

## THE ROLE OF LIMESTONE AND DOLOMITE TAILINGS' PARTICLE SIZE IN RETENTION OF HEAVY METALS FROM LIQUID WASTE

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### ABSTRACT

**Purpose.** The study aims at investigating the role of particle size of mineral tailings derived from limestone, limestone marble, dolomite and dolomitic marble in heavy metal adsorption, in both batch and fixed bed conditions, so as to estimate whether grinding and/or sieving is necessary for their utilization.

**Methods.** Fractions of different particle size have been studied. Adsorption has been examined in batch conditions from solutions of 5 mg/l Cd, 5 mg/l Pb, 100 mg/l Cu, 100 mg/l Zn, and their mixed solution simulating electroplating wastewater, and also in fixed bed conditions.

**Findings.** Total Cd and Cu adsorption is achieved on all the mineral fractions, whereas Pb and Zn show a difference up to 20% depending on particle size. Referring to the mixed solution, Cd and Zn adsorption is lower, whereas no significant differences in Cu and Pb adsorption are observed. Adsorption capacity rises up to 0.03 mg/g Cd, 0.60 mg/g Cu, 0.03 mg/g Pb, 0.60 mg/g Zn. In fixed bed conditions, metal adsorption greater than 93% is achieved. Furthermore, leaching not exceeding 4% indicates a good metal retention. Finally, Taguchi method has proven that the particle size effect is not so strong compared to other parameters, including solution concentration and time.

**Originality.** The particle size of mineral tailings has not yet been investigated as a parameter affecting heavy metal adsorption. Furthermore, heavy metal adsorption has been examined from separate metal solutions and not from a mixed one. The present study aims at contributing to these two research fields.

**Practical implications.** The differences in adsorption between mineral tailings' fractions with different particle size are not as high as to make grinding of minerals necessary.

**Keywords:** limestone, dolomite, marble, mineral tailings, heavy metal adsorption, Taguchi method

### 1. INTRODUCTION

Calcium carbonate ( $\text{CaCO}_3$ ) rocks are found throughout the world, accounting for more than 4% of the earth's crust, and are readily available. Due to its specific physicochemical properties, calcium carbonate contributes to the production of paper, plastics, paint/coatings/adhesives, as well in the fields of construction, environment, agriculture, food and pharmaceutical industry, where fineness and particle size distribution are optimally balanced (OMYA, 2014). Crumbled limestone and dolomite is applied as inert material, cement component, railway subbase, etc., increasing resistance to erosion and lifetime of construction (Tsirampides, 2008).

However,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in limestone and dolomite's structure make their surface active allowing ion-exchange, surface precipitation and co-precipitation of metal ions. This property makes carbonate minerals attractive sorbent materials for heavy metal removal from

waste streams. Research has focused on investigating the mechanisms of metal adsorption on carbonate minerals, either calcite or dolomite, through mainly batch adsorption experiments from single ion solutions.

In particular, calcite with extra fine particle size varying from 2 to 75  $\mu\text{m}$  has been investigated for Cd, Mn, Co, Zn (Zachara, Cowan, & Resch, 1991), Cu (Parsiegla & Katz, 1999; Parsiegla & Katz, 2000) and Pb adsorption (Rouff, Reeder, & Fisher, 2002; Rouff, Elzinga, & Reeder, 2004) in separate solutions, whereas dolomite powder has been investigated for Cd, Pb (Kocaoba, 2007) and Sr, Ba adsorption in separate solutions (Ghaemi, Torab-Mostaedi, & Ghannadi-Maragheh, 2011). Calcite with fine particle size rising up to 200  $\mu\text{m}$  has also been examined for Pb (Godelitsas, Astilleros, Hallam, Harissopoulos, & Putnis, 2003) and Zn adsorption (Freij, Godelitsas, & Putnis, 2005), whereas dolomite with similar particle size has been examined for Cu, Pb adsorption separately (Pehlivan, Özkan, Dinç, & Parlayici, 2009; Irani, Am-

jadib, & Mousaviana, 2011). Limestone with very coarse particle size (2.36 – 4.75 mm) has been investigated for Cd, Pb, Zn, Ni, Cu, Cr adsorption separately (Aziz, Adlan, & Ariffin, 2008), single-crystal calcite cleavage fragments (8 – 10 mm<sup>2</sup> by 2.0 – 2.5 mm thick) for Cd adsorption (Stipp, Hochella, Parks, & Leckie, 1992), calcite cleavage faces for Cd, Pb adsorption separately (Chada, Hausner, Stongin, Rouff, & Reeder, 2005), dolomite with coarse particle size (0.180-2mm) for Cr(VI) adsorption (Albadarina et al., 2012), polished dolomitic marble slices (1 × 1 cm<sup>2</sup>) for Co, Cd, Pb, Cr (Godelitsas, Kokkoris, & Misaelides, 2007) and U, Th adsorption in separate solutions (Godelitsas, Kokkoris, Chatzitheodoris, & Misaelides, 2008). Furthermore, limestone with coarse particle size (1.4 – 2.0mm) has been examined for Cd adsorption (Wang & Reardon, 2001) and calcite with finer particle size (0.2 – 1.0 mm) for Cd, Cr, Zn adsorption (García-Sánchez & Álvarez-Ayuso, 2002) in fixed bed conditions.

As it results from the aforementioned references, particle size has not yet been examined as a parameter, for adsorption from a liquid waste burdened with a number of metal ions, on carbonate minerals. The present study aims at investigating the effect of minerals' particle size on their behaviour in heavy metal adsorption and the retention mechanisms, so as to estimate, whether grinding and/or sieving is necessary for their further utilisation in such an application. To this direction, Taguchi method has also been applied, in order to compare the effect of particle size with other parameters, including solution concentration and time.

