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Preparation of a Chromatographic Solid Support on the Basis of Perlite, and Separation of Uranium on a Tributyl-Phosphate-Loaded Perlite Column

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ABSTRACT

The SiO_2 content of the mineral perlite, which is the 70–75% range, was converted to soluble silicates with NaOH. The acidification of soluble silicates in the perlite formed hydrogels which turned into xerogels upon drying. Several parameters, particle size, specific surface area, pore size and volume, and surface hydroxyl group density were investigated for perlite standardized by NaOH. The standardized perlite was silanized and loaded with 20% (w/w) tributyl phosphate before use as a reversed-phase column chromatograghy solid support for the investigation of the chromatographic behavior of UO_2^{2+} and Fe^{3+}.

Key Words. Perlite; RPC; TBP; UO_2^{2+}; Fe^{3+}

INTRODUCTION

Reversed-phase column chromatography (RPC) is an extremely versatile technique and has been applied successfully to the separation of various metals and organic compounds (1, 2).

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The application of RPC has received considerable attention because it combines the selectivity of liquid–liquid extraction and the advantages of chromatographic operation. In general, the efficiency of RPC separation depends on both the chemical and physical properties of the solid support and the stationary phase (3–5). A number of solid support have previously been used for RPC including silica, alumina, poly(styrene–divinyl benzene), and hydrophilic polymers (6, 7).

Perlite is a volcanic glassy rock with an amorphous structure and a pearly lustre. It is produced in commercially workable quantities from mines in the Aegean region of Turkey. It contains 70–75% SiO_2 which can be converted to soluble silicates by reaction with NaOH (8, 9). The soluble silicates in the mineral perlite were gelled by the addition of HCl according the method for obtaining silica gel for chromatographic purposes (10).

Hydrophobization of silica gel can be achieved by using either reactive organosilanes or hydrocarbons with functional groups suitable for polymerization (5).

Perlite prepared as described above can be silanized by reaction with dimethyldichlorosilane (DMCS) as used for silica gel and used as a support material for RPC.

EXPERIMENTAL

Chemicals and Reagents

Raw perlite was provided from the perlite mines of Etibank (Izmir, Turkey). All chemicals used were of analytical grade from E. Merck, Fluka, and Riedel.

Standardization of Perlite

Raw perlite of 100–200 mesh particle size was boiled with 3 M HCl for about an hour, then filtered and washed with distilled water until the filtrate gave a negative reaction for Cl^-. The product was dried in an oven at 110°C. Afterward this product was suspended in 3 M NaOH and heated at 100–110°C with stirring for about 90 minutes. Then the pH of the suspension was adjusted to 2 by the addition of 1/1 (v/v) HCl with stirring. The suspension was allowed to stand for 24 hours. Then it was filtered and washed with distilled water (in order to remove Cl^- from the suspension), 0.1% EDTA solution, and finally distilled water. It was dried in an oven at 150°C and sieved to obtain a 100–200 mesh particle size. This product was called "standardized perlite." The chemical and physical properties of raw perlite and standardized perlite are given in Table 1.

Silanization of Perlite

The standardized perlite was silanized with DMCS in toluene. The silanization was carried out under reflux in toluene for 6 hours. The product was

TABLE 1
The Chemical and Physical Properties of Raw and Standardized Perlites

Physical properties of raw perlite		Constituent	Chemical properties of Raw perlite (%)	Chemical properties of Standardized perlite (%)
Color:	Gray-black-white	SiO_2	73.3	87.3
pH:	7	Al_2O_3	12.23	2.75
Softing point:	800–1100°C	Fe_2O_3	1.14	0.53
Melting point:	1315–1390°C	MgO	0.09	0.04
Specific heat capacity:	0.20 kcal/kg·°C	CaO	0.56	0.30
Specific weight:	2.2–2.4 g/cm^3	$Na_2O + K_2O$	7.52	5.25
Free moisture:	0.5%	Heat loss	5.00	3.40
Relative moisture:	2–5%			
Heat loss:	0.5%			

separated by filtration, washed with acetone, and dried in an oven at 40°C overnight.

