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Marble wastes as amendments to stabilize heavy metals in Zn-Electroplating sludge

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Abstract. Powdered marble wastes (PMW) generated by Utique marble cutting industries (North of Tunisia) with abundant amounts were used in this study as low-cost materials to investigate the stabilization of heavy metals (Pb, Zn, Fe) in sludge generated from a local Zn-Electroplating factory. Powdered marble wastes were evaluated by means of chemical fractions of heavy metals in sludge and concentrations of heavy metals in leachate from columns to determine their ability to stabilize heavy metals in contaminated sludge. Results indicated that chemical fractions of heavy metals in sludge were affected by application of the PMW mineral materials and pH, however, the effects varied with heavy metals. Application of the powdered marble wastes mineral materials reduced exchangeable metals in the sequence of Pb (60.5%)>Fe (40.5%)>Zn (30.1%). X-ray diffraction and hydro-geochemical transport code PHREEQC analysis were successfully carried out to get a better understanding of the mechanisms of reactive mineral phases involved in reduced exchangeable heavy metals in sludge after PMW material amendments. Therefore, metal immobilization using powdered marble wastes materials is an effective stabilization technique for industrial metallic hydroxide sludge.

Keywords: powdered marble wastes; heavy metals; stabilization; sludge; Zn-Electroplating

1. Introduction

Zinc-Electroplating provides corrosion resistance to the steel fastener by acting as a barrier and sacrificial coating. Electroplating production is a widely used and most environmentally harmful industrial processes, during which a large volume of wastewater containing heavy metal ions such as copper, zinc, nickel, cadmium, lead and chromium is generated. All these metals are very toxic and cause great environmental damage (Wang *et al*. 2010). At only 30 to 40% of all metals used in plating processes are effectively used, waste effluents from acid-Zn^{2+}-plating lines are responsible for high amounts of Zn^{2+} encountered in electroplating discharges (Grebenyuk *et al*. 1996, Zhao *et*

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al. 1999, Dermentzis *et al*. 2014). Heavy metal pollution is an increasingly urgent problem all over the industrialized world. Unlike organic contaminants, heavy metals do not undergo microbial or chemical degradation and persist for a long time after their introduction. High concentrations of heavy metals in water, soils and air may cause long-term risks to ecosystems and humans (Alloway 1995, WHO 2007, Singh and Prasad 2015). Increasing awareness of the hazard that heavy metals can cause to the environment and to humans is presently pressuring society to comply with environmental regulations and develop management strategies to minimize their adverse impacts. Among available stabilization technologies (Bolan *et al*. 2014), immobilization using liming materials (Brallier *et al*. 1996, Garau *et al*. 2007), phosphate compounds (Basta and Mc Gowen 2004, Chen *et al*. 2007), organic matter (Kandil *et al*. 2012, Mendez *et al*. 2012) and metal oxides (Mench *et al*. 1994, Contin *et al*. 2007) could be an environmentally sustainable and cost-effective alternative, especially for contaminated industrial sites which result in the redistribution of contaminants from aqueous phase to solid phase, thereby reducing their bioavailability and transport in the environment.

Marble powder wastes are one of the major worldwide environmental problems. As a consequence of environmental and economical considerations, there is a growing demand for wastes to be reused or recycled. The objective of this study was to evaluate the effects of powdered marble wastes (PMW) as low cost, available mineral materials, on chemical transformation of heavy metals (Pb, Fe, Zn) and leachability reduction for the contaminated sludge collected from Zn-Electroplating factory.

