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Ba and Co Removal from Water by Elution Through Fixed Beds of Phillipsite- and/or Chabazite-Rich Tuffs

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ABSTRACT

The possibility of using phillipsite- and chabazite-rich tuffs as cation exchangers in the process of barium and cobalt removal from wastewaters was evaluated. Accordingly, fixed beds of phillipsite-rich Neapolitan yellow tuff grains and of chabazite-rich Orvieto-Bagnoregio ignimbrite grains were prepared. After exchanging them in Na^+ form, the relevant breakthrough curves were determined at room temperature, using 100 mg/L solutions for each cation. Some characteristic dynamic parameters were calculated from these curves, such as length of mass transfer zone, ion exchange capacity in dynamic conditions, dynamic selectivity and efficiency of the process, obtaining information on

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the conditions under which the process should be carried out. The data collected evidenced the good selectivity of both Na-exchanged zeolites for Ba and the poor selectivity for Co, confirming the results previously obtained in equilibrium conditions. The difficulty of eluting barium from the tuff beds during regeneration suggested a profitable employment of Italian phillipsite- and/or chabazite-rich tuffs in discontinuous processes, which are especially useful in the treatment of nuclear power plant wastes, in which the zeolitic sludge generated from Ba removal is usually stabilized–solidified in a cement matrix.

Key Words: Barium; Cobalt; Ion exchange; Zeolitised tuff; Phillipsite; Chabazite.

INTRODUCTION

Natural zeolites of sedimentary origin, usually referred to as zeolitic tuffs, are widespread in hundreds of deposits all over the world.[1] Among other applications, these materials have been proposed as ion exchangers to remove polluting cations from wastewaters, as alternative of the methods based on precipitation.[2] The advantage of the ion-exchange procedure is connected to the good affinity generally exhibited by natural zeolites toward most heavy metal cations[3] and on the very low cost of these materials, widely available in outcrops amounting to several million tons.[4]

Zeolites present in Italian deposits are mainly phillipsite and/or chabazite, and in minor extent, clinoptilolite.[4] Their utilization in separation processes has long since been proposed in fields of industrial and/or environmental significance.[4] Interesting results have been obtained, for instance, in the study of exchange equilibria involving several cationic pollutants of industrial (Ba, Cd, Co, Cu, Pb, Zn), municipal (NH_4), or nuclear (^{133}Ba, ^{60}Co, ^{137}Cs, ^{90}Sr) wastewaters.[5–10] As regards, in particular, Ba and Co, that are of either industrial (hydrometallurgy) or nuclear interest, phillipsite and chabazite exhibited a different behavior. Both zeolites showed a reasonable selectivity for Ba^{2+}, as demonstrated by the convex profiles of the respective isotherms and especially by the moderate (chabazite) to high (phillipsite) values of the relevant equilibrium constants.[9,10] Also, the whole cation exchange capacity of both zeolites was proved to be available for this cation. On the contrary, either phillipsite or chabazite showed a poor selectivity for Co^{2+}. In addition, the cation exchange capacity was not completely or very hardly utilized in this case.[9,10]

Research on the possible utilization of natural zeolites to remove Ba^{2+} or Co^{2+} from wastewater are very scarce in the literature, either with regard to equilibrium studies,[11] or as concerns application (see, e.g., Refs.[12–14]). It was, therefore, considered worthwhile to further investigate the $2Na^+ \rightarrow Ba^{2+}$ and $2Na^+ \rightarrow Co^{2+}$ exchange reactions in dynamic conditions (elution through zeolitised tuff beds), to evaluate the efficiency of the process in two opposite situations (one favorable in terms of cation exchange selectivity, the other unfavorable) and to estimate, accordingly, the real possibility of utilization of the two sedimentary zeolites in the field of barium and cobalt removal from wastewaters.

