Research Article

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Effect of limestone and dolomite tailings' particle size on potentially toxic elements adsorption

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Abstract: The aim of the study is the investigation of potentially toxic elements adsorption on limestone, dolomite and marble particles of different size. As parameters, rock particle size, solution concentration, contact time and presence of other elements in the solution have been investigated. Four fractions with different particle size ($-4\text{mm} + 1\text{mm}$, $-1\text{mm} + 315\mu\text{m}$, $-315\mu\text{m} + 90\mu\text{m}$, $<90\mu\text{m}$) have been studied. Batch experiments have been carried out at 20, 60, 120 min from monoelement and competitive Cd, Cu, Pb, Zn solutions at concentrations 5, 100, 500 mg/L, whereas fixed bed conditions have also been applied. In lower concentrations, adsorption reaches equilibrium after 60 min. 15% difference in Pb adsorption and 15-30% in Zn adsorption has been observed depending on particle size. However, according to Taguchi method particle size has not proven a determinative parameter, so as to make grinding and/or sieving necessary for their further utilisation. Cd and Zn adsorption from a competitive solution is lower, whereas Cu and Pb adsorption is similar. Adsorption capacity of materials rises up to 0.03 mg Cd/g, 0.60 mg Cu/g, 0.03 mg Pb/g, 0.60 mg Zn/g. In fixed bed conditions more than 93% element is adsorbed, of which only 4% is leached.

Keywords: Limestone, dolomite, marble, potentially toxic element, adsorption capacity, particle size

1 Introduction

The rapid development of industries such as mining, specifically electroplating, metal-finishing, paint and

plastic manufacturing, without effective control has resulted in a large accumulation of potentially toxic elements like heavy metals in soils, which are generally immutable, not degradable and persistent. In this field, the chemical behaviour of the mineral surfaces in aquatic environments and the elucidation of the mineral-water interface interactions have forced researchers on investigating the mechanisms of metal adsorption on carbonate minerals. Adsorption experiments on calcite or dolomite have taken place mainly from monoelement solutions in batch conditions [1]. The effect of pH of the materials is also an important property affecting their retention capacity of cations. H^+ adsorption at the mineral-water interface modifies the surface charge, the surface potential and the distribution of ions in the solution surrounding the solid by formation of complexes.

A wide range of divalent metallic cations, including common diagenetic tracers (e.g. Mg^{2+} , Mn^{2+} , Sr^{2+}) and important environmental contaminants (e.g. Ni^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+}), can potentially substitute for Ca^{2+} ions in the calcite structure [2]. Elements substitutions, vacancies, structural defects etc. result active surfaces allowing ion-exchange, surface precipitation and co-precipitation of ions. This property makes carbonate minerals attractive sorbent materials for potentially toxic element removal from waste streams.

Adsorption on calcitic minerals from monoelement solutions of Cd, Co, Cr, Cu, Ni, Pb and Zn has been investigated with encouraging results. In particular, the sorption selectivity of calcite with extra fine particle size ($<9\mu\text{m}$), has proven to follow the sequence $\text{Cd} > \text{Zn} > \text{Mn} > \text{Co} > \text{Ni} > \text{Ba} = \text{Sr}$ [3]. Pb adsorption on calcite with particle size, varying from 2 to 200 μm , has also proven effective, either by being strongly adsorbed on calcite surface or by precipitating as cerussite, hydrocerussite, plumbonacrite or hydroxy lead compounds [4–6]. In case of Zn a heterogeneous nucleation of Zn-bearing precipitate on calcite surface has been observed [7]. Limestone with very coarse particle size (2.36-4.75 mm) has also been investigated for beneficial removal of Cd, Pb, Zn, Ni, Cu, Cr from monoelement solutions exceeding 90% [8]. Cd adsorption and solid-state diffusion into the crystal

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takes place on single-crystal calcite cleavage fragments (8-10 mm² by 2-2.5 mm thick) [9], whereas Cd²⁺ uptake by calcite cleavage faces has proven more rapid than Pb²⁺ uptake [10]. Furthermore, Cd adsorption by direct precipitation as cadmium carbonate on limestone with coarse particle size (1.4-2.0 mm) has been observed in a two column siderite/limestone reactor [11]. Cd, Cr, Zn adsorption on calcite with finer particle size (0.2-1.0 mm) in both batch and fixed bed conditions is achieved respectively through Cd exchange with Ca, precipitation of Zn as hydrozincite Zn₅(OH)₆(CO₃)₂ and precipitation of Cr as an oxide hydrocarbonate coating [12].

Dolomite powder has been investigated for Cd and Pb adsorption from aqueous medium with encouraging results at pH 5 as an optimum value [13]. Cu and Pb adsorption from mono-element solutions on dolomite with fine particle size rising up to 200 µm exceeding 85% has been achieved through surface complexation and ion exchange [14, 15]. Co, Cd, Pb, Cr adsorption on polished dolomitic marble slices (1×1 cm²) has been achieved by formation of a Co-bearing film on its surface, adsorption and solid-state diffusion of Cd²⁺, extended overgrowth of crystalline Pb²⁺ carbonates and massive surface precipitation of amorphous Cr³⁺ hydroxide/oxyhydroxide [16].