2. Materials and methods

2.1 Materials preparation and characterization

Powdered marble wastes generated by Utique marble cutting industries (North of Tunisia) with abundant amounts were used in this study as low-cost materials to investigate the performance of a natural amendment for chemical transformation of heavy metals in the contaminated sludge from Zn-Electroplating factory. These mineral materials were washed with distilled water and dried in an oven at 110℃ for 24 h to ensure a constant weight. In order to get a better understanding of the characteristics of marble powder wastes, particle size distribution, and X-ray fluorescence analysis were performed on the surface of these solid matrixes. The micro-pore structure, the distribution of the pore size, pore volume and specific surface area of these mineral materials are measured by N_2 adsorption-desorption isotherms gained at liquid nitrogen temperature with a Micromeritics ASAP 2020 gas sorption analyzer. The Barrett-Joyner-Halenda (BJH) method was used to evaluate the average adsorption-desorption surface area, pore volume and pore diameter. The contaminated hydroxide metallic sludge was collected from a local Zn-Electroplating factory. Then, it was dried at room temperature and sieved to 2 mm particle size. The concentrations of heavy metals (Pb, Fe, Zn) in sludge were determinate by a flame atomic absorption spectrometry (Perkin-Elmer) after digestion with acid.

2.2 Leaching column tests

Four treatments were prepared for the column leaching study, one with the raw sludge (RS) sample. A control treatment (0) for each sludge with no amendment addition was also prepared and other with increasing amounts of powdered marble wastes at two rates (5 and 10%). Afterwards, 50 cm^3 of demineralized water were added to each column with a 10 mL/min flow rate. All samples were inserted in 30 cm long glass columns with an inner diameter of 1.5 cm. The bottoms of the columns were filled with 2 cm layer of gravels to keep the contaminated sludge in. All columns were 15 cm high. The top of the column was covered with a 2 cm layer of gravels to facilitate uniform flow. The mixtures were carefully homogenized. The effects of the amendments on the chemical immobilization of metals in sludge were evaluated by measuring chemical forms of heavy metals and leaching experiments (Simon et *al*. 2010). Each treatment was carried out in triplicates. The concentrations of heavy metals (Pb, Fe, Zn) were determinate by a flame atomic absorption spectrometry (Perkin-Elmer) after digestion with acid. Column leachates were filtered through a 0.45 μm membrane before analysis. Leachates were then acidified with trace metal grade HNO_3 to pH<2 prior to metal analysis (APHA 1992).

2.3 Analytical techniques

X-ray diffraction and hydro-geochemical transport code PHREEQC analysis were successfully carried out to get a better understanding on the mechanisms of reactive mineral phases involved in reduced exchangeable heavy metals and their solubility and mobility in sludge after PMW material amendments. Mineral phases present in these materials were analyzed using an X-ray diffractometer Cu Kα radiation PW 1710 Philips. The voltage and filament current were maintained at 40 kV and 40 mA respectively. The scan was obtained over 2θ range from 2 to 70° at the scan speed of 0.02. The hydro-geochemical transport code PHREEQC (Parkhurst and Appelo 2009), was used to simulate the effect of pH on mineral speciation and saturation indices after PMW materials amendments. The simulations have been performed from pH=3 to pH=11. Each mineral was allowed to precipitate if it became thermodynamically stable and the saturation index $Si_{[mineral]}$ of this phase was reached ($Si_{[mineral]}=0$). A saturation index of $Si_{[mineral]}>0$ would indicate oversaturated solutions. A saturation index of $Si_{[mineral]}<0$ would indicate unsaturated solutions.

3. Results and discussions

3.1 Materials characteristics

The characteristics of powdered marble wastes (PMW) were investigated using a combination of characterization techniques, including particle size distribution measured by N_2 adsorption-desorption isotherms at liquid nitrogen temperature, pH_{pzc} and X-ray fluorescence (Table 1).