MATERIALS AND METHODS

Materials

The tuff samples investigated came from two quarries, one in Marano (Naples), belonging to the huge formation of *Neapolitan yellow tuff* (TGN), and the other in Palombara-Lubriano (Viterbo), belonging to the formation of the Orvieto Bagnoregio ignimbrite (IOB) (Vulsini volcanic district, southern Tuscany-northern Latium), locally called *red tuff with black scoriae*.[4] The x-ray diffraction analysis (XRD), carried out on representative specimens of these tuffs using a Philips PW 1730 apparatus (rad. CuKα), equipped with a Philips 3710 counts unit, showed the presence mainly of phillipsite with minor amounts of chabazite, K-feldspar, analcime, and biotite in the TGN and of prevalent chabazite with small quantities of phillipsite and K-feldspar in the IOB. The quantitative mineralogical analysis was carried out also by XRD, using the technique denominated reference intensity ratio (RIR),[15] that is, an extension to mixtures with many components of the well-known technique based on the internal standard.[16] Table 1 reports the mineralogical composition of the two tuff samples examined. The bulk samples of the two zeolitic materials were then ground and screened. The 30 × 50 mesh grain-size fraction was used to prepare two fixed bed columns for dynamic runs.

Ion Exchange Runs

The cation exchange capacity (CEC) of the two zeolite tuffs (TGN and IOB) was determined using the cross-exchange method.[17] Accordingly, two 1-g tuff samples, placed on gooch filters, were percolated at about 60°C up to exhaustion by 1 M NaCl or KCl solutions, prepared by using Carlo Erba

Table 1. Mineralogical composition (percentage) of the two tuff samples examined.

Mineral	TGN[a]	IOB[a]
Phillipsite	48.5	5.5
Chabazite	7.9	45.5
Analcime	6.0	10.2
Feldspar	25.7	38.0
Biotite	0.2	0.6
Smectite	8.4	—
Glass	3.2	0.3

[a] TGN = Neapolitan yellow tuff; IOB = Orvieto Bagnoregio ignimbrite.

reagent-grade chemicals (purity 99.5%). The obtained monocationic forms (Na^+ or K^+) were then re-exchanged under the same conditions with potassium and sodium, respectively. Na^+ and K^+ concentrations in the effluents of the second exchange cycle, evaluated by atomic absorption spectrophotometry (AAS, Perkin Elmer AA 2100 apparatus), were used to calculate the mean CEC values. Experimental CEC values turned out to be 1.92 mEq/g and 1.89 mEq/g for TGN and IOB, respectively. These values are in good agreement with the calculated CEC values (2.00 mEq/g and 1.84 mEq/g, respectively), which were estimated from the phillipsite and chabazite contents (see Table 1), taking into account the reference values of the pure phases obtained from the literature (3.55 mEq/g for TGN phillipsite and chabazite[18] and 3.60 mEq/g for IOB phillipsite and chabazite[19]). The other cation exchanging tuff constituents (e.g., analcime, smectite, glass) were not considered in this computation, because they, due to their exiguity and low cation-exchange rate and/or capacity,[20,21] do not contribute to great extent to the CEC value.

Dynamic runs were carried out at room temperature (roughly 25°C) in fixed beds, obtained by allowing wet tuffs grain of zeolite tuffs to tightly accommodate into glass columns, partially filled with water. The columns were rapped until the bed depth showed no further reduction. Before starting elution with solutions containing the polluting cations, the two beds were converted in Na^+ form using a 1 M NaCl solution till the concentration of the other species present in the effluent was below 1 mg/L. Ba^{2+} and Co^{2+} solutions were passed through the columns at a constant flow rate, regulated by a peristaltic pump (Mod. P-3, Pharmacia Fine Chemicals). The eluted solutions were collected at fixed times with a fraction collector

(Mod. PF-3, Pharmacia Fine Chemicals) and analyzed by AAS. After exhaustion, the beds were regenerated before reuse (the same column was used for eluting either Ba^{2+} solutions or Co^{2+} solutions) using a 1 M NaCl solution, as mentioned before. Table 2 summarizes the column operating conditions for both phillipsite-rich tuff (TGN) and chabazite-rich tuff (IOB).