As it results from the aforementioned references, particle size has not been examined yet as a specific parameter, for adsorption from a liquid waste burdened with a number of potentially toxic elements, on carbonate minerals. Furthermore, adsorption from competitive solutions is still a field where bibliography also remains poor.

Reserves of carbonate rocks, appropriate as inert material, are abundant in Greece with 230 quarries in operation. Great quantities of tailings and by-products deriving from the extraction which is an economically important and widespread activity remain unexploited, since they are considered inappropriate due to their physical and chemical characteristics, referring to shape, purity, etc. [17]. In combination with great quantities, resulting from cutting, smoothing and polishing of marble, they may cause environmental problems.

The present study aims at investigating the effect of rocks' particle size on their behaviour in potentially toxic element adsorption and the retention mechanisms, so as to estimate, whether grinding and/or sieving is necessary for their further utilisation as base material of a landfill. To this direction, Taguchi method has also been applied, in order to compare the effect of particle size on potentially toxic element adsorption with other parameters, including solution concentration and contact time. The adsorption process has been studied from both mono-element and competitive solutions, so as to simulate real waste streams

in case the rocks are used for such an application. The nature of the adsorption isotherms has been also evaluated. Finally, the element 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 excavated from different depths and supplied by the company TITAN Group dealing with production, transport and trading of ready-mixed concrete and quarry products in Greece. On the other hand, samples of limestone marble and dolomitic marble have been supplied by quarries in Penteli of Attiki and Volakas of Drama in Greece respectively, resulting from both cutting and smoothing the exploited rock and remains of the exploited rock. 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 potentially toxic element adsorption, which is a critical parameter so as to estimate, whether grinding and/or sieving of the mineral tailings is necessary for their further utilisation, samples have been crashed and separated into their grain fractions by mechanical screening. The standard DIN 4188-1:1977-10 has been applied, including material division in four quadrants and cross selection of two quadrants constituting the sample, and subsequently sample dry sieving. Each sample has been divided into four fractions with particle sizes -4mm + 1mm, -1mm + 315µm, -315µm + 90µm and <90µm respectively. The particle size distribution of the samples is shown in Table 1, expressed as % retained material on each sieve.

For the qualitative element analysis X-Ray Fluorescence (XRF, ARL ADVANT XP) has been applied and samples have been prepared as fused beads. All the elements have been determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-MS, Perkin Elmer-ELAN 6100), except Cd, Cr, Cu, Ni, whose quantitative analysis has been also certified by Flame Atomic Absorption Spectrometry (AAS, VARIAN AA240FS) and samples have been digested with HCl, whereas lithium tetraborate fusion has been applied for any remaining material. The mineralogical composition of the samples has been determined by X-Ray Diffraction (XRD, Siemens D-500) with further analysis in a petrographic microscope (LEICA DMLP).

In order to investigate the adsorption mechanisms, further parameters have also been measured: pH accord-

Table 1: Particle size distribution of the samples.

particle size	% retained			
	limestone	limestone marble	dolomite	dolomitic marble
+ 4mm	15.30	17.14	33.38	6.38
−4mm + 1mm	54.73	43.45	30.80	12.68
−1mm + 315μm	15.23	15.04	18.79	8.41
−315μm + 90μm	4.76	14.98	10.08	61.13
−90μm	9.99	9.39	6.94	11.39

ing to ISO 6588-1:2012, porosity and specific surface area by N₂-adsorption (NOVA-2200 Ver. 6.11) and cation-exchange capacity (CEC) according to EPA 9081 [18], 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.

2.2 Methods

Sorption studies

Potentially toxic element sorption has been studied as a function of sample particle size, solution concentration and contact time, including experiments in both batch and fixed bed conditions in case of using such materials as base of a landfill.

Monoelement solutions containing Cd, Pb, Cu and Zn at 5, 100 and 500 mg/L have been prepared from Fluka analytical standard solutions of their nitrate salts. The pH of the solutions has been adjusted to 5 by adding HNO₃ or NaOH, as performed experiments have shown precipitation 37-98% of the aforementioned ions in a competitive solution by increasing pH from 5 to 8 [19].

The batch experiments have been carried out for all the aforementioned material fractions three times and the result is the mean value. In particular, 5 g of sorbent have been added to 30 mL of each solution in a 250 mL Erlenmeyer flask, under magnetic stirring at 400 rpm for 20, 60, 120 min, at room temperature. The sorbent has been removed by filtration and dried over night at 80°C, so as to be further subjected to leaching studies and XRD-Analysis. The filtrate's pH has been measured and the element concentration after sorption has been determined by AAS.

