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Removal naturally occurring radionuclides from drinking water using a filter specifically designed for Drinking Water Treatment Plants



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HIGHLIGHTS

• Filter system (green + silica sand) especially designed to remove radium was characterized.

- \bullet Mn in green sand was homogenously distributed (FE-SEM and $\mu\text{-PIXE}).$
- Ra adsorption kinetics adsorb 99% from raw water.
- Radium removal efficiency remained unchanged after passing a large water volume.
- It can also remove partially the uranium content.

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ABSTRACT

The occurrence of naturally occurring radionuclides in drinking water can pose health hazards in some populations, especially taking into account that routine procedures in Drinking Water Treatment Plants (DWTPs) are normally unable to remove them efficiently from drinking water. In fact, these procedures are practically transparent to them, and in particular to radium. In this paper, the characterization and capabilities of a patented filter designed to remove radium from drinking water with high efficiency is described. This filter is based on a sandwich structure of silica and green sand, with a natural high content manganese oxide. Both sands are authorized by Spanish authorities to be used in Drinking Water Treatment Plants. The Mn distribution in the green sand was found to be homogenous, thus providing a great number of adsorption sites for radium. Kinetic studies showed that the ²²⁶Ra adsorption on green sand was influenced by the content of major cations solved in the treated water, but the saturation level, about 96–99%, was not affected by it. The physico-chemical parameters of the treated water were unaltered by the filter. The efficiency of the filter for the removal of ²²⁶Ra remained unchanged with large water volumes passed through it, proving its potential use in DWTP. This filter was also able to remove initially the uranium content due to the presence of Fe₂O₃ particles in it, although it is saturated faster than radium.

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1. Introduction

The content of naturally occurring radionuclides may become an increasingly serious problem for drinking water supplies, due to the growing demand for new water resources (IAEA, 2003). Unless the corresponding water treatment systems are appropriately designed, a significant part of this radioactive content can

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.148 0045-6535/© 2016 Elsevier Ltd. All rights reserved. eventually be incorporated into the population, with the consequent risk to health. In areas unaffected by radioactive contamination events, such as those of Chernobyl or Fukushima, naturally occurring radionuclides are the main contributors to the Total Indicative Dose (TID) for the consumption of drinking water. Their occurrence can be high, mainly caused by the geological environment surrounding the water source (Otton, 1994; Baeza et al., 1995). As the routine procedures in Drinking Water Treatment Plants (DWTPs) have practically no effect on the removal of uranium and radium from drinking water (Baeza et al., 2012), they are ingested by the population as they drink. Anthropogenic causes, such as the



age and maintenance of pipelines in public water supplies, can also affect the radium content in drinking water, implying a health hazard to population (Fisher et al., 2000). The chemical toxicity of soluble uranium compounds in drinking water can surpass its potential low radiotoxic effects. The exposure to ingested uranium includes changes to bone structure and nephritis (Kurttio et al., 2002, 2005; Ansoborlo et al., 2015). Information on radium content in drinking water is particularly important as radium has a similar metabolic behavior as calcium in the body. An appreciable fraction of the radium acquired through drinking water is present in bones, where it contributes to the internal dose for all population (UNSCEAR, 1982; Tyler et al., 2013).

The use of specific substances for removing uranium and radium in water has often been studied from different approaches. A number of chemical methods were developed by adding substances to raw water in order to produce precipitation or coprecipitation of radionuclides. Such methods work very well for removing uranium (Baeza et al., 2012), but for the radium require very aggressive conditions in practice difficult to apply (Valentine et al., 1985; Baeza et al., 2008). Other methods are based on the use of specific materials, such as resins and adsorbents which produce a large adsorption. Examples of these substances would be the MnO₂-Coated Acrylic Fiber Filters (Moore, 1978), Radium Selective Complexer (DOW, 1986), BaSO₄-impregnated alumina (Clifford et al., 1988) and silica sand (Valentine et al., 1985). Silica sand is a material used as a filter bed to retain small solids that are in the water. It is usually employed as a filter bed in water treatment plants. Its ability to adsorb radium depends on working conditions and has many limitations. All methods above described require treatment of the adsorbent material for removal of radium, and in some cases the associated cost is high. Greensand is a natural manganese dioxide, commonly employed in removing iron and manganese from water through a filtration process, and capable to remove radium (Qureshi and Nelson, 2003). Soluble iron and manganese are oxidized and precipitated by contact with major oxides of manganese in greensand granules.