Computation of the Kinetic Parameters

The obtained S-shaped breakthrough curves were analyzed to obtain some dynamic parameters. First, the length of the mass transfer zone (MTZ), L_z, i.e., the fraction of bed depth in which cation exchange is supposed to occur under dynamic conditions was obtained.[22] In agreement with the mathematical model for the elution of fixed beds,[22] L_z can be computed from the following expression:

$$L_z = L_b \frac{V_t - V_b}{FV_t - (1 - F)V_b} \tag{1}$$

where L_b is the bed length, V_b is the breakthrough volume, V_t is the volume of the eluting solution at the bed exhaustion, and F is the symmetry index

Table 2. Columns operating conditions.

Equipment specifications	TGN	IOB	Service conditions	TGN	IOB
Column diameter (cm)	1.0	1.0	Influent Ba^{2+} concentration (mg/L)	98	98
Bed depth (cm)	40	39	Influent Co^{2+} concentration (mg/L)	100	100
Bed volume (cm^3)	31.40	30.61	Feed flow rate (mL/h) (Ba)	303	309
Tuff weight (g)	18.38	19.20	Feed flow rate (mL/h) (Co)	339	303
Grain size (mesh)	30 × 50	30 × 50	Holdup time[a] (min) (Ba)	6.2	5.9
Bulk density (g/cm^3)	0.58	0.63	Holdup time[a] (min) (Co)	5.6	6.1

[a] Time necessary to the influent solution to pass through the bed.

of the breakthrough curve, defined as:

$$F = \frac{\int_{V_b}^{V_t} (C_0 - C)\,dV}{C_0(V_t - V_b)}. \tag{2}$$

Here, C_0 and C are the original and the actual concentrations of the cation entering the zeolite framework, respectively. The integral at the numerator can be estimated from the breakthrough plot through a graphic integration of the area delimited by the abscissas axis, the horizontal line denoting the value of the original cation concentration, the vertical line having equation $V = V_b$, and the S-shaped curve. Given the uncertainty in evaluating the real values of V_b and V_t, the breakthrough and exhaustion volumes were estimated, according to a consolidate practice,[22,23] at 0.05 C_0 and 0.95 C_0. To be kept in mind, in addition, that the data obtained can be considered reliable, as long as $L_z < 1/2L_b$.[24]

The $Ba^{2+} - CEC$ and $Co^{2+} - CEC$, i.e., the exchange capacities of TGN and IOB tuffs in dynamic conditions (C_t), were estimated from a graphic integration (in a similar way as described previously), according to the following relationship:

$$C_t = \frac{\int_{0}^{V_t} (C_0 - C)\,dV}{\rho_b L_b A_s} \tag{3}$$

where ρ_b is the tuff density and L_b and A_s represent the length and the section of the tuff bed, respectively. The working exchange capacity (WEC or C_w), that is the profitable cation exchange capacity in the assumption that the maximum allowable concentration of the ingoing ion in the effluent is that reached at the breakthrough point, was estimated graphically, according to the relationship:

$$C_w = \frac{\int_{0}^{V_b} (C_0 - C)\,dV}{\rho_b L_b A_s}. \tag{4}$$

Knowing C_t, C_w and the total cation-exchange capacity (CEC), the dynamic selectivity (S), defined as the ratio between the $Ba^{2+} - CEC$ or $Co^{2+} - CEC$ and the total CEC, which appraises the tuff preference in dynamic conditions for the ingoing cation (i.e., Ba^{2+} and Co^{2+}), and the efficiency (E), namely, the ratio between WEC and total CEC, can be easily calculated:

$$S = \frac{C_t}{CEC} \tag{5}$$

$$E = \frac{C_w}{CEC}. \tag{6}$$

RESULTS AND DISCUSSION

Figures 1 through 4 show the breakthrough curves resulting from the elution of the two Na-pre-exchanged zeolite beds, made of chabazite-rich tuff (IOB) or phillipsite-rich tuff (TGN), with Ba^{2+} (see Figs. 1 and 2) and with Co^{2+} (Figs. 3 and 4), respectively. The breakthrough curves were plotted reporting in ordinates the normalized values of concentration, C/C_0, i.e., the ratio between the actual concentration of the effluent cation, C, and the original concentration of the same cation, C_0. In abscissas, the normalized values of volume of eluate (BV), i.e., the ratio between the actual volume of solution passed through the bed and the bed volume are given.

All the previous observations on selectivity were confirmed[9,10]: in fact, the S-shaped breakthrough curves presented by phillipsite and chabazite with Ba^{2+} (see Figs. 1 and 2) are sufficiently symmetrical and somewhat steep, both signs of good selectivity. On the contrary, the Co^{2+} breakthrough curves (see Figs. 3 and 4) present a clear asymmetry and are very smooth, an index of a poor selectivity or unselectivity. Table 3 summarizes the dynamic data calculated from the breakthrough curves reported in Figs. 1 through 4.

Inspecting the data of Table 3 points out that L_z, i.e., the length of MTZ, is small for Ba^{2+} ($< 1/2\ L_b$); whereas it is rather large for Co^{2+} ($> L_b$). This is an indirect confirmation[9,10] of the good selectivity of both tuffs for barium and the poor selectivity of both tuffs for cobalt. In addition, the data for the latter cation appear absolutely unreliable, inasmuch as $L_z > L_b$. The results regarding the cation-exchange capacity (see Table 3, fourth column) are also consistent with those concerning the occupancy of the extraframework cationic sites, worked out from the data collected in equilibrium conditions.[9,10] The values found for the exchange of Ba^{2+} for Na^+ in dynamic conditions (1.80 mEq/g for IOB and 1.74 mEq/g for TGN) are, in fact, very close to the CEC values determined for both tuffs (1.89 mEq/g for IOB and 1.92 mEq/g for TGN, see section, “Experimental”). The values confirm that Ba^{2+} can completely replace for Na^+ in chabazite or in phillipsite. Accordingly, dynamic selectivity S [see eq. (5)] is very high (0.95 and 0.91).

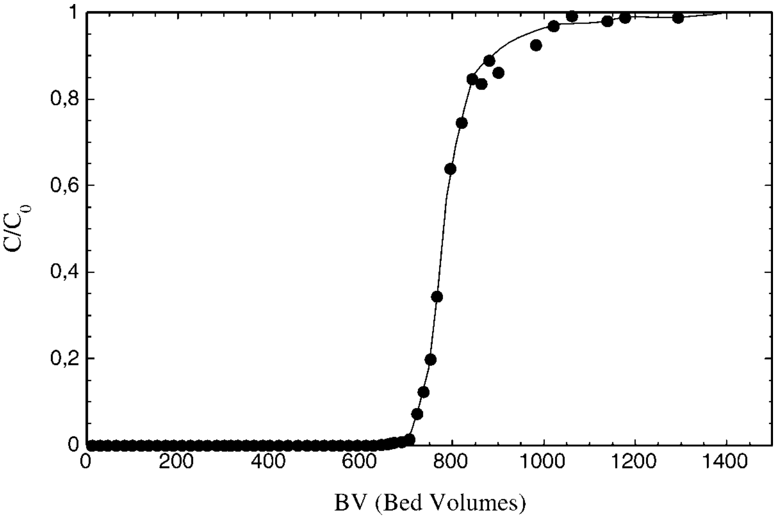

Figure 1. Ba breakthrough curve obtained by eluting the Na-exchanged IOB chabazite-rich tuff bed with a solution containing 98 mg/L Ba^{2+}.