In particular, mineral tailings, deriving from limestone and dolomite and their recrystallization products that is limestone marble and dolomitic marble respectively, have been examined. Adsorption has been studied from both separate and mixed metal solutions, so as to simulate real waste streams. Adsorption from mixed metal solutions is still a field where bibliography also remains poor. Both batch and fixed bed conditions have been applied, so as to better simulate real conditions in case the minerals are used as a substrate. Finally, the metal retention capacity of the mineral tailings has been estimated by leaching tests.

## 2. MATERIALS AND METHODS

### 2.1. Samples

Samples of limestone and dolomite have been supplied by a Company dealing with production, transport and trading of ready-mixed concrete and quarry products in Greece. Samples of limestone marble and dolomitic marble have been supplied by quarries, as cutting and smoothing by-products. It must be noted that these materials cannot be used or recycled by the specific companies, due to their inappropriate particle size.

In order to investigate the effect of sample particle size on metal adsorption, which is a critical parameter so as to estimate, whether grinding and/or sieving of the mineral tailings is necessary, the samples have been divided according to DIN 4188 in four fractions of the following particle sizes: –4 mm + 1 mm, –1 mm + 315 µm, –315 µm + 90 µm and –90 µm.

The chemical and mineralogical composition of the samples has been determined by X-Ray Fluorescence (XRF, ARL ADVANT XP), X-Ray Diffraction (XRD, Siemens D-500) and Flame Atomic Absorption Spectrometry (AAS, VARIAN AA240FS). In order to investigate the adsorption mechanisms, further parameters have also been measured: pH according to ISO 6588, porosity and specific surface area by N<sub>2</sub>-adsorption (NOVA-2200 Ver. 6.11) and cation-exchange capacity (CEC) according to EPA 9081, based on mixing the sample with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations, being then determined (SW-846..., 1986). In Table 1 the physico-chemical characteristics of the samples are presented.

**Table 1. Physicochemical characteristics of the minerals**

Parameter	Limestone	Limestone marble	Dolomite	Dolomitic marble
CaO (%)	55.40	55.00	31.90	33.10
MgO (%)	0.30	0.72	20.30	19.30
SiO <sub>2</sub> (%)	0.23	0.49	0.27	0.52
Al <sub>2</sub> O <sub>3</sub> (%)	0.22	0.36	0.26	0.24
Fe <sub>2</sub> O <sub>3</sub> (%)	0.12	0.12	0.18	0.13
K <sub>2</sub> O (%)	0.03	0.14	0.01	< 0.01
Na <sub>2</sub> O (%)	< 0.01	< 0.01	< 0.01	< 0.01
SO <sub>3</sub> (%)	0.05	0.01	0.02	< 0.01
Cu (mg/kg)	< 0.01	76.00	10.00	89.00
Mn (mg/kg)	70.00	180.00	< 0.001	< 0.001
Ni (mg/kg)	17.00	< 0.001	< 0.001	< 0.001
P (mg/kg)	340.00	270.00	50.00	33.00
Sr (mg/kg)	700.00	420.00	170.00	310.00
Ti (mg/kg)	44.00	220.00	< 0.001	< 0.001
Zn (mg/kg)	94.00	< 0.001	< 0.001	< 0.001
LoI (%)	43.60	43.20	47.50	46.70
pH	9.00	8.80	10.30	9.20
CEC (meq/100 g)	5.10	4.70	4.30	4.90

The XRD analysis of all samples confirms the presence of calcite, whereas with the use of a petrographic microscope (LEICA DMLP) apatite, moscovite, magnetite and manganese oxides have been also detected.

### 2.2. Sorption experiments

For the sorption experiments, separate solutions containing 5 mg/l Cd, 5 mg/l Pb, 100 mg/l Cu, 100 mg/l Zn, prepared from Fluka analytical standard solutions have been used. For the mixed solution all the above mentioned metal ions were used in the same concentrations. The metal concentrations have been selected so as to simulate wastewater deriving from electroplating, metal-finishing, paint and plastic manufacturing activities. The pH of the solutions has been adjusted to 5 by adding HNO<sub>3</sub> or NaOH, as performed experiments have shown precipitation 37 – 98% of the aforementioned metal ions in mixed solution by increasing pH from 5 to 8 (Farmaki, Vorrissi, Karakasi, & Moutsatsou, 2012).

The sorption studies included experiments in both batch and fixed bed conditions in case of using such materials as landfill substrates.

The batch experiments have been carried out for all the mentioned mineral fractions. In particular, 5 g of sorbent have been added to 30 ml of metal solution under magnetic stirring at 400 rpm for 1 h at room temperature.

The time of the experiments has been selected according to previous experiments (Farmaki, Demiris, & Moutsatsou, 2010; Farmaki & Moutsatsou, 2011). The sorbent has been removed by filtration, dried overnight at 80°C, and subjected to leaching tests and XRD-Analysis. The filtrate's pH has been measured and the metal concentration after sorption has been determined by AAS.

In order to estimate the effect of particle size compared to other parameters, including solution concentration and time, Taguchi method has been applied. Taguchi method combines standard experimental design and analysis techniques, resulting in consistency and reproducibility which are rarely found in other statistical methods. It reduces the number of the required experimental tests, determines the optimal values for various factors and estimates the effect of each factor. Three (3) factors have been selected for the present study (particle size, solution concentration, time) each one with 3 levels. In this case the L9 (3<sup>3</sup>) Taguchi design is proposed.