In this paper, the characterization of a patented filtration system for the removal of radium in water for human consumption is presented (patent publication number ES2564566A1). This system uses two types of natural substances, silica sand and greensand, which are permitted for use in drinking water. Thus, the elemental composition of the green sand was mapped using qualitative FE-SEM (Field Emission Scanning Microscopy) and quantitative μ -PIXE (Micro Particle Induced X-ray Emission). The radium adsorption was analysed by means of different experiments focused on: a) studying its kinetics on green sand; b) the variables affecting its adsorption in silica sand. Finally, experiences aimed to determine its use for treatment of large water volumes were also carried out.

2. Material and methods

2.1. Design and characterization of the filter

The filter was designed using adsorbing materials authorized by the Spanish Health Ministry to be used in water purification processes (BOE, 2003; BOE, 2009). It consists in a mixture of silica and green sand in a sandwich structure (1-4-2), as shown in Fig. 1. The green sand has a high Mn content, thus providing adsorption sites for radionuclides, especially for radium. The difference of this filter with other existing in the market are: i) it is radium specific, ii) its components are already approved by Spanish legislation to be used in DWTP, while some other resins are not authorized, iii) it is based in a sandwich structure, while other filters use only one component. The silica sand in the filter has a double utility. It holds the green sand and provides an extra filter bed in order to prevent



Fig. 1. Schematic diagram of the filter, with three layers: silica sand, green sand, and silica sand in 1-4-2 proportion.

drinking water from taking any colour and avoiding obstructions.

The elemental composition of the green sand was analysed in detail by a qualitative analysis by FE-SEM, using 30 keV electron beam. Nevertheless, quantitative µ-PIXE analysis was also performed. For the preparation of the samples, about 0.2 g of sample pressed into pellets of 11 mm of diameter on a boric acid substrate about 0.4 g using a pneumatic press (10 Ton). The measurements were performed at the Centro Nacional de Aceleradores micro-PIXE facility (García-López et al., 2000). A proton beam of 3.0 MeV energy, a current of 100 pA, and a spot size of $4 \times 4 \,\mu m^2$ was produced normal to the sample. A Si(Li) detector (area 80 mm², resolution 145 eV) was mounted at 135° for X-ray detection. For all measurements, a 50 µm thick Mylar filter was used between the sample and the Si(Li) detector improve the sensitivity of trace elements. Proton backscattered spectra (BS) were collected simultaneously with a surface barrier detector of an active area of 300 mm² at an angle of 37° to the beam. Samples were sprayed with low-energy electrons originated from a hot tungsten filament in order to avoid sample charging during the analysis. All signals produced during the proton beam irradiation were recorded together with the beam position using the OM_DAQ data acquisition system (Grime and Dawson, 1995). Elemental maps up from $25 \times 25 \,\mu\text{m}^2$ to $150 \times 150 \,\mu\text{m}^2$ were generated using the scanning mode in order to determine element distribution and to select the most convenient areas of analysis. Quantification was performed with the GUPIX-WIN V2.1 software package (Campbell et al., 2010).

