rural communities (Ouled Bou Aicha and Tazakourte) of about 5790 ha of which 65% are occupied by farmland (Figure 2). The climate is Mediterranean, bordering arid and semi arid with an average annual precipitation of 231 mm (10 years). Temperatures are characterized by great daily and seasonal variation with an average value of 11.5°C in January and 36.8°C in July.

MATERIALS AND METHODS

The sampling of the tailings was carried out in 2 sampling spots (S1, S2) and (S3, S4) respectively from each tailings reservoir TR1 (155 m/100 m/13 m) and TR2 (150 m/125 m/19 m) (Figure 2) by using a specially designed cylindrical stainless steel corer. After collection, the tailing samples were carefully transferred to clean and dry self-sealing polyethylene bags and transported to laboratory. After being air-dried in paper lined propylene trays at room temperature and disaggregated with a wooden roller, all samples were sieved through <2 mm or <100 µm.

The tailings samples from each zone were thoroughly mixed and
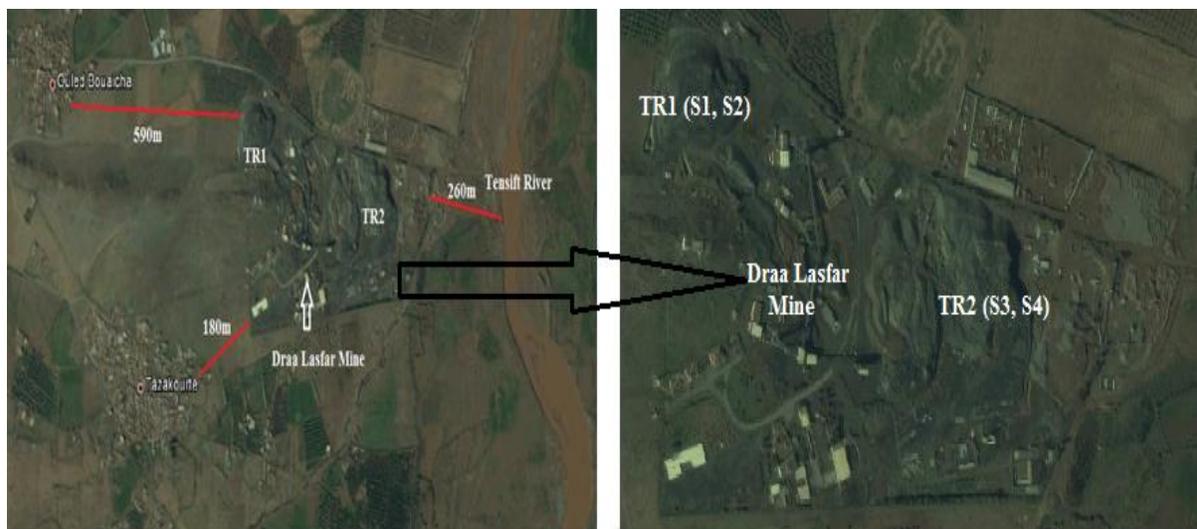
Figure 2. Panoramic sight of Draa Lasfar mine tailings.

homogenized by coning and quartering. Finally the tailings samples were stored at 4°C in tightly sealed polyethylene bags until its analysis. Due to the strong association and affinity of heavy metals with fine grained soil components, the <100 μm tailing fraction were selected for the sequential extraction and total chemical determinations (Pickering, 1986; Ramos et al., 1999; Cuong and Obbard, 2006). The <2 mm tailing fraction was used to determine the pH, electrical conductivity (EC), organic matter (OM), organic carbon (OC) and carbonate contents. The physical-chemical characterization consisted in the determination of the tailings sample pH, electrical conductivity (EC), organic matter content (OM) and the carbonate content. The soil pH was measured with the aid of pH meter while EC was done with the use of electrode meter (Badmus et al., 2014). Organic carbon content of the soil sample was estimated by following Walkey and Black method (1934). 10 g of sieved soil sample was taken into a 500 ml wide mouthed Erlenmeyer flask. To this, 10 ml of 1 N $K_2Cr_2O_7$ was added and swirled the flask gently to disperse the soil in the solution. 20 ml of Conc. H_2SO_4 was then added slowly followed by vigorous shaking for 1 min. Distilled water (200 ml) was added to the flask and the suspension was filtered. Few drops of o-phenanthroline indicator was then added to the filtered solution and titrated against 0.5 N $FeSO_4$ H_2O. Sample without soil was kept as a blank. The amount of organic carbon in the soil sample was calculated by using the following formula:

$$\text{Organic carbon (\%)} = \frac{(\text{milli equivalents } K_2Cr_2O_7 - \text{milli equivalents } FeSO_4) \times 0.003 \times 100}{\text{Soil weight (g)}} \times f$$

% Organic Matter = % Organic Carbon 1.724

Total heavy metal concentration was determined by atomic absorption spectroscopy after an acid digestion of samples. The methodology followed for the digestion consisted in weighting 1g dry sample and adding 3 ml HNO_3 (70%), 6 ml HCl (37%) and 3 ml HF (48%). The analyzed sample was placed in a sand bath to complete the digestion. After digestion, the sample solution was air-cooled and then diluted with deionized water.

The optimized sequential extraction procedure was applied to assess heavy metal fractionation in tailings samples (Wufem et al.,

2013). The sequential extraction was performed using five-step procedure (Fuentes et al., 2004). Additionally, a sixth step was added, which consisted of dissolving the final residue using the same digestion procedure for the total metal determination (Gleyzes et al., 2002; Avila et al., 2012).

(F1) Water Soluble: Soil sample extracted with 15 ml of deionized water for 2 h.
(F2) Exchangeable: The residue from water soluble fraction was extracted with 8 ml of 1M $MgCl_2$ (pH 7.0) for 1 h.
(F3) Carbonate-Bound: The residue from exchangeable fraction was extracted with 8 ml of 1M Ammonium acetate (adjusted to pH 5.0 with Acetic acid) for 5 h.
(F4) Fe-Mn Oxides-Bound: The residue from carbonate fraction was extracted with 0.04 M NH_2 OH. HCl in 25% (v/v) Acetic acid at 96°C with occasional agitation for 6 h.
(F5) Organic-Bound: The residue from Fe-Mn oxides bound fraction was extracted with 3 ml of 0.02M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was added and the mixture heated to 85°C for 3 hours, with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture heated again to 85°C for 3 h with intermittent agitation.
After cooling, 5 ml of 3.2 M NH_4 acetate in 20% (v/v) HNO_3 was added and the samples was made up to 20 ml with deionized water and agitated continuously for 30 min.
(F6) Residual: The residue from organic fraction after drying was digested in a conical flask with 10 ml of 7M HNO_3 on a hot plate for 6 h. After evaporation, 1 ml of 2 M HNO_3 was added and the residue after dissolution was diluted to 10 ml. The residue was washed with 10 ml of deionized water. After each successive extraction separation was done by centrifuging at 4000 rpm for 30 min. The supernatants were filtered and analyzed for heavy metals. All chemicals used were of reagent grade and pure deionized water was used throughout the experimentation. All plastic were soaked in 10% HNO_3.

RESULTS AND DISCUSSION

The results obtained for the tailing grain-size, pH, EC, OM, OC and $CaCO_3$ content measurements

Table 1. Mean values (%) of the grain-size analysis and geochemical parameters of different tailing samples from Draa Lasfar mine.