Particle Size Analysis

Particle size analysis was carried out using a Malvern Instruments Series 2600 combined with a computer. The particle size analysis of raw perlite and standardized perlite are given in Table 2. Figures 1 and 2 show the particle size distribution of raw perlite and standardized perlite, respectively.

In Table 2, the span is the measurement of the width of the distribution.

D[4,3]: This is the volume mean diameter. It is the diameter of the sphere having the same value as our real particle.
D[3,2]: This is the surface area mean diameter. It is the diameter of the sphere having the same surface area as our real particle.
D[v,0.9]: 90% of the distribution is below this value.
D[v,0.1]: 10% of the distribution is below this value.

TABLE 2
Particle Size Analysis

	Span	D[4,3]	D[3,2]	D[v,0.9]	D[v,0.1]	D[v,0.5]
Raw perlite	1.13	114.53 μm	37.03 μm	173.21 μm	35.60 μm	121.69 μm
Standardized perlite	0.91	118.97 μm	46.12 μm	173.92 μm	60.09 μm	124.70 μm

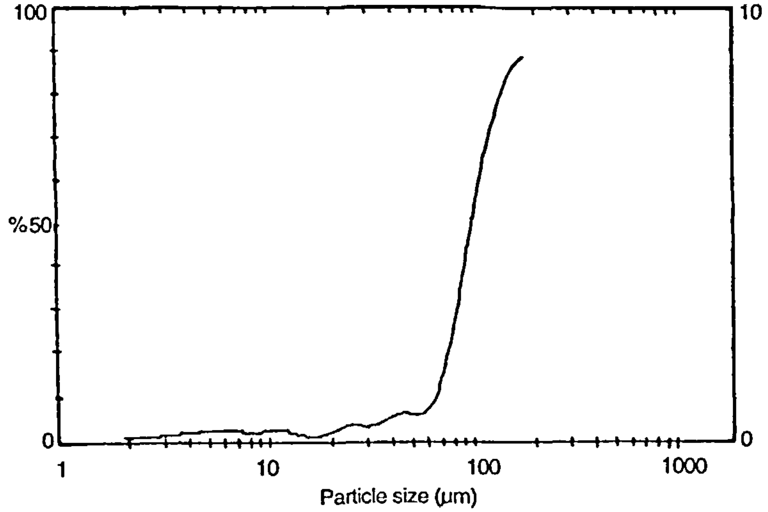

FIG. 1 Particle size analysis of raw perlite.

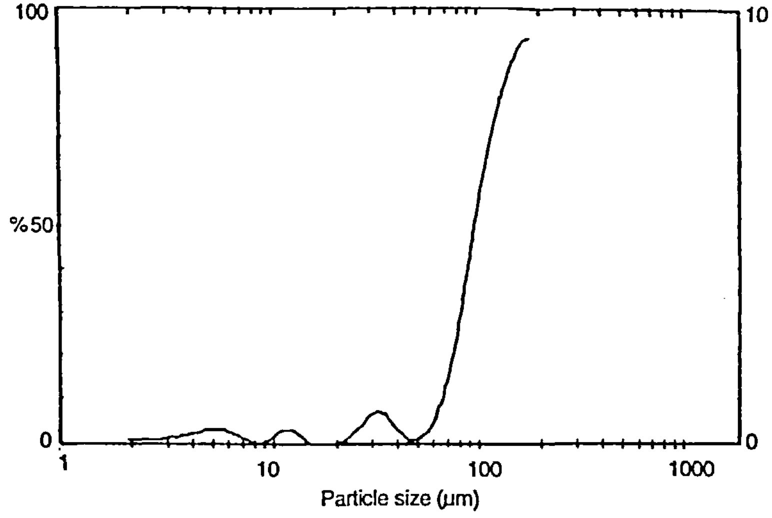

FIG. 2 Particle size analysis of standardized perlite.

