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Retention of radium from thermal waters on sand filters and adsorbents

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Abstract

This study was focussed on laboratory experiences of retention of radium from one thermal water on sand filters and adsorbents, trying to find an easy method for the elimination in drinkable waters polluted with this natural radio-nuclide. A thermal water from Cantabria (Spain) was selected for this work.

Retention experiences were made with columns of 35 mm of diameter containing 15 cm layers of washed river sand or 4 cm layers of zeolite A3, passing known volumes of thermal water at flows between 4 and 40 ml/min with control of the retained radium by determining the amount in the water after the treatment. The statistical analysis of data suggests that retention depends on the flow and the volume passed through the columns.

As additional adsorbents were used kaolin and a clay rich in illite. Jar-test experiences were made agitating known weights of adsorbents with the selected thermal water, with addition of flocculants and determination of radium in filtrated water after the treatment. Data suggest that retention is related to the weight of adsorbent used, but important quantities of radium seem remain in solution for higher amounts of adsorbents, according to the statistical treatment of data.

The elution of retained radium from columns or adsorbents, previously used in experiences, should be the aim of a future research.

Keywords: Retention of radium; Thermal waters; River sand; Adsorbents; Zeolite A3; Kaolin; Clay rich illite

1. Introduction

As a continuation of our research on retention of radioactive pollutants [1] in an attempt to find an easy method for their elimination in a drinking water treatment station [2], this work was focussed on the retention of radium by sand and adsorbents with the objective of its elimination from rivers naturally contaminated, susceptible to be used for drinkable water, or waters from radioactive springs, mainly thermal waters [3], to avoid contamination of rivers.

2. Methods

2.1. Thermal water selected

For this research thermal water from La Hermida (Cantabria, Spain). The main characteristics are as follows: temperature *in situ* 47.5 °C; dissolved oxygen 2.3 mg/l; 40% saturation; pH 5.68.

2.2. Substances used for retention experiences

- *River sand* from Arenas de Arija S.A. (Arija, Burgos, Spain) was used for retention experiences. The main characteristics, determined by us [1], were as follows:
  - Size analysis:

mm	%
>3.2	0
3.2–2.0	1.40
2.0–1.6	19.65
1.6–1.25	55.00
1.25–1.00	13.50
1.00–0.80	3.10
<0.80%	7.35

  - Arithmetical mean size: 1.38 mm.
  - Composition (by electronic microscope, data in atomic %): sand is mostly constituted by white particles (O 77.08; Al

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1.02; Si 21.66; K 0.25) with a few beige (O 75.78; Al 1.25; Si 22.84; Fe 0.13) and grey particles (O 63.62; Al 11.75; Si 24.64).
  - Real density: 2.60 g/ml. Apparent density: 1.43 g/ml. Porosity 45.07%.
  - Loss of weight at 110 °C 0.24%.
  - Resistance to acid: 0.15% of loss; CO_2 emission was not detected.
  - Cationic exchange capacity 3.12 mequiv./100 g.
- *Zeolite 3A* Molecular Sieve UOP Type 3A (Fluka) beads with diameter ∼2 mm, pore diameter 3 Å.
- *Kaolin* (Fluka).
- *Clay rich in illite*, with a content in illite close to 40%, according to data supplied by Instituto Geológico Minero (Spain).

2.3. Experiences of retention by sand river and zeolite 3A

These retention experiences were carried out with columns containing 200 g of sand or 25 g of zeolite, previously tried with distilled water overnight, passing three portions of 500 ml of the selected thermal water at three different flows (4, 10 and 20 ml/min). Each portion was evaporated very carefully to a volume close to 3 ml, passed to a Sterilin Petri disk (55 mm diameter and 12 mm high) containing activated charcoal, sealed tightly and stored until the moment of the measurement.

2.4. Retention by other adsorbents

Jar-test experiences with kaolin and clay rich in illite were carried out agitating for 10 min, 0.025, 0.050 or 0.100 g of adsorbents with 500 ml of the selected thermal water, with addition as flocculants of:

- one milliliter of solution with 0.5 g/l of Prosedim ASP 34 (an anionic flocculant of Degremont),
- two milliliters of solution with 15 g/l of ferric sulphate $9H_2O$ and
- three milliliters of solution with 6 g/l of $Ca(OH)_2$.

The determination of radium was made after filtration, careful evaporation, pass to a Petri disk containing activated charcoal, seal and store.

2.5. Measurements of Ra-226

As Ra-226 emits gamma rays at 186.21 keV with a very low photon emission probability (3.59%), measurements were performed [4,5] through Pb-214, its decay daughter, which results in a more exact activity calculation because the gamma ray emission of 351.93 keV from Pb-214 has a higher photon emission probability (37.6%). To achieve secular equilibrium between those two radio-nuclides 25 days from the sealing of the Petri disk must be waited. Radon retention in the decay chain is guaranteed with the use of activated charcoal. Measurements were made in a high-purity Ge detection spectrometer (XtRa from Canberra with 90% relative efficiency) with a calibration standard prepared from the reference solution QCY48 from ISOTRAK.