Variables	S1	S2	S3	S4
clay	25.7 ± 3.8	27.7 ± 4.5	29.1 ± 3.1	27.4 ± 3.5
Fine silt	18.1 ± 4.7	14.7 ± 3.7	13.5 ± 2.7	15.6 ± 2.7
Coarse silt	9.2 ± 3.5	10.5 ± 1.8	13.8 ± 1.5	13.1 ± 3.2
Fine sand	24.7 ± 3.7	21.4 ± 3.4	19.7 ± 3.1	19.2 ± 4.7
Coarse sand	22.5 ± 4.1	25.7 ± 5.8	23.9 ± 2.8	24.1 ± 8.4
pH	7.5 ± 0.5	7.4 ± 0.5	7.6 ± 0.5	7.2 ± 0.6
E.C ($\mu S.cm^{-1}$)	1782.7 ± 421.3	1549.5 ± 348.5	1257.9 ± 264.2	1865.4 ± 421.7
OM (%)	2.7 ± 1.0	3.5 ± 0.5	3.2 ± 1.7	2.3 ± 0.8
OC (%)	1.6 ± 0.6	2.0 ± 0.4	1.9 ± 1.0	1.3 ± 0.3
$CaCO_3$ ($mg.g^{-1}$)	181.5 ± 17.1	196.4 ± 32.1	162.1 ± 21.4	168.2 ± 22.5
SO_4^{2-}	3.7 ± 0.6	3.4 ± 0.4	3.9 ± 0.6	3.7 ± 0.6

Table 2. Mean total concentrations of heavy metals of different tailing samples of Draa Lasfar mine.

Variables	S1	S2	S3	S4
Cd ($mg.kg^{-1}$)	143.1 ± 12.7	127.8 ± 13.4	157.2 ± 8.8	96.7 ± 9.4
Cu ($mg.kg^{-1}$)	871.9 ± 25.8	971.2 ± 42.4	969.1 ± 38.7	950.9 ± 35.2
Pb ($mg.kg^{-1}$)	3381.7 ± 117.1	3144.5 ± 34.7	2942.7 ± 37.7	3108.8 ± 41.8
Zn ($mg.kg^{-1}$)	2478.5 ± 124.2	2123.7 ± 95.7	2268.1 ± 67.8	2398.4 ± 78.5

corresponding to the old Draa Lasfar tailing mine are presented in Table 1. These results show that OC of different tailing samples depends on the sand composition of tailings. The low OC values of different soils is related with the low rate of degradation by microbial-mediated processes due to the heavy metal contamination. These are also probably related to the poor absorbability of organics on negatively charged quartz (Aysha et al., 2015) which predominate in solid tailings of Draa Lasfar mine. In addition, the constant flushing activity by rain can support the low percentage of OC in these soils.

Results show also that Draa Lasfar mine tailing samples have neutral to alkaline pH for the majority of the samples. Neutral and alkaline pH in mining residues could be attributed to the presence of carbonates with a high concentration ranging from 162.1 to 196.4 mg g^{-1} for tailings, due primarily to the mixture of these mining residues with soil very rich in carbonates. The EC measurements revealed that all tailings samples presented high values ranging from 1257,9 to 1865.4 μS cm^{-1}. Results showed that the most alkaline tailings samples have the lower EC values. This correlation between high pH and low EC value can be explained by the presence of low amounts of sulfur ions that causes a decrease of the EC. Regarding the carbonate content, it can be stated that tailings with a pH of 7.1 and higher generally have high calcium carbonate content. Total element concentrations in the investigated soils varied in

a narrow range of values (Table 2). In this sense, alkaline tailing samples together with high amounts of OM and the presence of carbonates increase the retention of heavy metals in these tailing samples.

However, these values do not provide sufficient information of its potential hazardous effects on environment because the mobility and eco-toxicity of heavy metals depend strongly on their specific chemical forms or binding. Heavy metals may be distributed among many components of the tailings and may be associated with them in different ways (Aikpokpodion et al., 2013) and the determination of the heavy metals fractionation is useful in order to assess toxic effects. The chemical form of heavy metals in tailing components is of great significance in determining the potential bioavailability and translocation of the metals to other environmental compartments like water, soil, plant and microorganisms when physicochemical conditions are favorable (Cuong and Obbard, 2006).