2.2. Design of laboratory experiences

The efficiency of the filter to remove naturally occurring radionuclides, mainly uranium and radium, was tested in laboratory controlled conditions, by passing a known quantity volume of water, whose radium content was known, through the filter. Two different kinds of water with different physico-chemical parameters were used: distilled water and groundwater which is used as raw water in an operational DWTP. The ²²⁶Ra content in groundwater is about the same order of magnitude that tap water collected in areas of Iowa, USA (Fisher et al., 2000). These types of water were selected in order to analyse the influence of the concentation of major ions present in groundwater on the radionuclide adsorption by the filter, as the radionuclide content in water is usually at trace level (ppq for Ra). The use of the selected groundwater also provides information about the results to be expected in the actual use of the present filter in DWTPs.

The removal efficiency, R, was determined by the following equation:

$$R(\%) = \frac{\left|A_f - A_0\right|}{A_0} * 100 \tag{1}$$

where A_0 is the initial radionuclide content in the raw water before passing through the filter; and A_f is the final radionuclide content after passing through the filter. Both contents were expressed in Bq/L.

2.3. Radionuclide determination

To determine the uranium content, 232 U was first added as tracer to the water samples. Then uranium content was coprecipitated with Fe(OH)₃. The precipitate was re-dissolved in HCl 9 M, followed by separation in a column with Dowex 1 × 4 resin. Uranium was retained in the column, and subsequently eluted with HNO₃ 8 M. Finally, alpha sources were prepared by co-precipitation with NdF₃ (Sill, 1987). Radium content in the water was absorbed in MnO₂ precipitate, with ¹³³Ba as tracer. Then the precipitate was dissolved in HNO₃ 5 M, and uranium and thorium present in the samples were extracted with TBP (tributyl phosphate). Lastly, radium was co-precipitated as Ba(Ra)SO₄ (Baeza et al., 1998). Recovery was determined by γ -spectrometry of ¹³³Ba (302.85 and 356.01 keV) of the corresponding sources, using a germanium Ntype detector with a 25% relative efficiency, a 1.87 keV resolution for the 1332 keV ⁶⁰Co peak, and a peak-to-Compton ratio of 57.5:1.

Alpha spectrometries of uranium and radium samples were carried out using twelve different silicon detectors with a mean efficiency of 23.2% and a resolution of 38.7 keV for a source-detector distance of 6 mm. Activity levels were determined in mBq/L, but are easily converted to concentration units in μ g/L using the following factors: ²³⁸U (8.03 · 10¹); ²³⁴U (4.34 · 10⁻³) and ²²⁶Ra (2.73 · 10⁻⁵). Associated uncertainties were estimated using the 2 σ criterion.

The overall quality control of these radiochemical procedures was guaranteed by the accreditation of the laboratory to carry out radioactivity assays in environmental samples according to UNE-EN ISO/IEC 17025 (ISO, 2005). Different reference materials were also used to check the quality of the measurements: IAEA-381 for uranium and IAEA Soil 6 for radium and γ -spectrometry.

3. Results and discussion

3.1. Characterization of the filter components

The distribution of Mn, Si, and Fe elements within the green sand was mapped using qualitative FE-SEM micrographs, in which the elemental presence was identified by its K α lines, as shown in Fig. 2. The homogeneous Mn distribution is observed on the sample, although some aggregations of Si and Fe are also existing, due to the presence of SiO₂ and Fe₂O₃ grains. Table 1 shows the mineral and elemental composition of the green sand specified in the corresponding technical data sheet. It can be observed that this green sand is composed mainly of MnO₂, about 78%, with some quantities



Fig. 2. Scanning electron micrograph of green sand in false colour showing a) the main components of green sand; b) Si in blue; c) Mn in pink; and d) Fe in yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Mineral composition of the green sand used in the filter taken from the technical data sheet of the green sand, expressed as wt%, and its derived elemental composition and those of three samples analysed by PIXE technique, expressed as wt%. n.d. = not determined.