The results showed that the values of the pore size, pore volume and BET specific surface area of powdered marble wastes seem to be higher than siliceous sand materials and lower than iron minerals hydroxides materials like ferrihydrite, akaganeite, and hematite (Kumar *et al*. 2014). The X-ray fluorescence analyses (XRF) indicate that powdered marble wastes are formed by calcite with relatively high contents of CaO (Average percent of CaO≈55%). The crystalline phases identified by XRD are in agreement with the results obtained by chemical composition analysis (XRF). The pH_{pzc} of powdered marble wastes were determined to 8.2. Contaminated Sludge contained 2655 mg/kg of Zn, 2440 mg/kg of Fe, 47.9 mg/kg of Pb and 87.5 mg/kg of P_T and its pH value was 7.4. Higher values of Zn in metal hydroxides sludge from Zn-Electroplating factory

Table 1 Characterization of powdered marble wastes

Parameter	Value
BET Surface Area (m^2/g)	4.192
Pore Volume (cm^3/g)	0.010
Pore Size (Å)	99.423
pH_{pzc}	8.2
SiO_2	0.41
Al_2O_3	0.20
Fe_2O_3	0.09
CaO	54.11
MgO	0.15
K_2O	0.00
Na_2O	0.09
P_2O_5	0.04

exceed the limits of the Tunisian landfill standard in the specific waste disposal centers (Zn>400 mg/kg).

3.2 Results of leaching column tests

Results indicated that chemical fractions of heavy metals in sludge were affected by application of the powdered marble wastes mineral materials, however, the effects varied with heavy metals. Application of the powdered marble wastes mineral materials reduced exchangeable metals in the sequence of Pb (60.5%)>Fe (40.5%)>Zn (30.1%) (Fig. 1).

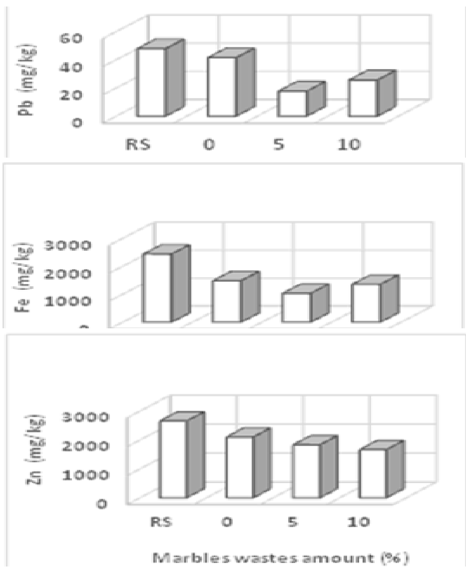

Fig. 1 Effect of powdered marble wastes stabilization on chemical fractions of heavy metals in sludge

Application of PMW amendments had also a significant effect on pH value of sludge. Sludge pH value increased slightly with increasing application rates of amendments due to the presence of carbonate in the PMW mineral material. The concentrations of heavy metals (Pb, Fe, Zn) in leachates from columns decreased as the leaching water volume increased. Addition of powdered marble wastes (PMW) mineral materials had significant effects of the metal concentrations in the leachates from the first leaching. Application of the powdered marble wastes mineral materials reduced metals leachabilities in the sequence of Pb (84.3%)>Fe (66.8%)>Zn (51%).

3.3 Comparison of Zn chemical fraction and leachability reduction

The results obtained are similar to others studies on chemical immobilization and leachability reduction of Zinc including alkaline- and phosphate-based materials that adsorb, chelate, or complex heavy metals in calcareous soils, acidic soils (Table 2) and in contaminated soils and activated sludge (Table 3). Among several materials used for chemical stabilization of heavy metals in contaminated soils and sludge, powdered marble wastes materials have more important Zn immobilization and leachability reduction than other phosphate-based materials (Natural zeolite, Iron ore, “Polifoska 15” fertilizer, Triple superphosphate and Diammonium phosphate).