Overall, Cd is well distributed among the different fractions in all tailing samples (Figure 3) and seems to be very available with more than 34.1 to 42.7% of this metal bound to the short-term mobile fraction F1 and F2 respectively. The long-term mobile fraction (F3, F4 and F5) homes more than 34.5 to 38.5% of Cd. The immobilized fraction (F6) traps about 18.3 to 24.5%.

Copper in tailings (Figure 4) is essentially bound to soluble (F1) and exchangeable fractions (F2) with more than 34.7 to 37% of the total metal content. Copper is
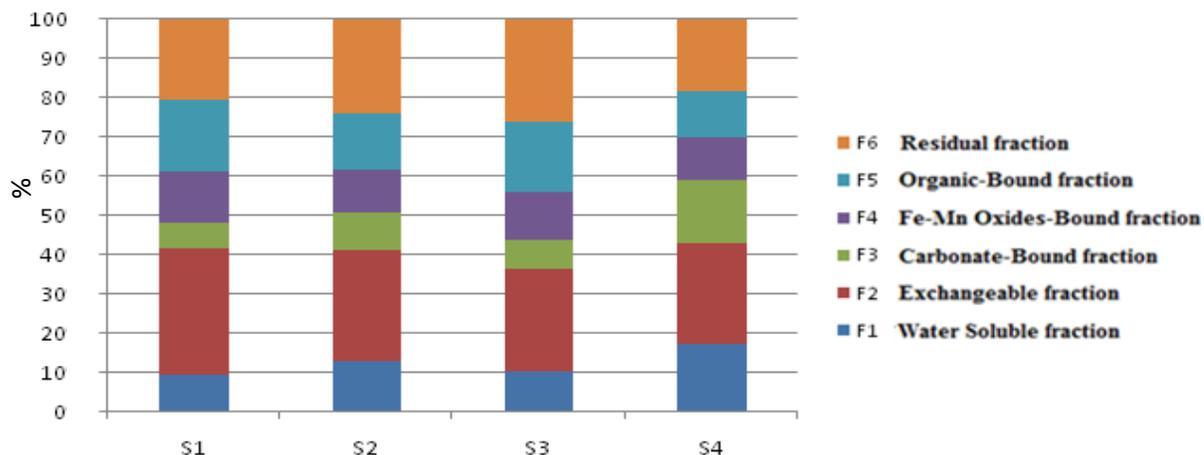
Figure 3. Relative distribution of Cd among six fractions (F1-F6) obtained by chemical extraction of studied tailing samples.
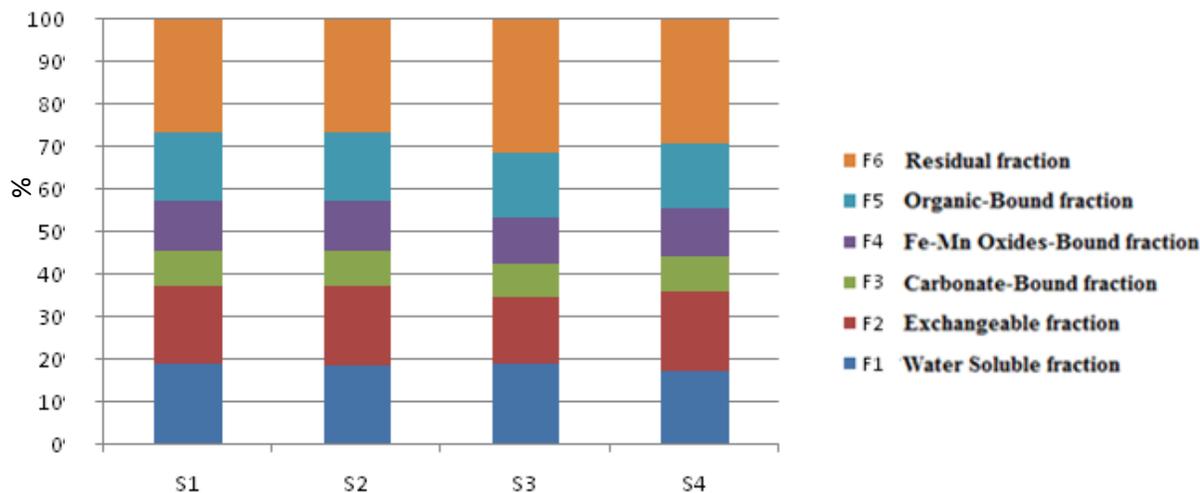
Figure 4. Relative distribution of Cu among six fractions (F1-F6) obtained by chemical extraction of studied tailing samples.