In Table 2 the set of the experimental tests proposed by the Taguchi method are shown. For the particle size 3 levels have been selected (–4 mm + 1 mm, –1 mm + 315 µm, –315 µm + 90 µm). The finest fraction –90 µm is excluded, taking into account that the adsorption on this fraction is known to be high, whereas the study aims at estimating whether coarser fractions' performance is satisfactory, in order to avoid grinding and/or sieving.

**Table 2. Experimental set according to L9 Taguchi design**

Particle size	Concentration (mg/l)	Time (min)
–4 mm + 1 mm	5	20
	100	60
	500	120
–1 mm + 315 µm	5	60
	100	120
	500	20
–315 µm + 90 µm	5	120
	100	20
	500	60

For the fixed bed experiments, particle size –1 mm has been selected, since the adsorption results appeared to be more satisfying. The particle size distribution is shown in Table 3. The experiments have been based on the principles of the BS EN 14405, determining the release of constituents from waste packed in a column with a leachant percolating through it, by using a continuous vertical up-flow (BS EN 14405, 2017). In particular, a plastic column of 30 cm height and 5 cm diameter has been used. A down flow at rate 1.25 ml/min has been set by using a pump so as to simulate the down flow of water in the soil. Twelve (12) consecutive filtrates of 100 ml have been collected. Their pH has been measured and the metal ion concentrations have been determined by AAS. A representative sample of the remaining sorbent has been collected, dried at 80°C overnight, and subjected to XRD-Analysis.

The adsorption capacity of each sorbent  $q$  (mg metal ion per g sorbent) and the % adsorption for each metal are determined according to relations (1) and (2) respectively:

$$q = \frac{c_i - c_f}{m} \cdot V ; \quad (1)$$

$$\text{adsorption}(\%) = 100 \cdot \frac{c_i - c_f}{m} \cdot V , \quad (2)$$

where:

$c_i$  – the initial solution concentration, mg/l;

$c_f$  – the final concentration after sorption, mg/l;

$m$  – the sorbent mass, g;

$V$  – the solution volume, l.

**Table 3. Particle size distribution of the minerals**

Particle size	% retained			
	Limestone	Limestone marble	Dolomite	Dolomitic marble
–1 mm + 315 µm	46.0	30.2	42.8	64.4
–315 µm + 90 µm	27.6	40.1	28.5	16.2
–90 µm	26.4	29.7	28.7	19.4

### 2.3. Leaching studies

After sorption studies the collected sorbents have been subjected to leaching studies, so as to investigate the strength of adsorption of metal ions on the sorbents, taking into consideration the principles of BS EN 12457-2, that is a batch compliance test providing information on leaching at a liquid to solid ratio 10 l/kg of granular wastes and sludges with a particle size below 4 mm (BS EN 12457-2, 2002). The % leaching of each metal ion retained on the sorbent is given by relation (3):

$$\text{leaching}(\%) = 100 \cdot \frac{c_{el} - v_{el}}{m \cdot q} . \quad (3)$$

where:

$c_{el}$  – the eluate concentration, mg/l;

$v_{el}$  – the eluate volume, l;

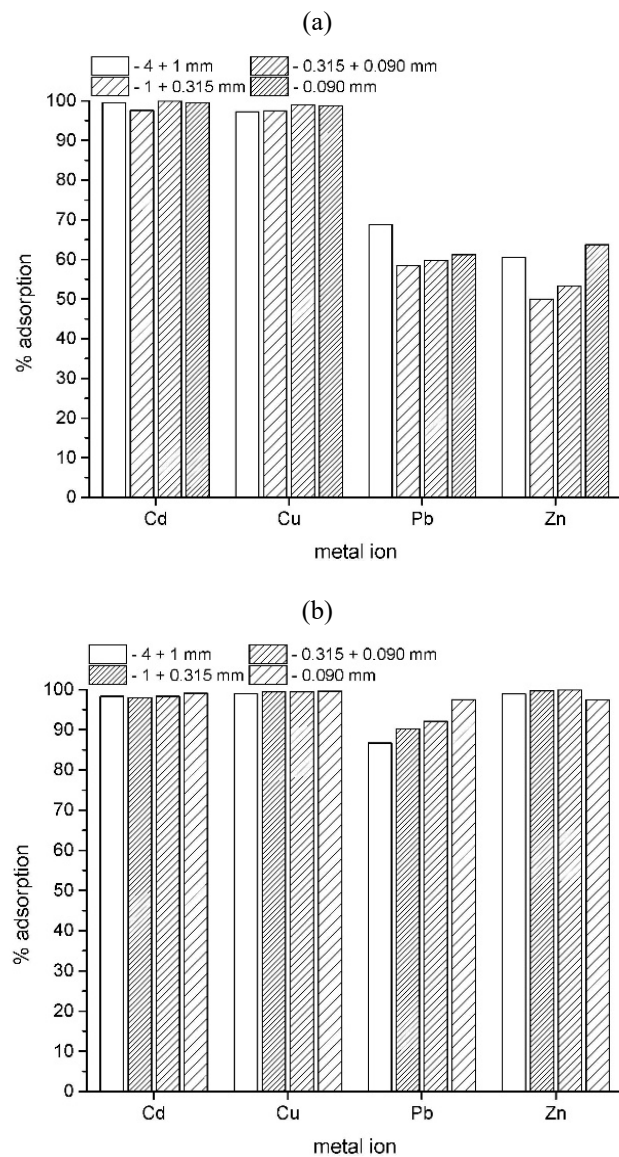
$m$  – the sorbent mass used for the leaching studies, g;

$q$  – the adsorption capacity of the sorbent, mg metal ion per g sorbent.