3. Discussion and conclusions

3.1. Retention of radium by river sand and zeolite A3

The accumulated retentions of radium by sand river and zeolite A3, shown in Figs. 1 and 2, increase with the volume of thermal water used in experiences and decrease with the flow of pass through the column.

Data could be adjusted [6] to the non-linear expression:

$$\text{accumulated retained Ra} = \frac{a \times \text{volume}}{1 + b \times \text{flow}}$$

with the following values for coefficients and significance:

	a	b	R^2
Sand river	0.000975	0.1855	0.8901
Zeolite A3	0.00150	0.0182	0.9991

The retention of radium by zeolite A3 is more important than the retention by sand river and less decreased by an increase of flow. The concordance between calculated and experimental values are shown in Figs. 3 and 4.

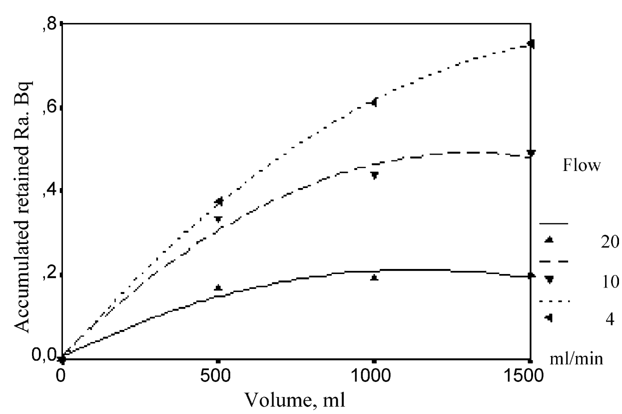

Fig. 1. Accumulated retention of radium by sand river.

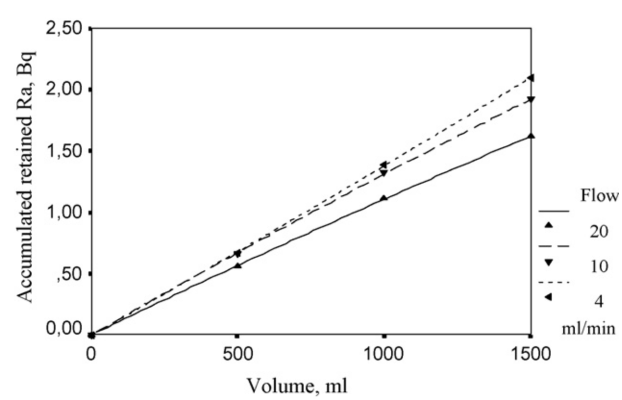

Fig. 2. Accumulated retention of radium by zeolite A3.

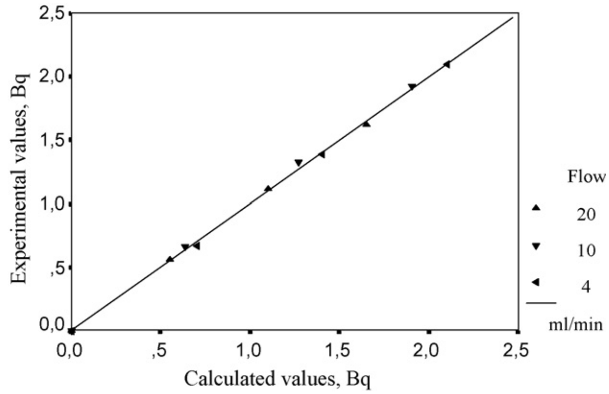

Fig. 3. Retention of radium by zeolite A3.

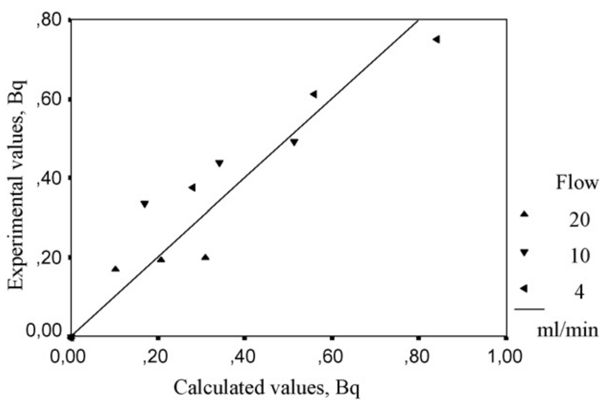

Fig. 4. Retention of radium by sand river.

The mean percent of retained radium as a function of volume, passed through the columns, is shown in Fig. 5. The retention by zeolite A3 is almost constant and more important than the retention by sand river, which decreases noticeably when the volume increases.

3.2. Retention of radium by other adsorbents

The amounts of radium retained by kaolin and the used clay rich in illite are shown graphically in Fig. 6.