also widely present (26.5 to 31.5%) in the residual fraction (F6). The oxidizable (F3), acid-soluble (F4) and reducible factions (F5) are represented by small percentages in these tailings, representing respectively about 7.9 to 8.5, 10.9 to 11.7 and 14.8 to 16%.

The high percentage of Cu in the residue is likely due to the fact that Cu is easily chemisorbed on or incorporated in clay minerals (Pickering, 1989). The significant Cu concentrations in organic phase can be justify by Cu affinity with OM, thus it can be hypothesized that Cu is bound to labile organic matter such as lipids, proteins, and carbohydrates. Lead distribution (Figure 5) in tailings is characterized by a strong dominance of this metal bound to long-term mobile fraction (F3, F4 and F5), with more than 50.4 to 60% of the total metal. The short-

term mobile fraction (F1 and F2) represents about 18 to 21.5%. The remaining fraction (F6) traps about 19 to 28% of the total metal.

The relatively high percentage of Pb in reducible phase is in agreement with the known ability of amorphous Fe–Mn oxides to scavenge Pb from solution (Yusuf, 2007). Thus, a high Pb percentage in the reducible fraction is a hazard for the aquatic environment because Fe and Mn species can be reduced into the porewaters during early diagenesis by microbially mediated redox reactions (Oluwatosin et al., 2008). Dissolution will also release Pb associated with oxide phases to the porewater possibly to the overlying water column and to benthic biota (Kabala and Singh, 2001). The major sources of Pb are from intensive human activities, including agriculture in the
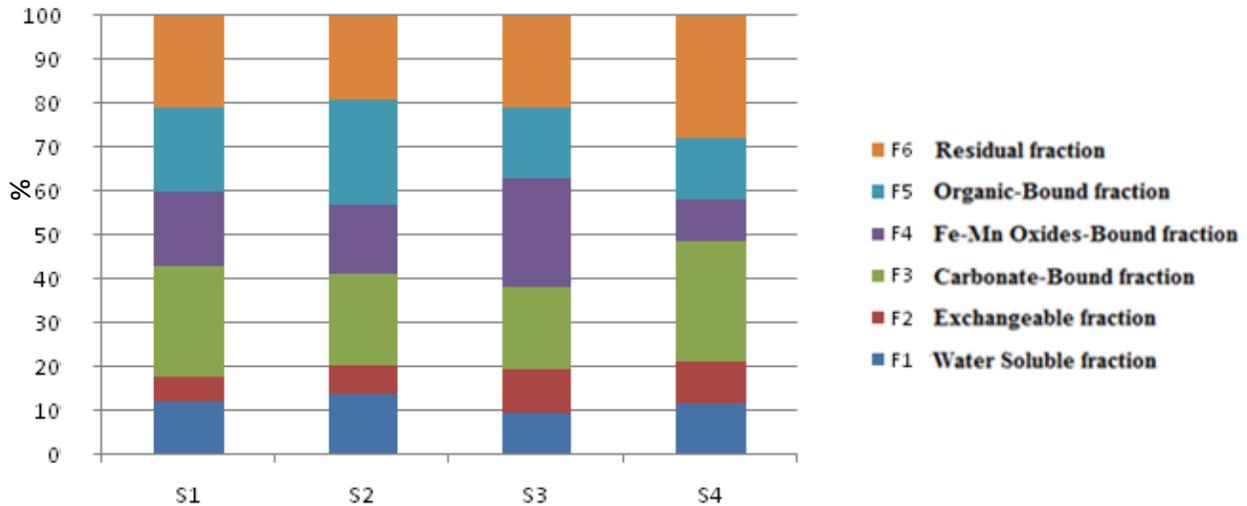
Figure 5. Relative distribution of Pb among six fractions (F1-F6) obtained by chemical extraction of studied tailing samples.
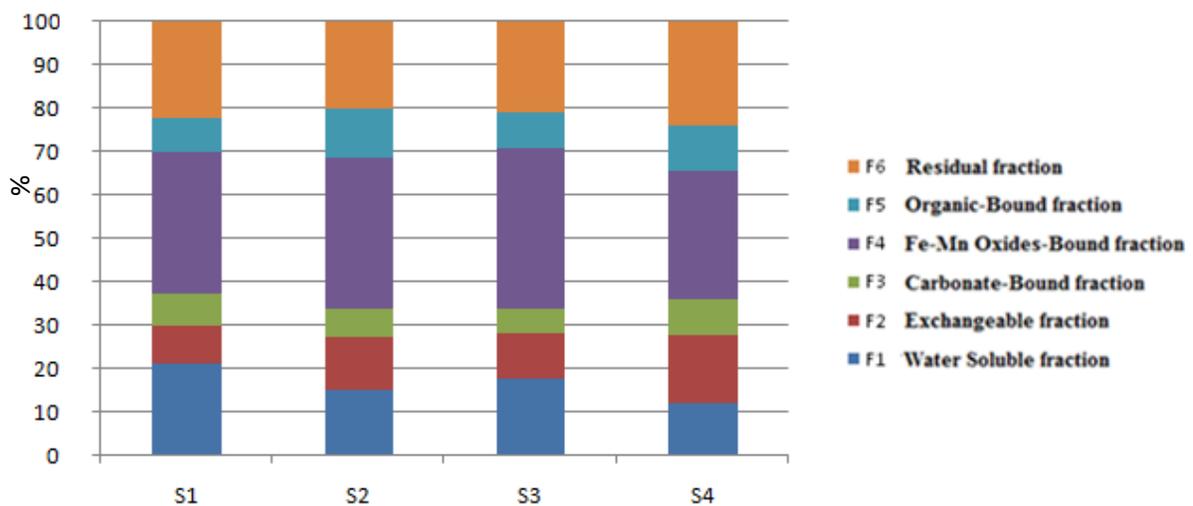