Green sand technical data				Green sand PIXE analysis			
Mineral	wt%	Element	wt%	Element	Sample 1 wt%	Sample 2 wt%	Sample 3 wt%
MnO ₂	78	Mn	49.3	Mn	54.26 ± 0.08	49.86 ± 0.11	54.30 ± 0.04
Fe ₂ O ₃	6.2	Fe	4.3	Fe	3.33 ± 0.13	6.12 ± 0.14	2.04 ± 0.11
SiO ₂	5.2	Si	2.4	Si	4.5 ± 0.7	7.1 ± 0.9	2.6 ± 0.4
Al_2O_3	3.1	Al	1.6	Al	n.d.	n.d	n.d.
				K	0.515 ± 0.013	1.558 ± 0.024	1.592 ± 0.011
				Ti	0.171 ± 0.009	0.182 ± 0.013	0.132 ± 0.007
				Cu	0.063 ± 0.007	0.058 ± 0.010	0.090 ± 0.005
				Zn	0.749 ± 0.008	0.200 ± 0.020	0.117 ± 0.005

of other minerals, less than 10%, Fe₂O₃, SiO₂, and Al₂O₃. The elemental composition of the technical data sheet was confirmed by the quantitative PIXE analysis of three green sand samples, whose results are also included in Table 1. For the PIXE analysis, elemental maps were produced with the proton microprobe in order to check their homogeneity and areas between 100×100 and $150 \times 150 \ \mu\text{m}^2$ size were selected for the spectrum acquisition. In the PIXE analysis, Al is non-detected and the Si concentrations differ significantly from the technical datum, due to use of the Mylar filter during the analysis, which improved the sensitivity for trace elements but attenuated signals from light elements. In the maps, local Ti accumulations were also identified due to the presence of TiO₂ grains in the green sand as it has been observed.

3.2. Kinetic studies on the radium adsorption

The analysis of the kinetics on the radium adsorption by the green sand was carried out with the two selected types of water. The first one was distilled water with pH 5.8, conductivity 2 μ S/cm and dry residue 4 mg/L. It was spiked with ²²⁶Ra, so that its final content was 0.10 Bq/L. The addition of 226 Ra did not change the chemical speciation of radium in solution, since it is mainly as Ra^{2+} in water at the selected pH (Salas et al., 2014). The selected groundwater was used as input water by a working DWTP. Due to the extremely low mass radium concentration (2.7 and 12 ppq respectively) of these activity levels, any concentration dependence of the adsorption can be considered negligible. Table 2 lists the main physico-chemical content of the selected groundwater, which had a greater cation and anion content than distilled water. Solidliquid ratio (green sand-water) for the kinetic tests was kept constant at 1:1600 (g:mL) for both types of water, and after the reaction time it was filtered through a 0.45 μ m pore filter. Fig. 3 shows the ²²⁶Ra adsorption kinetics by green sand in terms of the removal efficiency, R, for distilled water and groundwater. To further understand the radium adsorption kinetics on the filter, experimental data were fitted to a dynamic model based on pseudo-second-order rate equation (see eq. (2)) used to describe the adsorption of divalent metal ions onto peat (Ho, 2006).

$$\frac{t}{R} = \frac{1}{k_{p2} \cdot R_e^2} + \frac{1}{R_e} t$$
(2)

where R is the removal efficiency, which is equivalent to the amount adsorbed by the filter; R_e is the removal efficiency at equilibrium; t is the elapsed time, expressed in min; and k_{p2} is the pseudo-second-order rate constant of adsorption, expressed in min⁻¹. Fitting parameters were calculated by linear regression and R_e and k_{p2} were calculated by plotting t/R against t, and were: a) for distilled water $R_e = (99.16 \pm 0.11)$, $k_{p2} = (0.012 \pm 0.005)$ min⁻¹, $R^2 = 0.999$; and b) for groundwater $R_e = (101 \pm 5)$,