D[v,0.5]: This is the volume median diameter. It is not to be confused with the diameter, D[4,3]. 50% of the distribution is above and 50% is below this value. It divides the distribution exactly in half.

From Table 2, the average particle diameters for raw perlite and standardized perlite were 121.69 and 124.70 μm, respectively.

Determination of Specific Surface Area

The specific surface area measurement of raw perlite and standardized perlite was carried out using a Quantocrome B.E.T combined with a computer. The reproducibility of the specific surface area values is ±5%.

Determination of Mean Surface Hydroxyl Group Density

The method applied by Chertov et al. (11) for determination of the surface hydroxyl group density, $\alpha_{OH(s)}$, which is based on ion exchange of hydrogen on the surface for Ca^{2+} from $Ca(OH)_2$ solution, was used. The $\alpha_{OH(s)}$ data are presented in Table 3.

Preparation of TBP-Loaded Silanized Perlite

Loading of TBP (tributyl phosphate) was carried out by soaking the quantitatively weighed perlite in solutions of the appropriate concentration of TBP in acetone with occasional vigorous shaking for 2.5 hours to complete saturation of the perlite with the reagent. The acetone was removed using a vacuum evaporator. The amount of TBP loaded on standardized perlite was determined gravimetrically.

Apparatus

Glass columns of 8 and 4 mm internal diameter and 30 cm long were used. A separating funnel was fitted at the top of the column as a reservoir for the

TABLE 3
The Mean Surface OH Group Density for Perlite

Type of perlite (particle size: 75–150 μm)	Mean surface hydroxyl group density [$\alpha_{OH(s)}$], μmol/m^2
Raw perlite	1.05
Standardized perlite	3.20
Silanized perlite	1.80
Silicagel (22)	4.00

eluting solution. An empty glass column containing a glass-wool plug and a sealed plastic sleve on its tip was clamped vertically. HNO_3 (0.1 M), and the support were introduced into the column and packed in the column by gentle pressure with a glass rod. The air bubbles were removed using a vibrator. The flow rate was adjusted to 0.5 mL/min by use of a peristaltic pump.

The column prepared in this manner was used to study some essential separation parameters for UO_2^{2+} and Fe^{3+}.

Determination of the Percent Extraction (%*E*) and the Distribution Ratio of Uranium (D_u)

The percent uptake (%E) of uranium(VI) by the TBP-loaded perlite was calculated from the following equation:

$$\%E = [(C_b - C_a)/C_b] \times 100$$

where C_b and C_a are the concentrations of metal ion in the bulk solution and after extraction, respectively.

The distribution ratio of uranium(VI) could be determined from the following equation:

$$D_u = \frac{\%E \text{ by the mmoles of TBP loaded on 1 g dry perlite}}{(100 - \%E)/\text{volume of aqueous phase}}$$

Plate Height and Distribution Coefficient Measurements

The number of free column volumes to peak maximum k' (or the capacity factor) was calculated from the position of the peak maximum using the following equation:

$$k' = (V_{max} - v_m)/v_m$$

where V_{max} is the eluate volume to peak maximum and v_m is the retention volume or mobile phase volume (column void volume). The void volume was measured using a methyl red indicator solution (3).

The distribution coefficient K_d was calculated from k' or v_m by means of the following equations:

$$K_d = k'(v_m/v_s)$$

$$V_{max} = v_m + K_d v_s$$

where k' and v_m are the same as defined above, and v_s is the volume of the stationary phase. Distribution coefficients measured under the same experimental conditions but with two different columns were reproducible within ±5% when $k' > 1$.