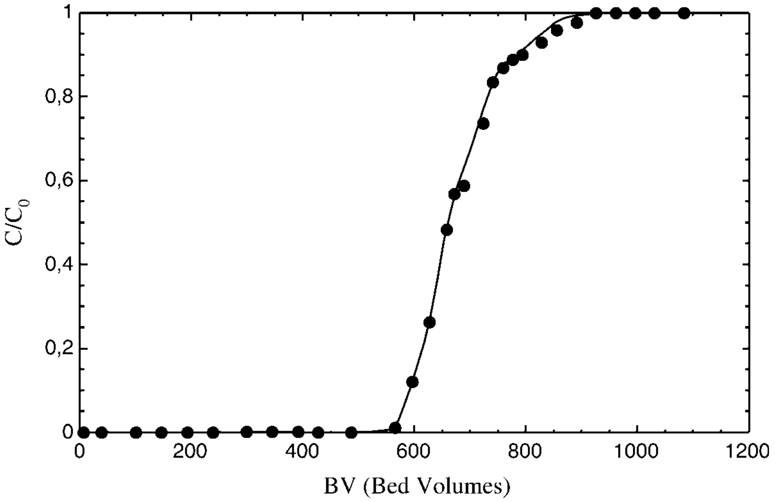

Figure 2. Ba breakthrough curve obtained by eluting the Na-exchanged TGN phillipsite-rich tuff bed with a solution containing 98 mg/L Ba^{2+}.

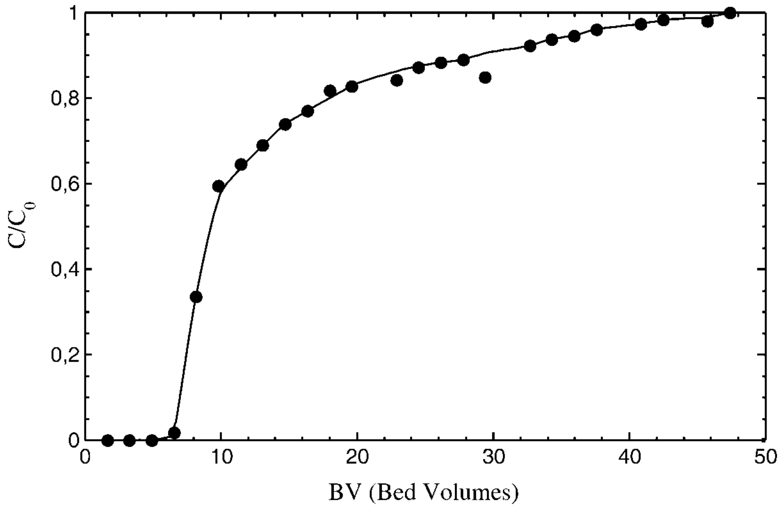

Figure 3. Co breakthrough curve obtained by eluting the Na-exchanged IOB chabazite-rich tuff bed with a solution containing 100 mg/L Co^{2+}.