### 3. RESULTS AND DISCUSSION

In Figure 1 the effect of particle size on metal ion adsorption on limestone and dolomite from separate metal ion solutions is indicatively illustrated.

As it is resulted, no significant difference in Cd and Cu adsorption can be observed between the fractions of different particle size while for Pb and Zn, the difference rises up to 20%. In particular, Pb and Zn adsorption on limestone seems to be higher on the coarsest fraction –4 mm + 1 mm and on the finest one –90 µm. This could be attributed to the greater pore diameter that may compensate for the greater specific surface area of the finest fraction, as it has been resulted from porosity measurements (coarsest fraction:  $d = 264 \text{ Å}$ ,  $S = 0.187 \text{ m}^2/\text{g}$ ; finest fraction:  $d = 96 \text{ Å}$ ,  $S = 1.18 \text{ m}^2/\text{g}$ ). On the other hand, Pb adsorption on dolomite is by 10% higher on the finest fraction than on the coarsest one, due to its greater specific area, whereas no significant difference in Zn adsorption can be observed.



**Figure 1.** Adsorption (%) of metal ions as a function of particle size from separate metal ion solutions on: (a) limestone; (b) dolomite

In general, the fractions of coarser particle size exhibit in most cases a satisfactory performance, comparable to that of the finer ones. This fact leads to the encouraging conclusion that a grinding and/or sieving process for achieving a fine particle size is not worth the cost. A similar performance is also observed in limestone and dolomitic marbles.

In order to certify this result, Taguchi method has been applied, estimating the effect of particle size in comparison with solution concentration and time. In Table 4 the effect of each parameter is shown, as resulting from the Taguchi method.

As it is obvious, the effect of particle size on adsorption of Pb and Zn on all studied minerals is much lower than the one of other parameters. Cd adsorption seems to be determined by concentration in case of limestone and its marble, whereas in case of dolomite the effect of particle size and time is similar and not the strongest one.

**Table 4.** Effect of particle size, concentration and time on heavy metal adsorption on limestone, limestone marble and dolomite, as resulting from the Taguchi method

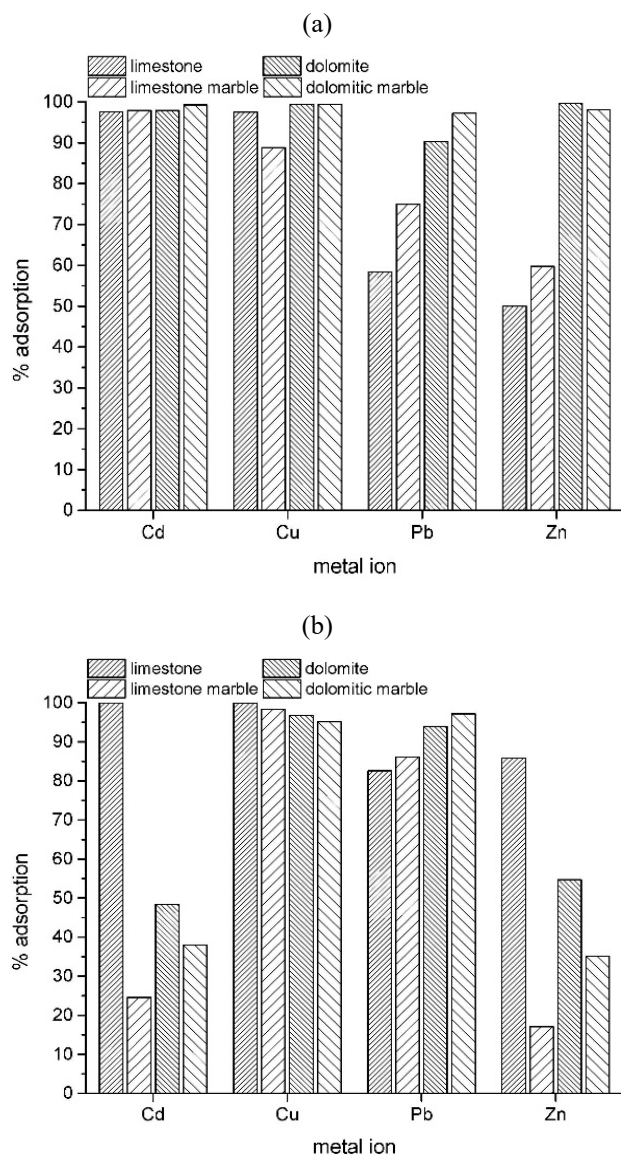
Metal ion	% effect			
	Particle size	Concentration	Time	Other
Limestone				
Cd	19.18	43.57	17.67	19.58
Cu	23.71	22.54	28.55	25.2
Pb	0.60	98.09	0.58	0.73
Zn	5.36	21.67	46.88	26.09
Limestone marble				
Cd	31.93	40.20	1.04	26.83
Cu	13.23	34.74	10.12	41.91
Pb	2.08	94.11	1.85	1.96
Zn	2.86	45.18	45.04	6.92
Dolomite				
Cd	24.84	16.64	20.18	38.34
Cu	16.09	12.54	54.94	16.43
Pb	1.35	98.05	0.23	0.37
Zn	11.10	66.77	20.42	1.71

Cu adsorption seems to be determined by concentration in case of limestone marble and by time in case of dolomite, whereas in case of limestone all parameters have a similar effect on adsorption. Therefore, in almost all cases particle size is proven not to be the most determinative parameter in adsorption.