In order to simulate wastewater deriving from electroplating, metal-finishing, paint and plastic manufacturing activities, batch experiments have also been carried out in a competitive solution containing 5 mg/L Cd, 5 mg/L Pb, 100 mg/L Cu and 100 mg/L Zn. Sorption has been studied under the aforementioned conditions, whereas as contact

time 60min has been selected, since at this time an acceptable adsorption has been achieved.

The adsorption capacity (Eq. 1) of the sorbents in batch experiments has been determined according to the following relation:

$$q = \frac{C_i - C_f}{m} \cdot Vq \quad (1)$$

(mg element per g sorbent) the adsorption capacity of the sorbent, C_i (mg/L) the initial concentration of each element in the solution and C_f (mg/L) the final concentration of each element in the solution after sorption, m (g) the mass of the sorbent used and V (L) the volume of the solution.

The % adsorption (Eq. 2) for each element has been determined, in both batch and fixed bed conditions, according to the following relation:

$$\text{adsorption}(\%) = 100 \cdot \frac{C_i - C_f}{C_i} \quad (2)$$

Furthermore, in order to describe potentially toxic element adsorption on the different grain fractions of the examined materials, adsorption capacity has been studied as a function of concentration. Langmuir and Freundlich parameters have been calculated from the respective curves fitted to the experimental data, so as to find out how adsorption proceeds at higher solution concentrations (up to 500mg/L), since the aforementioned isotherm models have already been applied for the studied materials at lower concentrations (<<5mg/L) [3, 8, 14].

Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. Langmuir isotherm is given by the following relation (Eq. 3):

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (3)$$

where q_m (mg/g) is the maximum adsorption capacity related to the monolayer adsorption capacity, b the Langmuir model constant. However, for the determination of favorability of sorption process the dimensionless constant

separation factor (R_L) is important, being defined by the following relation (Eq. 4):

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

where C_o (mg/L) is the initial concentration of the elements. The R_L indicates the type of isotherm, being either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich isotherm is applied for non-ideal and reversible sorption, which is not limited to the formation of a monomolecular layer, and is determined by the following relation (Eq. 5):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

where (mg/g) and n are the Freundlich parameters. A value $n > 1$ indicates that element adsorption is favorable, whereas $n < 1$ indicates unfavorable adsorption and $n = 1$ linear adsorption.

For the estimation of particle size effect in comparison with other parameters, including solution concentration and contact 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. As factors for the present study, three (3) parameters that is particle size, solution concentration and contact time have been selected, each one with 3 levels. In this case the L9 (3^3) 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 only been included ($-4\text{mm} + 1\text{mm}$, $-1\text{mm} + 315\mu\text{m}$, $-315\mu\text{m} + 90\mu\text{m}$). The finest particle size $<90\mu\text{m}$

has not been included, taking into account that the adsorption on this fraction is known to be high and the goal of the present study is to estimate whether the performance of the coarser fractions is satisfactory, in order to avoid grinding and/or sieving.

For the fixed bed experiments, samples of particle size $< 1\text{mm}$ (including fractions $-1\text{mm} + 315\mu\text{m}$, $-315\mu\text{m} + 90\mu\text{m}$ and $<90\mu\text{m}$) have been used, as the adsorption results appeared to be more satisfying. The experiments have been based on the principles of the EN 14405 [20], determining the release of constituents from waste packed in a column with a leachant percolating through it, by using a continuous vertical up-flow. However, the conditions of the standard have been changed according to the needs of adsorption, since the standard refers to leaching and not adsorption. In particular, a plastic column of 30 cm height and 5 cm diameter has been used and a down flow at rate 1.25 mL/min has been set by using a peristaltic 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 concentration of elements has been determined by AAS and ICP-AES. After collecting all the filtrates, a representative sample of the sorbent has been collected and dried at 80°C overnight, so as to be further subjected to XRD Analysis.

Leaching studies

After sorption studies, the collected sorbents have been subjected to leaching studies, so as to investigate the strength of adsorption of elements on the sorbents, taking into consideration the principles of EN12457-2 [21], 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. In particular, de-ionised water has been applied as leachant under stirring for 24 h at 10 rpm. The pH and element concentration of the eluate have been determined and % leaching of each element retained on the sorbent is given by the following relation (Eq. 6):

$$\text{leaching (\%)} = 100 \cdot \frac{C_{el} \cdot V_{el}}{m \cdot q} \quad (6)$$

where C_{el} (mg/L) the concentration of each element in the eluate, V_{el} (L) the volume of the eluate, m (g) the mass of the sorbent used for the leaching studies and q (mg element per g sorbent) the adsorption capacity of the sorbent.