 $k_{p2}=(0.00015\pm0.00007)\ min^{-1},\ R^2=0.988.$ Associated uncertainties were estimated by quadratic propagation from fitting results. The removal efficiency at equilibrium, R_e , was approximately the same for both types of water and very close to total adsorption. The effect of the ion content of the water was reflected in the interval of time elapsed, which was related to the pseudosecond order adsorption rate, k_{p2} . The higher content of ions in groundwater delayed the ^{226}Ra adsorption by the green sand. Therefore, k_{p2} value for groundwater was about two orders of magnitude lower than for distilled water. The delay effect of radium adsorption in waters with increasing water salinity has been reported previously for a MnO_2 resin (Moon et al., 2003). Therefore, the use of low flow and long column heights are recommended to increase the contact time.

3.3. Adsorption of naturally occurring radionuclides in silica sand

The filter is composed of green sand between two layers of silica sand. In order to analyse if silica sand contributes to the removal of radium, a column experiment filled with the same amount of silica sand than that of green sand used in the filter (300 g) and passed distilled water spiked with ²²⁶Ra (0.10 Bq/L) and groundwater with natural content of ²²⁶Ra and ^{234,238}U (see Table 2). Two different sets of experiences were carried out: in the first of them the pH of distilled and groundwater were adjusted to 6, and in the second the groundwater was passed through the silica sand column at pH 6

Table 2

Physico-chemical and radioactive composition of the groundwater used in the laboratory experiences to remove uranium and radium by the designed filter.

Radiological parameters of original groundwater used for tests								
Radionuclide		Activity	Content					
²²⁶ Ra ²³⁸ U ²³⁴ U		$\begin{array}{l} 0.44 \ \pm \ 0.08 \ \ Bq/L \\ 0.26 \ \pm \ 0.04 \ \ Bq/L \\ 1.30 \ \pm \ 0.17 \ \ Bq/L \end{array}$	12 ± 2 pg/L 21 ± 3 μg/L 5.6 ± 0.7 ng/L					
Physico-chemical parameters of ground water used for tests								
Parameter	Original groundwater	Treated groundwater after filter	Treated groundwater without filter					
σ at 20 °C pH at 25 °C Dry residue 100 °C HCO ₃ Cl ⁻ SO ₄ NO ₃ Al Ca K Fe Na	1082 μS/cm 7.8 744 mg/L 351 mg/L 172 mg/L 172 mg/L 114 mg/L <5 mg/L <50 μg/L 80 mg/L 1.8 mg/L <50 μg/L 54 mg/L	1076 μS/cm 7.8 743 mg/L 351 mg/L 172 mg/L 115 mg/L <5 mg/L <50 μg/L 73 mg/L 1.7 mg/L <50 μg/L 55 mg/L	1010 μS/cm 7.9 744 mg/L 345 mg/L 174 mg/L 121 mg/L <5 mg/L <50 μg/L 75 mg/L 1.6 mg/L <50 μg/L 50 mg/L					



Fig. 3. Analysis of the ^{226}Ra adsorption kinetics by green sand with two different types of water: a) distilled water with low content of cations and anions dissolved (dry residue 4 mg/L, $\sigma = 2$ µS/cm); and b) ground water with higher ion content (dry residue 475 mg/L, $\sigma = 741$ µS/cm).

and original pH. These pH values were selected because they are typical for working conditions in a DWTP, in which the filter is designed to be used. The effect of pH on removal of uranium and radium in groundwater was previously reported in Baeza et al. (2008). Fig. 4 shows the results uranium and radium adsorption by silica sand from these experiences. When distilled water passed through the silica sand column, it retained the ²²⁶Ra present in the water with high effectivity. However, when groundwater passed through it, the removal efficiency for ²²⁶Ra dropped after 3 L, being practically negligible thereafter. This different behavior can be explained due to the salt content of both types of water used (Moon et al., 2003). In the case of distilled water, with minimum salt content (dry residue 4 mg/L), adsorption sites in silica sand were able to adsorb the 226 Ra present at trace levels (ppq). However, when groundwater (dry residue 475 mg/L) passed through the column, these sites were completely occupied by ions of the major constituents, and therefore there are less sites available to be occupied by radium, which is at trace level (ppg). As groundwater also contained 234,238 U, it was observed that followed a similar pattern to that of radium. In the range of assayed pH values of the groundwater did not affect the removal efficiency of the silica sand, as the pH 6 and original (pH 7.8) gave similar results (see Fig. 4b and c).