Comparing adsorption behaviour of limestone and dolomite, as it results from Figure 1, Cd and Cu adsorption does not differ significantly, whereas Pb and Zn adsorption is obviously much higher on dolomite than on limestone, by 20 and 40% respectively. This could be attributed to the Mg content of dolomite. In particular, comparing the ionic radii of  $Mg^{2+}$  (0.72 Å),  $Ca^{2+}$  (1.00 Å) and  $Zn^{2+}$  (0.74 Å), it is obvious that the similar ionic radius of  $Zn^{2+}$  favours the exchange with  $Mg^{2+}$  rather than with  $Ca^{2+}$  (Shannon, 1976; Al-Degs, El-Barghouthi, Issa, Khraisheh, & Walker, 2006). According to Wang & Xu (2001) estimation of partition coefficients for divalent and trivalent metal cation sorption on carbonate minerals, including calcite and magnesite, the partition coefficient for Pb sorption on magnesite ( $\log K_d = 4.26$ ) is higher than the one for Pb sorption on calcite ( $\log K_d = 2.5$ ), implying that Pb sorption is favoured on magnesite and, therefore, on dolomite than on calcite and, therefore, on limestone (Lee, Dyer, Sparks, Scrivner, & Elzinga, 2006).

Taking into consideration that in some cases a divergence in performance is observed for the  $-4 \text{ mm} + 1 \text{ mm}$  fraction in comparison with the other fractions, in combination with the fact that the performance of the fractions of finer particle size is not considerably better, the results concerning only the  $-1 \text{ mm} + 315 \mu\text{m}$  fraction are further presented. The selection of the  $-1 \text{ mm} + 315 \mu\text{m}$  fraction is also reinforced by previous experiments of our laboratory, indicating its better performance compared to the  $-4 \text{ mm} + 1 \text{ mm}$  fraction in metal concentrations 5, 100 and 500 mg/l (Farmaki, Demiris, & Moutsatsou, 2010; Farmaki & Moutsatsou, 2011). For the same reasons, for the experiments in fixed bed conditions, which simulate real conditions, the fraction  $-1 \text{ mm}$  has been selected.

As it can be observed in Figure 2, the adsorption of metal ions (Cd, Cu, Pb, Zn) from separate solutions differs a lot from their adsorption from a mixed solution. In particular, Cd and Cu adsorption from separate solutions on all the minerals is significantly high, varying from 89 to almost 100%. Pb and Zn adsorption on dolomite and its marble is higher, rising up to 90 – 100%, whereas it varies from 50 to 75% on limestone and its marble. In contrast, Cu and Pb adsorption from a mixed solution on all the minerals is high and in some cases even higher than their adsorption from separate solutions, whereas Cd and Zn adsorption from a mixed solution on all the minerals, except limestone, is significantly lower than their adsorption from separate solutions, varying from 17 to 55%.



**Figure 2. Adsorption (%) of metal ions from (a) separate metal ion and (b) mixed solutions on the  $-1\text{ mm} + 315\text{ }\mu\text{m}$  fraction of the minerals**

The difference observed in metal adsorption from separate and mixed solutions on the minerals being studied could be attributed to the nature of both metal ions and minerals. In particular,  $\text{Cu}^{2+}$  ions are adsorbed very strongly and fast (within 1min) on calcite surface,

which is the main mineralogical phase of all the studied minerals, since  $\text{Cu}^{2+}$  ions are smaller than  $\text{Ca}^{2+}$  ions and are incorporated into the crystal lattice (Parsiegla & Katz, 1999). Furthermore, the formation of Cu carbonate and Cu hydroxide complexes contributes to retention of  $\text{Cu}^{2+}$  ions on calcite surface (Parsiegla & Katz, 2000).  $\text{Pb}^{2+}$  adsorption on calcite is also rapid within the first minute, but continues slowly, indicating a primary reversible  $\text{Pb}^{2+}$  binding to the calcite surface, possibly via a co-precipitation mechanism, and some re-arrangement of Pb at the surface, perhaps due to enhanced dilute solid-solution formation with time (Rouff, Reeder, & Fisher, 2002). Rapid  $\text{Zn}^{2+}$  adsorption on calcite appears to occur within 12 hours via exchange of  $\text{Zn}^{2+}$  and  $\text{ZnOH}^+$  with surface-bound  $\text{Ca}^{2+}$  and formation of hydrated complex  $(\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2)$  being stabilized on calcite surface by chemical forces and incorporated in calcite structure by recrystallization (Zachara, Kittrick, & Harsh, 1988; Zachara, Cowan, & Resch, 1991).  $\text{Cd}^{2+}$  is adsorbed on calcite preferably than  $\text{Zn}^{2+}$  by forming a phase behaving as a surface precipitate (Zachara, Cowan, & Resch, 1991).  $\text{Cd}^{2+}$  is rapidly and reversibly adsorbed and diffused in calcite surface within 24 hours and slowly and less reversibly during the next 7 days, due to solid solution formation (Davis, Fuller, & Cook, 1987).

In Table 5 the adsorption capacity  $q$  (mg of metal ion per g of sorbent) of all the minerals, that is limestone and its marble, dolomite and its marble, for all the metal ions (Cd, Cu, Pb, Zn) from both separate and mixed solutions is given.