TABLE 4
Chemical Composition (in %) of the Solid Packings Used for RPC

Packing	Heat loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	$K_2O + Na_2O$
Chromosorb W (16)	0.3	88.9	4.00	1.60	0.20	0.20	0.60	0.60	3.60
Volcanic slag (16)	3.9	61.0	15.98	2.60	0.65	0.92	6.20	3.30	6.20
Treated volcanic slag (16)	2.8	96.5	0.10	—	—	—	Trace	Trace	0.30
Perlite (USSR) (16)	5.6	73.7	12.88	1.72	—	—	1.40	1.45	4.58
Perlsorb-I (16)	2.4	94.2	0.09	0.38	—	—	0.36	—	2.54
Etibank raw perlite	5.0	73.3	12.23	1.14	—	—	0.56	0.09	7.52
Our packing	3.4	87.3	2.75	0.53	—	—	0.30	0.04	5.25

The height equivalent to a theoretical plate H or HETP was calculated from the following equation:

$$N = L/H = 8V_{\max}^2/w^2 = V_{\max}^2/\sigma^2$$

where N is the number of plates, $V_{\max}$ is the same as defined above, w is the width of the peak at $1/e$ times the maximum solute concentration, σ is the standard deviation of the elution curve, and L is the length of the column bed.

RESULTS AND DISCUSSIONS

The chemical composition of perlite appears to be quite similar to glass. The data in Table 1 show standardized perlite was highly enriched in silica, but alumina and iron(III) oxides were appreciably diminished. The catalytically active oxides were reduced to minimum values. The data in Tables 4 and 5 show that certain characteristics of chromatographic packings made from rocks were superior to those of diatomite origin.

TABLE 5
The Specific Surfaces and Mechanical Strength for Different RPC Packings

Packings	Specific surface (m^2/g)	Mechanical strength (kg/cm^2)
Chromosorb W (16)	1.0	53.4
Tsvetochrom 1K (16)	2–3.5	61.6
Volcanic slag treatment (16)	1.2	60.8
Perlsorb 1 (16)	1.1	61.8
Expanded perlite of Etibank	—	24.8
Our packing	9.2	60.5

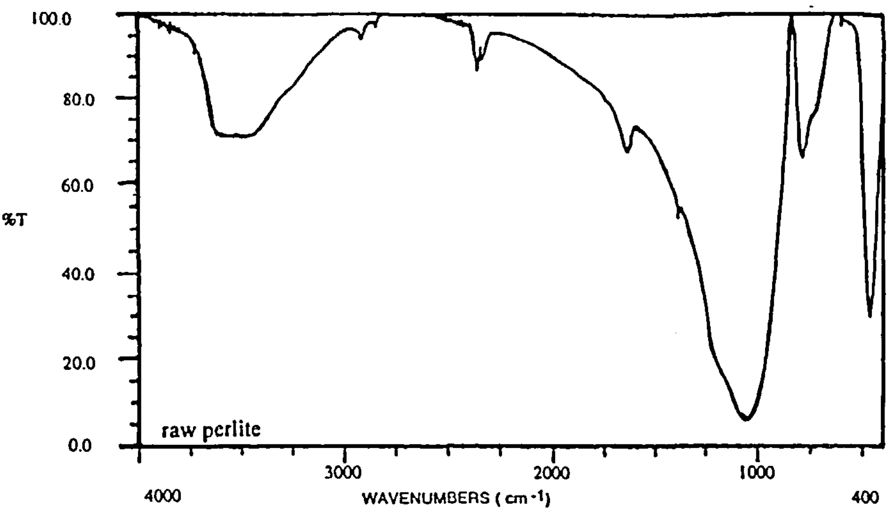

FIG. 3 IR spectra (Mattson 1000 FT-IR Spectrometer) of raw perlite.

The packings based on perlite had greater mechanical strength than Chromosorb W. The perlite prepared had a large specific surface area which allows good column efficiency to be obtained.

Studies on separation effectiveness, flow rate, column permeability, death volume, column capacity, etc. showed that the most suitable particle size fraction of perlite was between 75 and 150 μm.