Table 2: Set of experimental tests according to L9 Taguchi design.

particle size	concentration (mg/L)	contact time (min)
$-4\text{mm} + 1\text{mm}$	5	20
	100	60
	500	120
$-1\text{mm} + 315\mu\text{m}$	5	60
	100	120
	500	20
$-315\mu\text{m} + 90\mu\text{m}$	5	120
	100	20
	500	60

Table 3: Physicochemical characteristics of the samples.

parameter	limestone	limestone marble	dolomite	dolomitic marble
CaO (%)	55.4	55.0	31.9	33.1
MgO (%)	0.30	0.72	20.3	19.3
SiO ₂ (%)	0.23	0.49	0.27	0.52
Al ₂ O ₃ (%)	0.22	0.36	0.26	0.24
Fe ₂ O ₃ (%)	0.12	0.12	0.18	0.13
K ₂ O (%)	0.03	0.14	0.01	< 0.01
Na ₂ O (%)	< 0.01	< 0.01	< 0.01	< 0.01
SO ₃ (%)	0.05	0.01	0.02	< 0.01
Cu (mg/kg)	< 0.01	76	10	89
Mn (mg/kg)	70	180	< 0.001	< 0.001
Ni (mg/kg)	17	< 0.001	< 0.001	< 0.001
P (mg/kg)	340	270	50	33
Sr (mg/kg)	700	420	170	310
Ti (mg/kg)	44	220	< 0.001	< 0.001
Zn (mg/kg)	94	< 0.001	< 0.001	< 0.001
LOI (%)	43.6	43.2	47.5	46.7
pH	9.0	8.8	10.3	9.2
CEC (meq/100g)	5.1	4.7	4.3	4.9

Table 4: CEC of sample fractions with different particle size.

particle size	CEC (meq/100g)			
	limestone	limestone marble	dolomite	dolomitic marble
–4mm + 1mm	4.45	3.70	4.65	3.66
–1mm + 315µm	5.50	3.20	3.47	4.74
–315µm + 90µm	5.05	3.34	4.47	4.73
–90µm	4.90	4.75	4.28	4.92
total	5.07	4.72	4.26	4.93

3 Results

At first, the physicochemical characteristics of the samples are presented in Table 3, whereas CEC and porosity are analytically presented for each fraction of the materials in Tables 4 and 5 respectively.

Concerning the mineralogical characteristics of the samples, XRD analysis has confirmed the presence of calcite. Further analysis in a petrographic microscope has led to detection of apatite, muscovite and magnetite, whereas manganese oxides have been first detected by SEM analysis and then certified in the petrographic microscope. In all the dolomitic samples dolomite has also been detected. After adsorption on the materials formation of new crystalline phases has not been detected. This could be attributed to their low concentration.

In order to investigate the adsorption mechanisms, Langmuir and Freundlich isotherm models have been applied for all the material fractions. In Tables 6a–6d their parameters and correlation coefficients R^2 are presented. As it is obvious, in almost all cases that is adsorption of all the examined elements (Cd, Cu, Pb, Zn) on all the fractions of all the materials, Langmuir isotherm model cannot be applied, since correlation coefficients are very low, which is also confirmed by negative Q_{max} and b values that cannot correspond to a physical meaning. On the other hand, correlation coefficients ~ 1 indicate better application of Freundlich isotherm model. However, the value n tends to be 1, indicating rather a linear adsorption on the materials, except Cd adsorption on the coarsest fraction (–4mm + 1mm) of limestone marble which is favorable according to Langmuir isotherm model, since the correlation coefficient tends to 1 and is greater than the one of Freundlich model and $0 < R_L < 1$. The linear adsorption, observed almost in

Table 5: Porosity of sample fractions with different particle size.

particle size	specific surface area S_{BET} (m ² /g)	pore volume V_p (cm ³ /g)	mean pore diameter d_p (Å)
limestone			
–1mm + 315µm	0.164	0.002	218.2
–90µm	1.175	0.003	95.9
limestone marble			
–1mm + 315µm	0.149	0.001	160.2
–90µm	0.862	0.002	98.3
dolomite			
–1mm + 315µm	0.139	0.001	30.8
–90µm	1.182	0.003	42.9
dolomitic marble			
–1mm + 315µm	0.127	0.002	41.0
–90µm	0.740	0.006	46.4

Table 6a: Langmuir and Freundlich isotherm parameters for Cd adsorption on limestone, dolomite and marble.