Figure 6. Relative distribution of Zn among six fractions (F1-F6) obtained by chemical extraction of studied tailing samples.

drainage basin (Rodriguez et al., 2009). In addition, a substantial contribution from the factories located in the upstream of the Tensift river dealing with Pb play a vital role in soils contamination by heavy metals as referred by Sarkar et al. (2007).

Zinc in tailings (Figure 6) is essentially bound to Fe–Mn oxide phase (F4) with more than 32 to 39% of the Zn content. This result can be justified by the high stability of Zn on oxides. Iron oxides adsorb considerable amounts of Zn and these oxides may also occlude Zn in the lattice structures (Banerjee, 2003). Zinc is also widely present (21 to 26%) in the residual fraction (F6). The water soluble (F1) and exchangeable fractions (F2) are represented by relatively small percentages in these

tailings (about 13 to 22% and 9 to 14% respectively).

Conclusions

Environmental pollution by heavy metals originated from functional mines can become a very important source of contamination both in soil and water. Therefore, the characterization of chemical and physical properties tailings is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste. Taking into consideration the high mobility and potential bioavailability of heavy metals in this fraction and their total concentration, it can

be concluded that Draa Lasfar mine tailings could have potentially hazardous effects on the environment. Cadmium and copper were predominantly associated with short-term mobile fraction (F1 and F2) while lead was largely associated with long-term mobile fraction (F3, F4 and F5) and Zn was essentially bound to Fe–Mn oxide phase (F4).

Conflict of Interest

The authors have not declared any conflict of interest.

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