Table 2 Chemical fraction of Zn (%) after PMW mineral amendments

Amendments		Metal immobilization	Reference
Calcareous soil	Limestone	52.74	Zhang and Pu (2011)
	Rock phosphate	28.42	
	Palygorskite	64.38	
	Calcium magnesium phosphate	49.66	
Acidic soil	Limestone	41.98	
	Rock phosphate	40.68	
	Palygorskite	43.77	
	Calcium magnesium phosphate	18.46	
Contaminated Sludge	Powdered marble wastes	30.1	This study

Table 3 Leachability reduction of Zn (%) after PMW mineral amendments

Amendments		Leachability reduction	Reference
Contaminated soils	Natural zeolite	16	Szrek *et al*. 2011
	Iron ore	33	
	“Polifoska 15” fertilizer	36	
	Triple superphosphate	28	
	Diammonium phosphate	37	
	Carbonate de calcium	68	Simon *et al*. 2010
Activated sludge	Cement+Bentonite	75	Katsioti *et al*. 2008
Contaminated Sludge	Powdered marble wastes	51	This study

Alkaline materials used as chemical immobilization treatments include calcium oxides, fly ash, and calcium and magnesium carbonates can reduce heavy metal solubility in soil and sludge by increasing their pH and concomitantly increasing metal sorption and consequently lower the risk of polluted soils and contaminated sludge limiting metal leaching and bioavailability for crops (Katsioti *et al*. 2008, Simon *et al*. 2010).

3.4 Mechanisms of metal stabilization

X-ray diffraction and hydro-geochemical transport code PHREEQC analysis were successfully carried out to get a better understanding on the mechanisms of reactive mineral phases involved in reduced exchangeable heavy metals in sludge after PMW amendment. X-ray diffraction showed Pyromorphite ($Pb_5 (PO_4)_3 Cl$), Kehoite ($(Zn, Ca) Al_2P_2H_6O_{12}\ 3H_2O$) and Adamite ($Zn_2 (OH) AsO_4$) mineral phases that may control respectively lead and zinc solubility (Fig. 2).

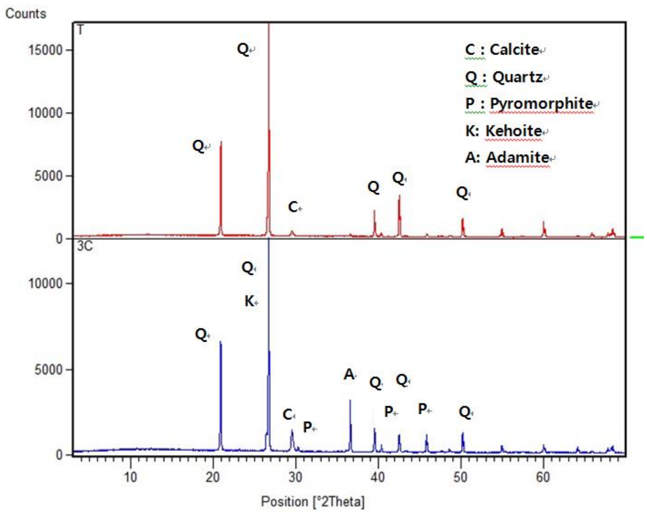

Fig. 2 X-ray diffraction analysis of raw and stabilized sludge with PMW amendments

The PHREEQC model is used to explain the chemical immobilization phenomena of heavy metals in sludge. Saturation indices (SI) of carbonates and hydroxides metals mineral phases at pH-controlled with PHREEQC are calculated (Table 4). The simulation shows that pH values had a significant effect on oxidation, dissolution, precipitation, re-dissolution of heavy metals in sludge. The chemical speciation of the mineral of carbonates and hydroxides metals mineral phases is pH dependent. Under acidic conditions ($3<pH<7$), precipitation of metals occurs as hydroxides ($Pb(OH)_2$, $Fe(OH)_3$, $Zn(OH)_2$). Under high pH conditions ($pH>9$), dissolution of soluble hydroxycarbonates metals (Pb, Fe, Zn) occurred, and thus increase significantly its mobility.