**Table 5. Adsorption capacity of the  $-1\text{ mm} + 315\text{ }\mu\text{m}$  fraction of the minerals in separate and mixed solutions of metal ions**

Sorbent material	Solution	Adsorption capacity, $q$ (mg/g sorbent)			
		Cd	Cu	Pb	Zn
Limestone	Separate	0.03	0.58	0.03	0.30
	Mixed	0.03	0.60	0.02	0.51
Limestone marble	Separate	0.03	0.53	0.03	0.36
	Mixed	0.01	0.59	0.026	0.10
Dolomite	Separate	0.03	0.60	0.03	0.60
	Mixed	0.01	0.58	0.03	0.33
Dolomitic marble	Separate	0.03	0.59	0.03	0.59
	Mixed	0.01	0.57	0.03	0.21

In general, no significant differences in adsorption capacity are observed between each mineral (limestone, dolomite) and its marble. Limestone and dolomite and their marbles have a similar adsorption capacity for Cd, Cu and Pb, rising up to 0.029 – 0.030 mg Cd per g, 0.53 – 0.60 mg Cu per g and 0.029 – 0.030 mg Pb per g, whereas dolomite and its marble have a higher adsorption capacity for Zn, rising up to 0.58 – 0.60 mg Zn per g, than that of limestone and its marble, rising up to 0.30 – 0.36 mg Zn per g. This could be attributed to the ionic radius of  $\text{Zn}^{2+}$ , which is similar to the one of  $\text{Mg}^{2+}$  compared to the one of  $\text{Ca}^{2+}$ , favouring thus its exchange with  $\text{Mg}^{2+}$  rather than with  $\text{Ca}^{2+}$ , as it has already been mentioned (Shannon, 1976; Al-Degs, El-Barghouthi, Issa, Khraisheh, & Walker, 2006).

Differences are observed also in the adsorption capacity achieved for each metal ion in separate solutions and a mixed solution. In particular, a decrease by 45–75% in adsorption capacity of all the minerals, except limestone, is observed for Cd and Zn in a mixed solution. In case of limestone and its marble, a decrease in adsorption capacity for Pb by 14–17%, and, in case of limestone, an increase in adsorption capacity for Zn by 40% is observed. The differences in adsorption capacity between separate and mixed solutions are in accordance with the ones observed in adsorption %, being attributed to the different nature of both metal ions and minerals, as it has already been analyzed.

The leaching of the metal ions (Cd, Cu, Pb, Zn) being retained on all the minerals, after adsorption in batch conditions, does not exceed 4%, indicating that they are sufficiently retained on the minerals' surface. This result seems encouraging for the further use of the minerals as substrates in landfills.

In Figures 3 and 4 the pH of the eluate and the adsorption (%) of the metal ions (Cd, Cu, Pb, Zn) during adsorption on all the mineral tailings, that is limestone and its marble, dolomite and its marble, in fixed bed conditions, are respectively illustrated.

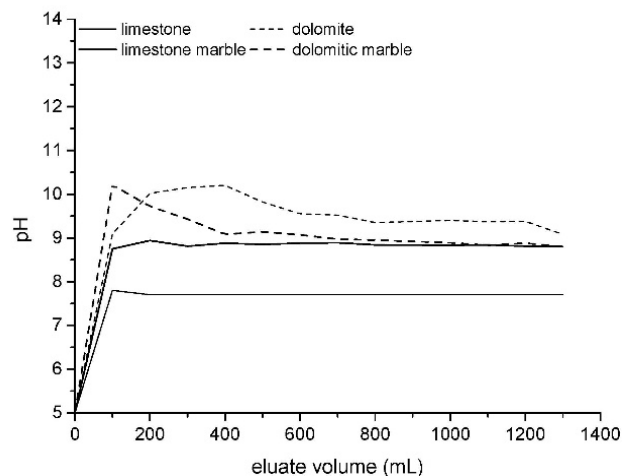


Figure 3. Eluate pH during metal ion adsorption on the minerals in fixed bed conditions

Concerning the pH of the eluate during adsorption in fixed bed conditions, an initial increase at the first eluate (100 mL) and then its stabilization is observed for all the minerals.