particle size	Langmuir				Freundlich		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
limestone							
–4mm + 1mm	$9.542 \cdot 10^{-1}$	$6.292 \cdot 10^{-3}$	0.241	0.905	0.969	0.004	1.000
–1mm + 315µm	–8.190	$-5.540 \cdot 10^{-4}$	1.383	0.415	1.009	0.004	1.000
–315µm + 90µm	–8.496	$-5.387 \cdot 10^{-4}$	1.369	0.416	0.988	0.004	1.000
–90µm	–8.347	$-5.463 \cdot 10^{-4}$	1.376	0.415	0.948	0.003	0.995
limestone marble							
–4mm + 1mm	$3.762 \cdot 10^{-1}$	$2.949 \cdot 10^{-2}$	0.064	0.942	1.452	0.009	0.767
–1mm + 315µm	1.595	$3.182 \cdot 10^{-3}$	0.386	0.892	1.149	0.006	0.961
–315µm + 90µm	–8.696	$-5.252 \cdot 10^{-4}$	1.356	0.407	0.916	0.004	0.999
–90µm	–9.074	$-5.048 \cdot 10^{-4}$	1.338	0.377	0.918	0.004	0.999
dolomite							
–4mm + 1mm	$-1.035 \cdot 10^{-1}$	$-4.412 \cdot 10^{-4}$	1.283	0.300	0.923	0.004	0.998
–1mm + 315µm	–8.217	$-5.534 \cdot 10^{-4}$	1.383	0.419	0.912	0.004	0.999
–315µm + 90µm	6.072	$7.986 \cdot 10^{-4}$	0.715	0.418	1.016	0.005	0.984
–90µm	$2.801 \cdot 10^{-1}$	$1.680 \cdot 10^{-4}$	0.923	0.041	0.974	0.004	0.992

all cases, is not in contrast with references [3, 8, 14], where either Langmuir or Freundlich model is applied at much lower concentrations (<5 mg/L), but adsorption tends to become linear as concentration increases.

In Figure 1a-1c potentially toxic element adsorption on limestone, dolomite and marble from mono-element solutions of different concentration is illustrated as a function of time. Results for dolomitic marble are not presented in this Figure, because they have been carried out only for the fraction –1mm + 315µm, since as it results from Figure 1a-1c it performs better than the coarsest one –4mm + 1mm in most cases, after adsorption reaches equilibrium (2 h).

The finest ones have not been selected, since their better performance is expected, whereas the goal of the present study is to investigate whether the coarsest ones perform as well as the finest ones, in order to avoid grinding of the materials.

As it is obvious from the Figures 1a-1c, adsorption from solutions with very low concentration (5 mg/L) stabilizes after 1 h. Adsorption on limestone at 100 mg/L stabilizes for all elements after 1 h, except in case of Zn whose adsorption increases slightly after 1 h. Adsorption on limestone marble at 100 mg/L is similar with that on limestone, whereas an important increase in Cd and Cu adsorp-

Table 6b: Langmuir and Freundlich isotherm parameters for Cu adsorption on limestone, dolomite and marble.

particle size	Langmuir				Freundlich		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
limestone							
–4mm + 1mm	–8.333	$-5.463 \cdot 10^{-4}$	1.376	0.419	0.914	0.004	0.999
–1mm + 315 μ m	–8.163	$-5.548 \cdot 10^{-4}$	1.384	0.437	0.913	0.004	0.999
–315 μ m + 90 μ m	–8.340	$-5.466 \cdot 10^{-4}$	1.376	0.428	0.914	0.004	0.999
–90 μ m	–8.525	$-5.349 \cdot 10^{-4}$	1.365	0.408	0.915	0.004	0.999
limestone marble							
–4mm + 1mm	$1.176 \cdot 10^{-2}$	$3.884 \cdot 10^{-5}$	0.981	0.002	0.960	0.004	0.993
–1mm + 315 μ m	–7.564	$-5.832 \cdot 10^{-4}$	1.412	0.524	0.910	0.003	1.000
–315 μ m + 90 μ m	–8.224	$-5.528 \cdot 10^{-4}$	1.382	0.424	0.910	0.004	0.999
–90 μ m	–8.143	$3.854 \cdot 10^{-5}$	0.981	0.421	0.910	0.003	0.999
dolomite							
–4mm + 1mm	–6.553	$-6.534 \cdot 10^{-4}$	1.485	0.417	0.897	0.003	0.999
–1mm + 315 μ m	–8.299	$-5.498 \cdot 10^{-4}$	1.379	0.422	0.913	0.004	0.999
–315 μ m + 90 μ m	–7.468	$-5.251 \cdot 10^{-4}$	1.356	0.422	0.906	0.003	0.999
–90 μ m	–7.698	$-5.817 \cdot 10^{-4}$	1.410	0.424	0.908	0.003	0.999

Table 6c: Langmuir and Freundlich isotherm parameters for Pb adsorption on limestone, dolomite and marble.