3.5 Discussions

The solubility and mobility of heavy metals in contaminated industrial sludge is quite different

Table 4 Saturation indices (SI) of mineral phases at pH-controlled calculated with PHREEQC

Mineral phases	pH3	pH5	pH7	pH9	pH11
Cerrusite ($PbCO_3$)	2.24	2.24	2.24	2.08	0.68
Siderite ($FeCO_3$)	3.09	3.12	3.12	-0.96	-6.99
Smithsonite ($ZnCO_3$)	2.10	2.13	2.15	1.90	-0.23
Lead hydroxide $Pb(OH)_2$	1.67	1.88	2.04	4.73	4.02
Iron hydroxide $Fe(OH)_3$	-0.76	1.16	5.35	6.33	4.74
Zinc hydroxide $Zn(OH)_2$	1.60	1.84	2.02	3.92	3.89

and therefore the risk of leaching into groundwater. Different sorption/dissolution processes are influenced by many factors: pH, redox potential, type of sludge constituents, cations exchange capacity, etc. and a single mechanism rarely accounts for the immobilization of heavy metals in contaminated industrial sludge. The fixation efficiency depends on not only the amount of the mineral amendments mixed to the sludge, but also the species of the metals. Cations mobility is one of the most important properties that can evaluate their environmental fate. Different metals have the distinct mobility and certainly it is not easy to find the uniform fixation agents to reduce the bioavailability of heavy metals.

Metal binding is probably due to precipitation of metal hydroxycarbonates. Cazalet (2012) also showed that carbonates can regulate the pH of mineral materials and thus impose a slightly alkaline pH values. In weakly basic conditions, the metal ions are stable in the form of carbonates and hydroxycarbonates. Contaminant immobilizing amendments decrease heavy metal element solubility and leaching by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes with organic ligands, surface precipitation and ion exchange (Zhang and Pu 2011). When powdered marble wastes enters the contaminated industrial sludge, $CaCO_3$ partly dissolves and the dissolution process reduces the H^+ concentration in the sludge solution, increasing the pH and oxidation of Fe^{2+} to Fe^{3+}; which also reacts with hydroxide ions precipitating iron, lead and zinc hydroxides. The close association of Ca with P suggests that Pb precipitation occurred on the surface of $Ca(H_2PO_4)_2$ particle. The main mechanism of Pb immobilization is via dissolution of P and subsequent precipitation of a Pyromorphite mineral phase. However, immobilization mechanisms for other metals may be different from that of Pb. Xu and Schwartz (1994) suggested that the dominant sorption process involving Zn interaction with hydroxyapatite was surface complexation of Zn with functional groups such as P-OH and coprecipitation of Zn with Ca into the apatite structure. Coprecipitation of zinc with calcium, occurs in the form of zinc-calcium phosphate (Song et *al*. 2008). The coprecipitation mechanism is probably more important for Zn sorption than for Pb since its ionic radius is closer to Ca than that of Pb. Solubility products of zinc phosphate are much greater than that of lead phosphate, and more soluble Pb was available for the precipitation formation than Zn. Therefore, lead phosphate was probably formed prior to zinc (Zhang and Pu 2011).

4. Conclusions

In this study, powdered marble wastes materials were used as natural amendments to stabilize heavy metals (Pb, Fe, and Zn) in sludge collected from Zn-Electrplating factory in order to decrease metal mobility and leachability, and to transform soluble metals to residual metal fraction. Sludge pH is one of the most important factors that can affect the mobility and bioavailability of heavy metals in sludge. Application of the PMW mineral materials reduced exchangeable metals in the sequence of Pb (60.5%)>Fe (40.5%)>Zn (30.1%) and reduced metals leachabilities in the sequence of Pb (84.3%)>Fe (66.8%)>Zn (51%). X-ray diffraction and hydro-geochemical transport code PHREEQC analysis were successfully carried out to get a better understanding on the mechanisms of reactive mineral phases (oxidation, dissolution, precipitation and complexation processes) involved in reduced exchangeable heavy metals in sludge after PMW amendment. This study has indicated the direction for further development of in situ immobilization method for metal contaminated industrial sludge. Further research should investigate the potential of powdered marble wastes amendment to reduce the metals availability in field conditions and over a longer term.

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