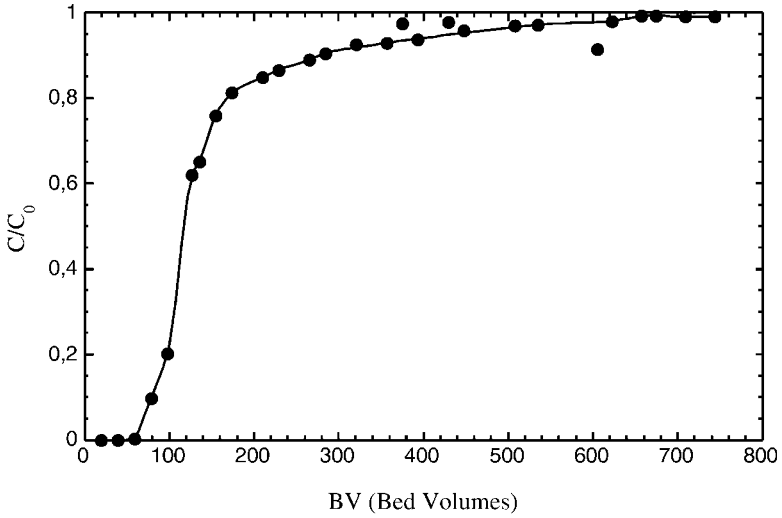

Figure 4. Co breakthrough curve obtained by eluting the Na-exchanged TGN phillipsite-rich tuff bed with a solution containing 100 mg/L Co^{2+}.

Table 3. Dynamic data from breakthrough curves.

$C_{0(Ba^{2+})}$ (mg/L)	$C_{0(Co^{2+})}$ (mg/L)	L_z (cm)	C_t (M^{2+} − CEC)[a] (mEq/g)	C_w (WEC) (mEq/g)	S[b] (C_t/CEC)	E[c] (C_w/CEC)
98[d]		14.7[d]	1.80[d]	1.39[d]	0.95[d]	0.74[d]
	100[d]	55.3[d]	0.84[d]	0.30[d]	0.44[d]	0.16[d]
98[e]		18.7[e]	1.74[e]	1.27[e]	0.91[e]	0.66[e]
	100[e]	52.8[e]	0.92[e]	0.41[e]	0.48[e]	0.21[e]

[a] M = Ba or Co.
[b] S = dynamic selectivity.
[c] E = overall efficiency.
[d] IOB.
[e] TGN.

On the contrary the Co^{2+} − CEC for IOB (0.84 mEq/g) is equal to only 44% of the reference CEC value. Similarly, that for TGN (0.92 mEq/g) corresponds to 48% of the calculated CEC value, in agreement with the reduced occupancy of the cation sites by Co^{2+} in both zeolites and the poor selectivity demonstrated by phillipsite and chabazite in equilibrium condition for this cation.[9,10] These considerations on selectivity are further confirmed by the data of the fifth and seventh columns of Table 3. The WEC values are, in fact, rather high for both tuffs in the case of Ba^{2+}, whereas they are very low for Co^{2+}. Accordingly, the process efficiency E [see eq. (6)] is good for the former cation (0.74 and 0.66 for IOB and TGN, respectively); whereas the performance in the case of Co^{2+} removal is definitely low: only 0.16 and 0.21 for the two materials, respectively. Figures 5 through 8 report the regeneration curves after bed exhaustion using a 1 M NaCl solution. The high selectivity of both chabazite and phillipsite for barium is further confirmed here, considering that regenerant volumes of about 15 L (490 BV) and 20 L (640 BV) are needed for eluting roughly 90% of barium contained in IOB and TGN beds, respectively (see Figs. 5 and 6). To obtain roughly 70% regeneration, which is the figure usually accepted in full-scale plants, it would be necessary to use regenerant volumes of about 10 L (330 BV) and 15 L (470 BV), respectively, two values very close to the relative breakthrough volumes (see Figs. 1 and 2). To be noticed is that the observed difficulty in leaching Ba from the TGN bed recalls, to some extent, the findings of Barrer and Munday, who reported that cation exchange of Ba^{2+} for Na^{+} in phillipsite was irreversible.[25] The regeneration of Co-exhausted tuff beds is, of course, easier (to obtain roughly 70% regeneration, would require about 8 L (260 BV) and 4 L (130 BV) of