The mean surface hydroxyl group densities given in Table 3 show that all kinds of perlite had lower $\alpha_{OH(s)}$ values than silica gel. However, increasing the $\alpha_{OH(s)}$ from raw perlite to standardized or silanized perlite was favorable for fixing the chelating agent.

Another parameter for studying the adsorbents used in RPC is the hydroxyl group density which gives knowledge about the adsorbent polarity. The IR spectra of standardized perlite showed that there were great differences in the intensities of transmittance of raw perlite and standardized perlite between 3750 and 3000 cm^{-1}. These differences were attributed to the vibration of hydrogen-bonded hydroxyl groups at the surface (10). In addition, a 10% aqueous suspension of raw perlite has a pH between 7.5 and 8.0. However, a 10% aqueous suspension of standardized perlite has a pH value about 5.0. These results show that standardized perlite has many more hydroxyl groups than raw perlite. The bands at 1250–1300 cm^{-1} are certainly due to P═O vibration, whereas those at 1700–1800 cm^{-1} belong to ester vibration, and those at 2400–2500 cm^{-1} are due to P—H vibration (Figs. 3–5).

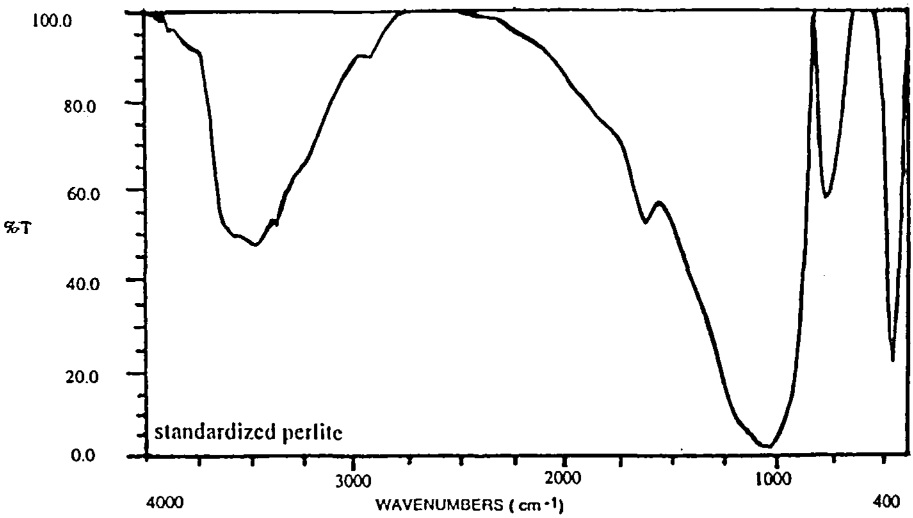

FIG. 4 IR spectra (Mattson 1000 FT-IR Spectrometer) of standardized perlite.

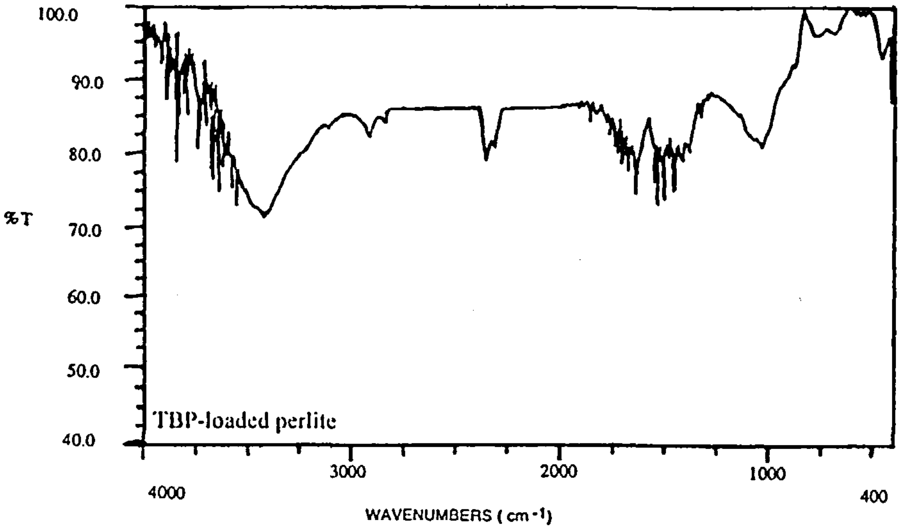

FIG. 5 IR spectra (Mattson 1000 FT-IR Spectrometer) of TBP-loaded perlite.