particle size	Langmuir				Freundlich		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
limestone							
–4mm + 1mm	$-1.252 \cdot 10^{-1}$	$-3.952 \cdot 10^{-4}$	1.246	0.429	0.938	0.004	1.000
–1mm + 315 μ m	–9.328	$-5.013 \cdot 10^{-4}$	1.334	0.427	0.921	0.004	0.999
–315 μ m + 90 μ m	–7.740	$-5.782 \cdot 10^{-4}$	1.407	0.424	0.909	0.003	0.999
–90 μ m	–6.570	$-6.521 \cdot 10^{-4}$	1.484	0.423	0.897	0.003	0.999
limestone marble							
–4mm + 1mm	$-1.706 \cdot 10^{-1}$	$-3.025 \cdot 10^{-4}$	1.178	0.428	0.952	0.004	1.000
–1mm + 315 μ m	$-1.335 \cdot 10^{-1}$	$-3.747 \cdot 10^{-4}$	1.231	0.419	0.940	0.004	1.000
–315 μ m + 90 μ m	–5.970	$-6.962 \cdot 10^{-4}$	1.534	0.422	0.890	0.003	0.998
–90 μ m	$-1.328 \cdot 10^{-1}$	$-3.762 \cdot 10^{-4}$	1.232	0.418	0.940	0.004	1.000
dolomite							
–4mm + 1mm	–6.053	$-6.905 \cdot 10^{-4}$	1.527	0.424	0.891	0.003	0.999
–41mm + 315 μ m	–8.389	$-5.446 \cdot 10^{-4}$	1.374	0.430	0.914	0.004	0.999
–315 μ m + 90 μ m	–6.456	$-6.607 \cdot 10^{-4}$	1.493	0.425	0.896	0.003	0.999
–90 μ m	–6.105	$-6.866 \cdot 10^{-4}$	1.523	0.417	0.892	0.003	0.998

tion on the coarsest fraction is observed at 2 h. Adsorption on dolomite at 100 mg/L also stabilizes after 1 h, except in case of Zn whose adsorption on the finer fractions decreases slightly or more intensely after 2 h. At 500 mg/L Cd and Pb adsorption on limestone and its marble stabilizes after 1h, whereas Cu and Zn adsorption increases. In case of limestone marble a slight decrease in Cd and Cu adsorption on the coarsest fractions is observed. Adsorption on dolomite increases almost in all cases after 1 h, except

Pb adsorption which stabilizes, and Cd adsorption on the fine fraction –315 μ m + 90 μ m, which decreases after 1 h.

Concerning the particle size effect, at 5 mg/L no significant difference in adsorption on all material fractions with different particle size is observed after 1 h, except a difference between all material fractions by up to 15% observed in Pb adsorption. At 100 mg/L respectively significant differences in adsorption on material fractions with different particle size are observed only in case of Zn adsorption on

Table 6d: Langmuir and Freundlich isotherm parameters for Zn adsorption on limestone, dolomite and marble.

particle size	Langmuir				Freundlich		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
limestone							
–4mm + 1mm	$-2.632 \cdot 10^{-1}$	$-1.503 \cdot 10^{-4}$	1.081	0.182	0.969	0.004	1.000
–1mm + 315 μ m	$4.587 \cdot 10^{-1}$	$8.533 \cdot 10^{-5}$	0.959	0.986	0.988	0.004	1.000
–315 μ m + 90 μ m	$-2.841 \cdot 10^{-1}$	$-1.375 \cdot 10^{-4}$	1.074	0.925	0.995	0.003	1.000
–90 μ m	–5.208	$-6.068 \cdot 10^{-4}$	1.436	0.812	0.998	0.092	0.995
limestone marble							
–4mm + 1mm	–4.965	$-5.923 \cdot 10^{-4}$	1.421	0.586	0.960	0.003	0.992
–1mm + 315 μ m	$-2.604 \cdot 10^{-1}$	$-1.632 \cdot 10^{-4}$	1.089	0.185	0.966	0.004	0.999
–315 μ m + 90 μ m	$-2.004 \cdot 10^{-1}$	$-2.068 \cdot 10^{-4}$	0.241	0.241	0.961	0.004	0.999
–90 μ m	$1.650 \cdot 10^{-1}$	$2.515 \cdot 10^{-4}$	0.888	0.405	1.007	0.004	0.998
dolomite							
–4mm + 1mm	3.619	$1.353 \cdot 10^{-3}$	0.596	0.605	1.045	0.005	0.975
–1mm + 315 μ m	–5.345	$-6.599 \cdot 10^{-4}$	1.492	0.701	0.948	0.003	0.992
–315 μ m + 90 μ m	5.750	$7.865 \cdot 10^{-4}$	0.718	0.477	1.021	0.004	0.987
–90 μ m	–7.479	$-5.643 \cdot 10^{-4}$	1.393	0.482	0.914	0.003	0.999

Table 7: Effect of particle size, concentration and contact time on potentially toxic element adsorption on limestone, limestone marble and dolomite, as resulting from the Taguchi method.

element	% effect			
	particle size	concentration	contact 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

all the materials, which is in the order of 20-30%. However, it is not the finest fractions that exhibit the best behaviour and the coarsest one the worst behaviour for all materials. At 500 mg/L significant differences are observed after 2 h for Zn adsorption on material fractions with different particle size, however not exceeding 15% in case of limestone and its marble and rising up to 50% in case of dolomite. Furthermore, differences in Cd adsorption at 500 mg/L are

observed between the fractions, however not leading to an obvious result.

In general, after equilibrium is achieved (2 h), the fractions of coarser particle size exhibit in most cases a comparable performance to that of the finer ones. In order to certify this result, Taguchi method has been applied, estimating the effect of particle size in comparison with solution concentration, contact time and other parameters, including temperature, pH, solution environment. In Table 7

500 mg/L

500 mg/L

Figure 1a: % Adsorption of potentially toxic elements as a function of time on limestone fractions of different particle size from mono-element solutions at 5, 100, 500 mg/L.