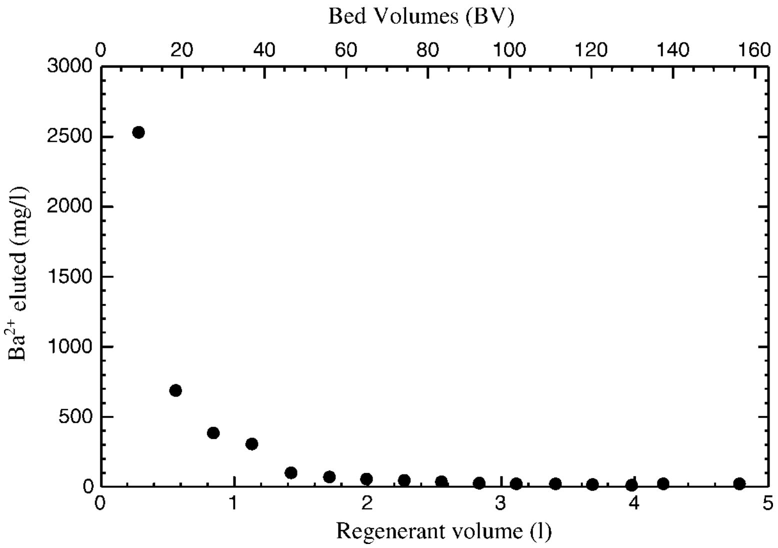

Figure 5. Elution curve of Ba^{2+} from the exhausted IOB chabazite-rich tuff bed by a 1 M NaCl regenerant solution.

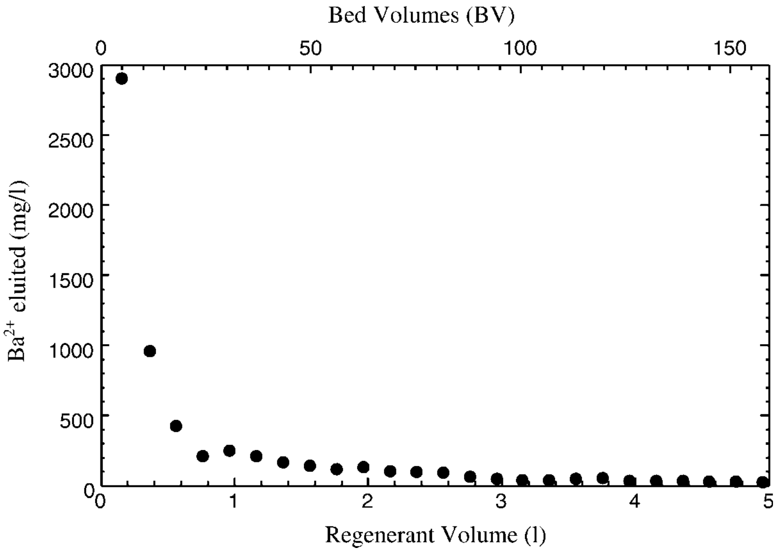

Figure 6. Elution curve of Ba^{2+} from the exhausted TGN phillipsite-rich tuff bed by a 1 M NaCl regenerant solution.

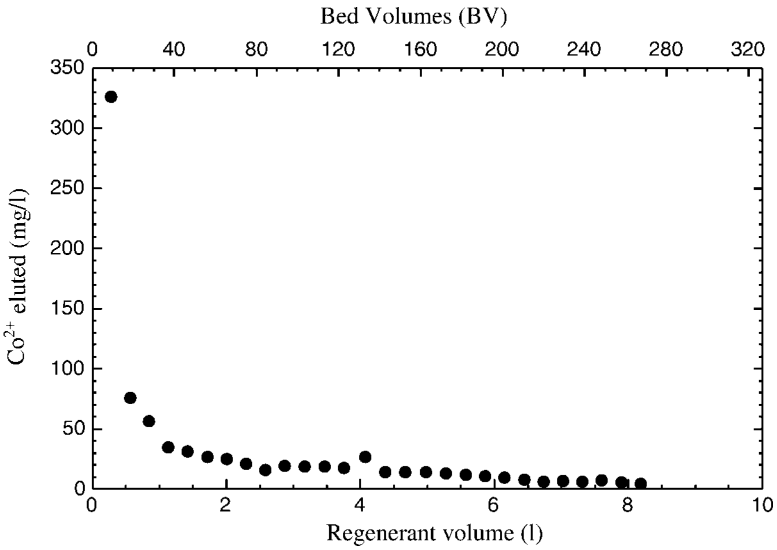

Figure 7. Elution curve of Co^{2+} from the exhausted IOB chabazite-rich tuff bed by a 1 M NaCl regenerant solution.