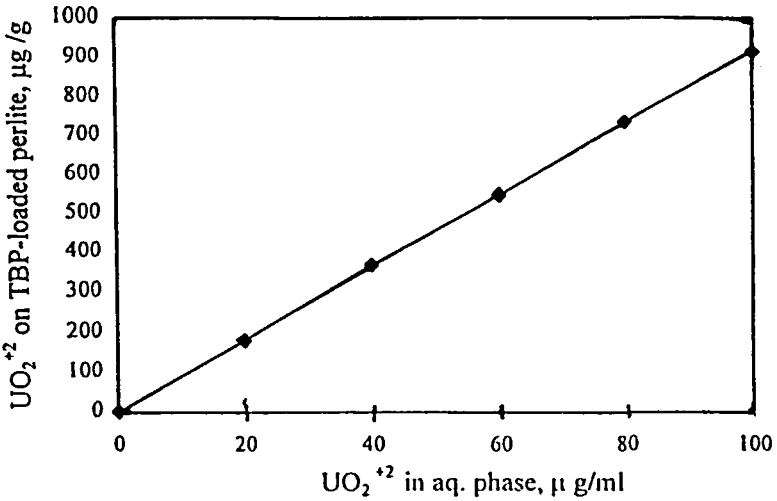

FIG. 6 Isotherm for the adorption of the UO_2^{2+} on TBP-loaded perlite.

The fractions of adsorption of different sorbates on solid packings prepared from volcanic slags and perlites were compared. The TBP adsorption fractions were the same or in some cases less than those of the highly commercialized support Chromosorb W (4, 12).

The uptake of the UO_2^{2+} and Fe^{3+} by loaded perlite was found to depend on their concentrations in the aqueous phase. Thus, in separate experiments, UO_2^{2+} and Fe^{3+} in different concentrations were shaken with loaded perlite. It can be seen from Fig. 6 that the uptake of UO_2^{2+} by TBP-loaded perlite was fast. Analyses of the aqueous phase for UO_2^{2+} and Fe^{3+} gave the curve in Fig. 7. The curves were approximately symmetrical with a relatively sharp peak. The elution curves for UO_2^{2+} and Fe^{3+} were satisfactorily separated, and the purity of UO_2^{2+} was approximately 96%.

Table 6 shows the effect of TBP loading on the height equivalent to a theoretical plate H or HETP at 25°C. The HETP was found to be 2.0 mm. This value was reproducible within ±5%. The particle size of the support was held constant at 100 μm. The capacity factors and distribution coefficients for Fe^{3+} and UO_2^{2+} were 0.36–0.30 and 1.96–1.63, respectively. The increase in HETP with a increase in TBP loading was expected. However, the magnitude of the effect was much smaller than that given by other authors (12–14).

It can be seen from Table 6 that a pronounced augmentation in column behavior did not occur until 10 w/w was exceeded. The high values of HETP, even for a 10-w/w TBP loading, indicate a rather large pore capacity for the