Figure 1b: % Adsorption of potentially toxic elements as a function of time on limestone marble fractions of different particle size from mono-element solutions at 5, 100, 500 mg/L.

Figure 1c: % Adsorption of potentially toxic elements as a function of time on dolomite fractions of different particle size from mono-element solutions at 5, 100, 500 mg/L.

the effect of each parameter is shown, as resulting from the Taguchi method.

As it results from Table 7, the effect of particle size on Zn adsorption on all studied materials is much lower than the one of other parameters. Pb adsorption is obviously determined by solution concentration. 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 contact time is similar and not the strongest one. Cu adsorption seems to be determined by concentration in case of limestone marble and by contact 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 has been proven not to be the most determinative parameter in adsorption.

As it has already been explained, since the performance of the fractions – 1mm + 315µm, – 315µm + 90µm and <90µm is better than that of the coarsest one – 4mm + 1mm in most cases, for the experiments in fixed bed conditions, which simulate real conditions, the fraction <1mm, including all the aforementioned finest fractions, has been selected.

As it can be observed in Figure 2, the adsorption of potentially toxic elements (Cd, Cu, Pb, Zn) from mono-element solutions differs a lot from their adsorption from a competitive solution. In particular, Cd and Cu adsorption from mono-element solutions on all the materials 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 competitive solution on all the materials is high and in some cases even higher than their adsorption from mono-element solutions, whereas Cd and Zn adsorption from a competitive solution on all the materials, except limestone, is significantly lower than their adsorption from mono-element solutions, varying from 17 to 55%. Furthermore, a significant difference is observed in Cd and Zn adsorption from a competitive solution on limestone and its marble. In particular, Cd and Zn adsorption is three times lower on limestone marble than on limestone.

In Table 8 the adsorption capacity q (mg of element per g of sorbent) of all the samples, that is limestone and its marble, dolomite and its marble, for all the studied elements (Cd, Cu, Pb, Zn) from both mono-element and competitive solutions is given.

In general, no significant differences in adsorption capacity are observed between each rock (limestone, dolomite) and its marble. Limestone and dolomite and their marbles have a similar adsorption capacity for Cd and Cu, rising up to 0.030 mg Cd per g and 0.53-0.60 mg Cu per

Table 8: Adsorption capacity of the fraction $-1\text{mm} + 315\mu\text{m}$ of the samples in monoelement and competitive solutions of potentially toxic elements.

sorber material	solution	adsorption capacity q (mg/g sorber)			
		Cd	Cu	Pb	Zn
limestone	monoelement	0.030	0.59	0.018	0.30
	competitive	0.030	0.60	0.025	0.52
limestone marble	monoelement	0.030	0.53	0.022	0.36
	competitive	0.007	0.59	0.026	0.10
dolomite	monoelement	0.030	0.60	0.029	0.60
	competitive	0.015	0.58	0.028	0.33
dolomitic marble	monoelement	0.030	0.60	0.029	0.59
	competitive	0.011	0.57	0.029	0.21

Figure 2: Adsorption % of potentially toxic elements from (a) monoelement solutions and (b) a competitive solution on the fraction $-1\text{mm} + 315\mu\text{m}$ of the materials. **Figure 3:** Eluate pH during potentially toxic element adsorption on the samples in fixed bed conditions.

g, whereas dolomite and its marble have a higher adsorption capacity for Pb and Zn, rising up to 0.029 mg Pb per g and 0.59–0.60 mg Zn per g, than that of limestone and its marble, rising up to 0.018–0.022 mg Pb per g and 0.30–0.36 mg Zn per g.

Differences are observed also in the adsorption capacity achieved for each element in monoelement solutions and a competitive solution. In particular, a decrease by 45–75% in Cd and Zn adsorption capacity of all the materials is observed in a competitive solution, except limestone, whose Cd adsorption capacity remains the same and Zn adsorption capacity increases by 73%. No significant differences in Cu adsorption capacity of all materials and also in Pb adsorption capacity of dolomite and its marble are observed, whereas in case of limestone and its marble, an increase in Pb adsorption capacity by 18–39% is observed. The differences in adsorption capacity between mono-

Figure 4: Adsorption % of potentially toxic elements Cd (a), Cu (b), Pb (c), Zn (d) on the samples in fixed bed conditions.

ment and competitive solutions are in accordance with the ones observed in adsorption %.

The leaching of the elements (Cd, Cu, Pb, Zn) being retained on all the materials, after adsorption in batch conditions, does not exceed 4%, indicating that they are sufficiently retained on the rocks' surface.

In Figure 3 and 4 the pH of the eluate and the adsorption % of the potentially toxic elements (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.