3.4. Removal efficiency of radium and uranium by the designed filter

The efficiency of the filter (see Fig. 1) to remove the radium and uranium from input water in a DWTP was tested in laboratory conditions by passing up to about 1000 L of raw water through it and taking samples at different time intervals. The selected water was the groundwater used in the previous experiences (see Table 2). Fig. 5 shows the removal efficiency, R, for ²²⁶Ra and ^{234,238}U as the water volume passed through the filter increased. The removal of ²²⁶Ra was extremely high, in the range 96–99%, regardless of the volume that already had passed through the column. This reduction was caused by the adsorption of ²²⁶Ra by MnO₂ particles present in the green sand used. The fact that the column was able to remove significantly the ²²⁶Ra present in about 1000 L implies the presence of a high number of adsorption sites due to the high content of MnO₂ in the green sand composition.



Fig. 4. Adsorption of naturally occurring radionuclides by the silica sand used in the filter in: a) distilled water with added ²²⁶Ra at pH 6; and groundwater with a natural content of ²²⁶Ra and ^{234,238}U at pH 6 and 7.8.

However, the filter's removal efficiency for uranium is limited, showing a decreasing trend as the volume of water passed through the column increased. The adsorption of uranium from aqueous media may be related with the presence of iron and iron oxides



Fig. 5. Removal effectivity of the filter, expressed as percentage, for different volumes of groundwater with high content of naturally occurring ²²⁶Ra and ^{234,238}U.

(Noubactep et al., 2006). In previous research, the presence of iron oxides in coagulation-flocculation processes in water was found to benefit uranium removal. (Baeza et al., 2008, 2012). According to the technical data sheet, the green sand has about 6% of Fe₂O₃ in its composition, and therefore there may be some adsorption sites available for uranium in it. Thus, the initial reduction of the 234,238 U content in the water was probably due to its adsorption on those sites. Later, as they were saturated, uranium removal efficiency decreased significantly.

4. Conclusion

The presence of large quantities of naturally occurring radionuclides in drinking water, in particular radium and uranium, can pose a radiological hazard to the population. Different techniques and procedures have been proposed in the literature, with different degrees of successfulness and implementation in operating DWTPs. This paper presents the characterization of a patented filter designed to be used in these plants:

- This filter consists of a sandwich structure of green and silica sands, both of which are authorized by Spanish legislation to be used in DWTPs.
- Green sand is a natural manganese dioxide sand, which was found to be homogeneously distributed using FE-SEM and μ -PIXE techniques.
- Adsorption kinetic of ²²⁶Ra adsorption on green sand showed at equilibrium, the green sand was able to adsorb about 99% of the radium present in solution.
- The adsorption kinetic was fitted to a pseudo-second-order dynamic model and the adsorption rate, k_{p2}, was influenced by the content of major cations solved (distilled water > groundwater)
- Silica sand presented adsorption sites for radium in distilled water, but were occupied by ions of major constituents when considering higher salinity water.
- Laboratory experiences seems to indicate that the use of the designed filter could stand the treatment of large volumes of water without any change in its physico-chemical parameters, and with high removal rates.

Therefore, the filtration system has a high effectiveness in

eliminating radio and an easy implementation in DWTPs, as well as for domestic use, providing drinking water with unmodified physico-chemical parameters. It has also the benefit that radium is prevented from entering the pipelines in public water supplies, thus avoiding the hazard of its accumulation in pipe scales.

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