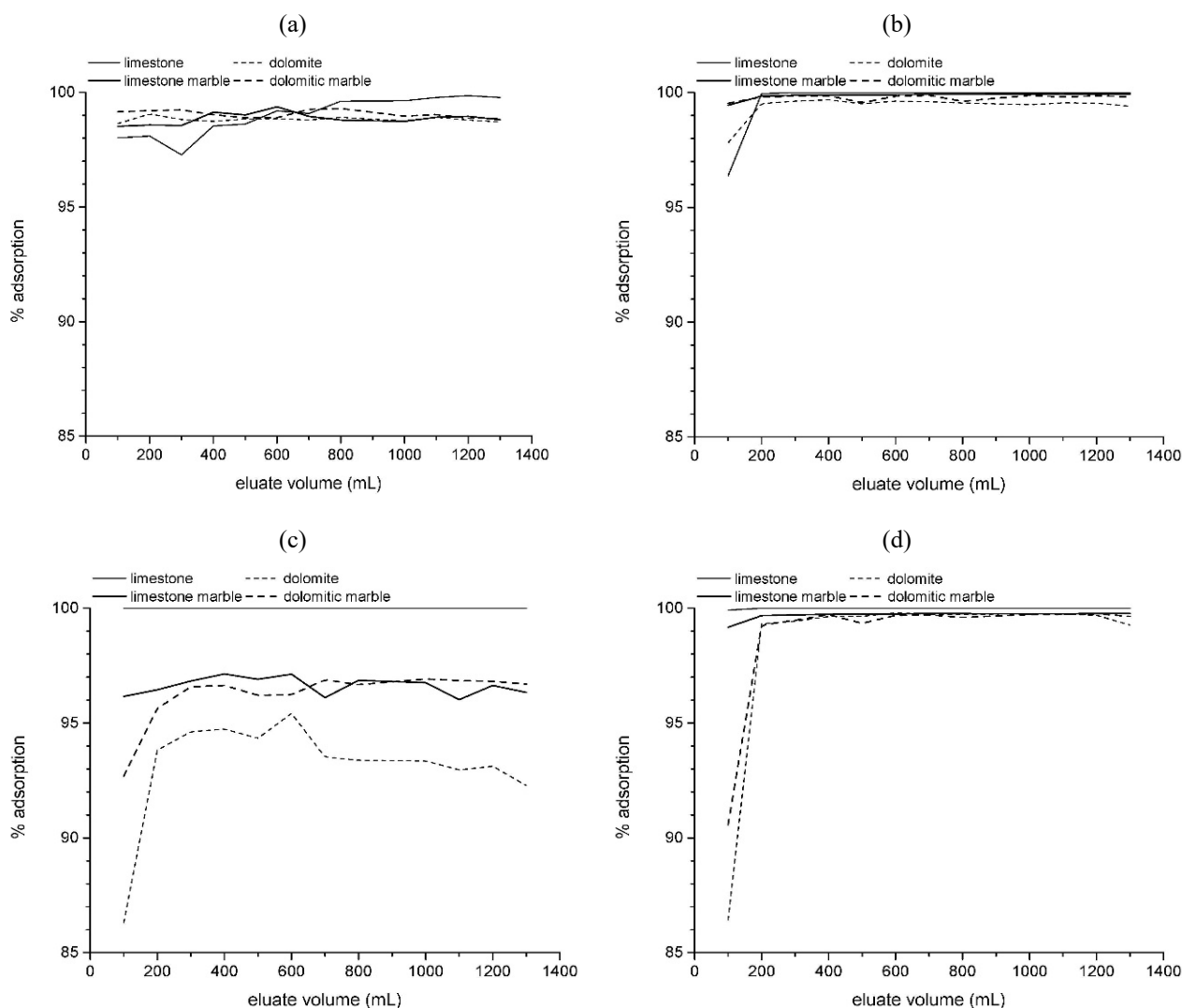


Figure 4. Adsorption (%) of metal ions (Cd, Cu, Pb, Zn) on the minerals in fixed bed conditions: (a) Cd; (b) Cu; (c) Pb; (d) Zn



The pH is stabilized at a different point for each mineral. For limestone and its marble it is stabilized at 7.7 – 9.0, whereas for dolomite and its marble at 9.0 – 9.5.

As it is obvious, since the first 200 ml of solution have passed through the bed, the adsorption on all the minerals is in most cases stabilized at its maximum, varying from 93 to almost 100%. Furthermore, the initial metal ion adsorption, estimated by the first eluate, is satisfying coming up to 86 – 99%. Total adsorption of Cu and Zn is achieved on all the minerals in fixed bed conditions. In case of Cd and Pb a variance in adsorption is observed until 800 ml of solution has passed through the bed, however, it cannot be considered significant, since it is in the order of 1 – 2%. Dolomite and its marble and limestone marble exhibit a lower performance in Pb adsorption in fixed bed conditions, however satisfying, since it is greater than 93%.

In comparison with batch experiments, all the minerals exhibit a much better performance in metal ion adsorption in fixed bed conditions. This could be attributed to both the available contact time allowing thus the almost total adsorption of the metal ions.

#### 4. CONCLUSIONS

In conclusion, the behaviour of mineral tailings, deriving from limestone and its marble, dolomite and its marble, in heavy metal adsorption (Cd, Cu, Pb, Zn) seems to be encouraging for their potential utilization in an environmental application.

Concerning their metal adsorption capacity, limestone differentiates from dolomite, whereas no significant differentiation between each mineral and its marble has been observed. In separate metal ion solutions the adsorption capacity of limestone and its marble follows the order  $Cu > Zn > Pb = Cd$ , and that of dolomite and its marble follows the order  $Cu = Zn > Pb = Cd$ , whereas in a mixed waste all the minerals follow the order  $Cu > Zn > Pb > Cd$ , except limestone following the order  $Cu > Zn > Cd > Pb$ .

The role of particle size has not proven such important as to make grinding of the minerals necessary, a fact that relieves their further utilization from an extra financial burden. Furthermore, limited leaching of metal ions adsorbed on the mineral surface constitutes an extra benefit for their utilization as landfill substrates.

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## ВПЛИВ РОЗМІРІВ ЧАСТИНОК У ВАПНЯНИХ ТА ДОЛОМІТОВИХ ХВОСТАХ НА ВИЛУЧЕННЯ ВАЖКИХ МЕТАЛІВ ІЗ РІДКИХ ВІДХОДІВ

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**Мета.** Дослідження впливу розмірів частинок у хвостах збагачення вапняку, вапняного мармуру, доломіту та доломітового мармуру на процес адсорбції важких металів у нерухомому шарі для оцінки доцільності технології подрібнення й/або просіювання в подальшому використанні металів.

**Методика.** Для виконання досліджень зразки вапняку та доломіту доставлені компанією, що займається виробництвом і продажем готових бетонів, а також кар'єрами у Греції. Хімічний і мінералогічний склад зразків був визначений рентгенівської флуоресценцією (XRF, ARL ADVANT XP), рентгенівської дифракцією (XRD, Siemens D-500) та атомно-абсорбційною спектрометрією (AAS, VARIAN AA240FS). Для дослідження механізму адсорбції були виміряні наступні параметри: рН відповідно до ISO 6588, пористість і питома площа поверхні за допомогою N<sub>2</sub>-адсорбції (NOVA-2200, версія 6.11) та катіонообмінна ємність (CEC) відповідно до EPA 9081 на основі змішування зразка з надлишком розчину ацетату натрію, в результаті якого потім визначались додані катіони натрію для матричних катіонів. Для сорбційних експериментів були використані окремі розчини, які містять 5 мг/л Cd, 5 мг/л Pb, 100 мг/л Cu, 100 мг/л Zn, отримані з аналітичних стандартних розчинів Fluka. Після сорбційних досліджень зібрані сорбенти були піддані дослідженням вилуговування.