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 materials. The pH is stabilized at a different point for each

material. For limestone and its marble it is stabilized at 7.7-9, whereas for dolomite and its marble at 9-9.5.

As it is obvious from Figure 4, as the first 200 mL of solution have passed through the bed, the adsorption on all the materials is in most cases stabilized at its maximum, varying from 93 to almost 100%. Furthermore, even the initial adsorption, estimated by the first eluate, coming up to 86-99%, is considered high. Total adsorption of Cu and Zn is achieved on all the materials 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%.

4 Discussion

According to the aforementioned presentation of the experimental results, when equilibrium is achieved after 2 h, no significant differences in adsorption on fractions with different particle size can be observed, except in case of Cd and Zn at higher solution concentrations and Pb at low concentration. However, the differences observed do not indicate that in any case the coarsest fraction exhibits the worst performance. In contrast, coarser fractions exhibit in most cases a satisfactory performance, comparable to that of the finer ones.

This fact has also been certified by application of Taguchi method, indicating that the particle size could not be considered as the determinative parameter in potentially toxic element adsorption on the studied materials. This is also in accordance with the fact that there is no statistically significant difference in CEC among the fractions with different particle size of each material, as it has been determined using SPSS software. This result leads to the encouraging conclusion that a grinding and/or sieving process for achieving a fine particle size of the rocks is not considered necessary, relieving thus their further application from an extra financial burden.

As far as it concerns the adsorption capacity of the studied materials, limestone differentiates from dolomite in Zn adsorption, which could be attributed to the ionic radius of Zn^{2+} , which is similar to the one of Mg^{2+} compared to the one of Ca^{2+} , favouring thus its exchange with Mg^{2+} rather than with Ca^{2+} , as it has already been mentioned [26, 27]. However, no significant differentiation between each rock and its marble has been observed.

Another view of potentially toxic element adsorption on carbonate minerals on which focuses the present study is adsorption from a competitive solution, in order to simulate real waste streams. Preferable Cu and Pb adsorption from a competitive solution in comparison to Cd and Zn adsorption on the studied materials could be attributed to the adsorption mechanisms for the studied elements. In particular, Cu^{2+} ions are adsorbed very strongly and fast (within 1 min) on calcite surface, since Cu^{2+} ions are smaller than Ca^{2+} ions and are incorporated into the crystal lattice [22]. Furthermore, the formation of Cu carbonate and Cu hydroxide complexes contributes to retention of Cu^{2+} ions on calcite surface [23]. Pb^{2+} adsorption on calcite is also rapid within the first minute, but contin-

ues slowly, indicating a primary reversible 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 [4]. Rapid Zn^{2+} adsorption on calcite appears to occur within 12 hours via exchange of Zn^{2+} and ZnOH^+ with surface-bound 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 [3, 24]. Cd^{2+} is adsorbed on calcite preferably than Zn^{2+} by forming a phase behaving as a surface precipitate [3]. 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 [25]. Taking into account that dolomite consists of layers of carbonate separated by alternating layers of calcium and magnesium ions [14], its performance in competitive solution, being similar to that of calcite, could be explained.

However, the above mentioned adsorption order of the elements from a competitive solution on calcite, as resulting from references, differentiates from the adsorption capacity of the materials. In particular, the adsorption capacity in a competitive solution for limestone follows the order $\text{Cu} > \text{Zn} > \text{Cd} > \text{Pb}$, for dolomite the order $\text{Cu} > \text{Zn} > \text{Pb} > \text{Cd}$ and for marbles the order $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$. Zn seems to be more preferred than Pb and Cd, in contrast to references. However, this could be attributed to the different initial concentrations (100 mg/L Zn, 5 mg/L Pb, 5 mg/L Cd), leading to a higher Zn adsorption capacity.

A significant difference observed in Cd and Zn adsorption from a competitive solution on limestone and its marble could be attributed to the adsorption mechanism of each element and the specific characteristics of each material. In particular, the higher porosity and greater pore volume of limestone, as it results from Table 5, favours the solid-state diffusion of Cd in its structure, which is its main adsorption mechanism [16, 25]. On the other hand, Zn is sorbed on carbonate minerals by both ion exchange and precipitation [12, 24]. Therefore, the higher CEC of limestone could partially explain the higher Zn adsorption on it.

Another encouraging result is that leaching of the elements adsorbed on the rock surface is very low rising up to 4%, which constitutes an extra benefit for their utilisation as base material of a landfill.

Finally, the application of fixed bed conditions has led to satisfying potentially toxic element adsorption. In comparison to batch experiments, almost total adsorption of the elements is achieved in all cases, attributed to the available contact time. Even if such a comparison is not

suggested, however it could constitute a first estimation of rocks' behaviour in real conditions, in case they are utilised as landfill base.

In conclusion, the behaviour of mineral tailings, deriving from limestone and its marble, dolomite and its marble, in potentially toxic element adsorption (Cd, Cu, Pb, Zn) investigated in the present study, seems to be encouraging for their potential utilisation in an environmental application.

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