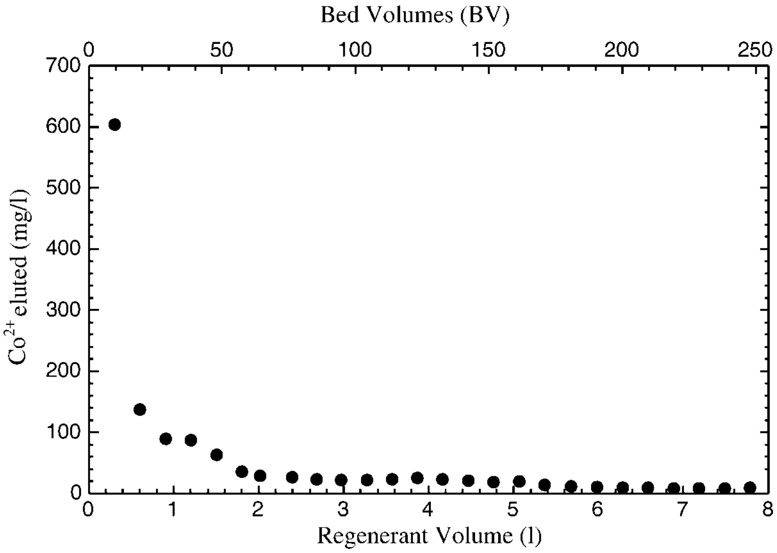

Figure 8. Elution curve of Co^{2+} from the exhausted TGN phillipsite-rich tuff bed by a 1 M NaCl regenerant solution.

the regenerant solution, respectively, but also in this case, very far from the needs of an industrial application (see Figs. 7 and 8).

CONCLUSION

Confirming the data of the previous study on equilibrium reactions,[9,10] the results collected during the present investigation demonstrate the possibility to use phillipsite- or chabazite-rich tuffs, pre-exchanged in sodium form, as cation exchangers for barium removal from wastewaters. Dynamic data from breakthrough curves indicate a little higher dynamic selectivity and efficiency of the chabazite-rich tuff, compared to phillipsite-rich tuff. In fact, some 19 g of IOB sample were able to depurate 683 BV of a solution containing about 100 mg/L Ba^{2+}; whereas the same amount of TGN sample was able to remove the polluting cation from 544 BV of the same solution. On the whole, it may be stated that Italian tuffs, rich in both zeolites,[4] can be used efficiently in the said process. The same is not true for cobalt, given the poor selectivity of both zeolites for this cation and the low efficiency of the overall removal process.

Regeneration of Ba^{2+}-saturated tuff beds proved to be not very effective, as apparently Ba^{2+} is so strongly bound to both zeolites that to remove it, e.g., 70% of barium, from the exhausted IOB bed, about 330 BV of regenerant must be used; whereas some 470 BV are required to remove the same barium amount from the exhausted TGN bed. These values are unacceptable to obtain a favorable performance of the exchange processes. This difficulty can be overcome choosing a discontinuous process in which the ion exchanger (zeolitised tuff) is used only once to remove the polluting species from the wastewater. The resulted sludges of this operation could be stabilized–solidified in a cement matrix, taking also advantage of the pozzolanic properties exhibited by tuff.[1] This procedure, which has successfully been adopted recently in several cases,[26] would be particularly timely in the case of wastewaters of nuclear power plants, where the stabilization–solidification of radioactive wastes in cement matrices is a consolidated practice.[1,3]

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