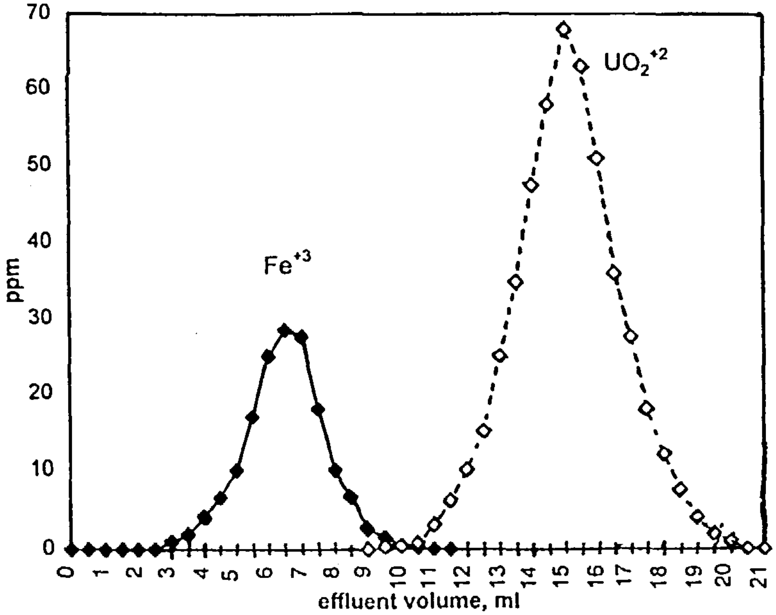

FIG. 7 Chromatogram of the UO_2^{2+} and Fe^{3+} on TBP-loaded perlite.

perlite support. Since the efficiency of extraction chromatographic column is influenced to some extent by the thickness of the stationary liquid film on or in the support, the data in Table 6 indicate that stationary phase diffusion is not a major contributor to band spreading in the 10–17-w/w range.

The data in Table 7 show a slight change in HETP with increasing column internal diameter. The flow rate, temperature, and capacity factor were held constant. If transcolumn effects were important, one would expect an effective increase in plate height with increasing internal diameter (15).

TABLE 6
The Effect of TBP Loading on the HETP

mmol TBP/g perlite	w/w TBP	HETP (mm)
0.12	3.1	1.3
0.53	12.3	1.8
0.62	14.2	1.9
0.76	16.8	2.0

TABLE 7
The Effect of Column Diameter on the HETP

i.d. (mm)	A (cm^2)[a]	w/w TBP	HETP (mm ± 8%)	K_d (±5%)
8.0	0.50	16.8	2.0	1.63
4.0	0.13	16.8	1.8	1.55

[a] A = cross section of column.

The practical usefulness of a column packed with TBP-loaded perlite can be tested by measuring its breakthrough capacity. Obviously, a column with a high breakthrough capacity will be used in many applications. Breakthrough capacity was defined as the amount of UO_2^{2+} or Fe^{3+} that could be retained on the column when they were allowed to pass through it at a rate of 0.5 mL/min until UO_2^{2+} or Fe^{3+} were first detected in the effluent solution. After reaching the breakthrough volume, elution was continued and the breakthrough capacities were 4.6 mg UO_2^{2+}/g-support and 1.4 mg Fe^{3+}/g-support.

Perlite is an abundant, cheap, and easily standardized material. The experimental results were compared with packings used by other authors, and it was concluded that the TBP-loaded perlite column shows approximately the same selectivity and rapidity (16–21).

CONCLUSION

The aim of this work was to prepare a perlite-based chromatographic packing having certain advantages compared with those of diatomite origin. The packings were compared as to minimum content of catalytically active oxides of the type M_2O_3, low adsorptive activity, high mechanical strength, high surface hydroxyl group density, and high specific surface area.

Nondiatomite originated alumina silicate systems were selected as the base material. The results are in good agreement with literature data and the effectiveness parameters for UO_2^{2+} distribution on a reversed-phase column loaded with the perlite–TBP system.

The TBP–perlite columns prepared by first allowing the column material to be wetted by the aqueous phase to form a slurry, followed by the application of pressure to form the bed, gave more uniform bed compaction and vastly improved column behavior.

The use of TBP-loaded perlite as a reversed-phase chromatographic solid support therefore appears to be useful for the separation of uranium from iron, especially in light of the fact that 25 cycles of elution experiments were carried out without a loss of efficiency.

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