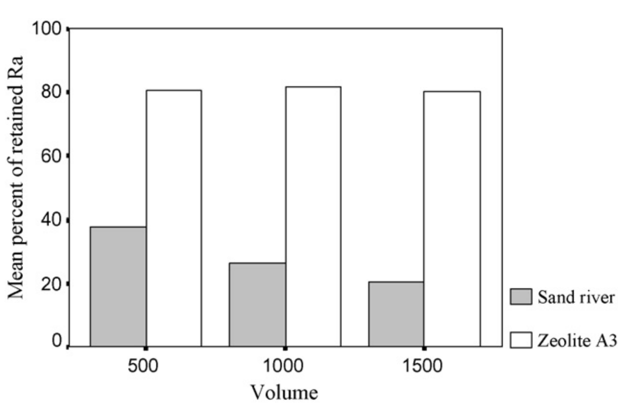

Fig. 5. Mean percent of retained radium vs. volume.

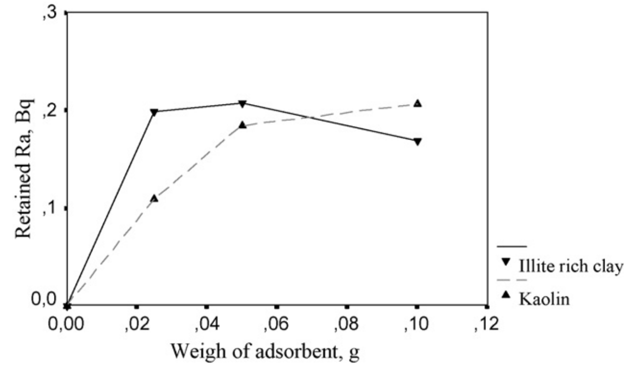

Fig. 6. Retention of radium vs. weight of adsorbents.

Data of retention of radium were statistically adjusted [6] to the non-linear expression:

$$\text{Ra retained} = \frac{a + b \times \text{weigh of adsorbent}}{c + d \times \text{weigh of adsorbent}}$$

The results of calculation were as follows:

	a	b	c	d	R^2
Kaolin	−3.66	29110	3503	101600	0.9882
Clay rich in illite	−0.0273	36.11	2.01	153.80	0.8552

The concordance between experimental and calculated values is shown in Fig. 7.

The observation of Fig. 6 and the form of the non-linear expression suggest that the amounts of retained Ra tend to constant values for great weights of adsorbents. These values can be calculated as the quotients b/d, respectively, 0.2865 and 0.2348 Bq. Having into account that experiences were made with 500 ml of thermal water, containing 0.7797 Bq, the maximum percentages of retained Ra with these adsorbents would be 36.74 and 30.11%.

The mean percentages of retained radium are shown in Fig. 8 as a function of the weight of adsorbents. The retentions by both are small.

3.3. Theoretical considerations

The retention of studied pollutant on the tried adsorbents may be due to the size of the cavities where pollutant is trapped

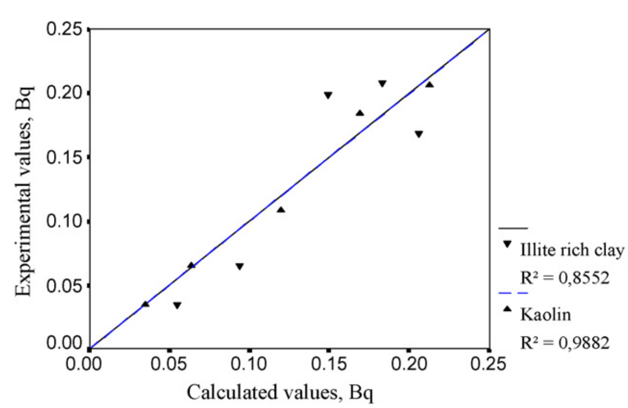

Fig. 7. Retention of radium by other adsorbents.

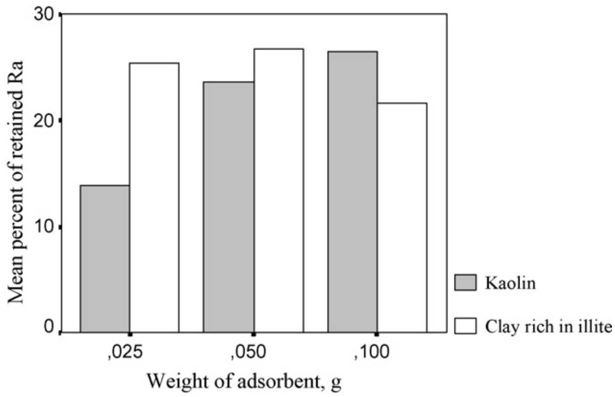

Fig. 8. Mean percent of retained radium vs. weight of adsorbent.

(this must be the case of zeolite A3), to the absorption on the surface or to the formation of insoluble compounds (rest of tried adsorbents).

Zeolite A3 has the best retention, though its practical use is conditioned to the possibility of its recuperation by elution of the retained radium. This will be the aim of a future research.

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