**Результати.** У процесі досліджень була досягнута повна адсорбція Cd і Cu з усіх мінеральних фракцій, проте до 20% адсорбції Pb і Zn визначалася розмірами частинок. Встановлено, що величина адсорбції Cd і Zn нижче у змішаному розчині, але при цьому даний показник для Cu і Pb залишається без змін. Поглинаюча здатність зростає до 0.03 мг/г Cd, 0.60 мг/г Cu, 0.03 мг/г Pb, 0.60 мг/г Zn. В умовах нерухомого шару досягається до 93% адсорбції металів. Більше того, витік, що не перевищує 4%, свідчить про ефективність вилучення металів. Доведено за методом Тагучі, що вплив розмірів частинок не є настільки значним, щоб не враховувати роль інших параметрів, таких як концентрація розчину і час. Вилуговування іонів металів (Cd, Cu, Pb, Zn), що зберігаються на всіх мінералах після адсорбції в періодичних умовах, не перевищує 4% та вказує на



те, що вони досить зберігаються на поверхні мінералів. Це є важливим результатом для подальшого використання мінералів у якості субстратів на полігонах.

**Наукова новизна.** Вперше розміри частинок у хвостах збагачення мінералів розглянуті як параметр, який впливає на процес адсорбції важких металів, при цьому даний процес вивчений також щодо окремих розчинів металів, а не тільки їх суміші.

**Практична значимість.** Виявленні відмінності у показниках адсорбції для фракцій частинок різного розміру не такі значущі, щоб обумовлювати необхідність їх подрібнення в технологічному процесі.

**Ключові слова:** вапняк, доломіт, мрамур, хвости збагачення, адсорбція важких металів, метод Тагучі

## ВЛИЯНИЕ РАЗМЕРОВ ЧАСТИЦ В ИЗВЕСТКОВЫХ И ДОЛОМИТОВЫХ ХВОСТАХ НА ИЗВЛЕЧЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ЖИДКИХ ОТХОДОВ

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**Цель.** Исследование влияния размеров частиц в хвостах обогащения известняка, известкового мрамора, доломита и доломитового мрамора на процесс адсорбции тяжелых металлов в неподвижном слое для оценки целесообразности технологии измельчения и/или просеивания в дальнейшем использования металлов.

**Методика.** Для выполнения исследований образцы известняка и доломита доставлены компанией, занимающейся производством и продажей готовых бетонов, а также карьерами в Греции. Химический и минералогический состав образцов был определен рентгеновской флуоресценцией (XRF, ARL ADVANT XP), рентгеновской дифракцией (XRD, Siemens D-500) и атомно-абсорбционной спектрометрией (AAS, VARIAN AA240FS). Для исследования механизма адсорбции были измерены следующие параметры: pH в соответствии с ISO 6588, пористость и удельная площадь поверхности с помощью N<sub>2</sub>-адсорбции (NOVA-2200, версия 6.11) и катионообменная емкость (CEC) в соответствии с EPA 9081 на основе смешивания образца с избытком раствора ацетата натрия, в результате которого затем определялись добавленные катионы натрия для матричных катионов. Для сорбционных экспериментов были использованы отдельные растворы, содержащие 5 мг/л Cd, 5 мг/л Pb, 100 мг/л Cu, 100 мг/л Zn, полученные из аналитических стандартных растворов Fluka. После сорбционных исследований собранные сорбенты были подвергнуты исследованиям выщелачивания.

**Результаты.** В процессе исследований была достигнута полная адсорбция Cd и Cu из всех минеральных фракций, однако до 20% адсорбции Pb и Zn определялась размерами частиц. Установлено, что величина адсорбции Cd и Zn ниже в смешанном растворе, но при этом данный показатель для Cu и Pb остается без изменений. Поглощающая способность возрастает до 0.03 мг/г Cd, 0.60 мг/г Cu, 0.03 мг/г Pb, 0.60 мг/г Zn. В условиях неподвижного слоя достигается до 93% адсорбции металлов. Более того, утечка, не превышающая 4%, свидетельствует об эффективности извлечения металлов. Доказано по методу Тагучи, что влияние размеров частиц не является настолько значительным, чтобы не учитывать роль других параметров, таких как концентрация раствора и время. Выщелачивание ионов металлов (Cd, Cu, Pb, Zn), сохраняющихся на всех минералах после адсорбции в периодических условиях, не превышает 4% и указывает на то, что они достаточно сохраняются на поверхности минералов. Это является важным результатом для дальнейшего использования минералов в качестве субстратов на полигонах.

**Научная новизна.** Впервые размеры частиц в хвостах обогащения минералов рассмотрены как параметр, оказывающий влияние на процесс адсорбции тяжелых металлов, при этом данный процесс изучен также в отношении отдельных растворов металлов, а не только их смеси.

**Практическая значимость.** Вывявленные различия в показателях адсорбции для фракций частиц различного размера не столь значимы, чтобы обуславливать необходимость их измельчения в технологическом процессе.

**Ключевые слова:** известняк, доломит, мрамор, хвосты обогащения, адсорбция тяжелых металлов, метод Тагучи

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