



Fly ash sorbent modified with KMnO_4 for the separation of important radionuclides

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Abstract

The main aim of this work was to develop a suitable sorbent for the separation and determination of ^{226}Ra through ^{133}Ba (radio tracer) in water samples using fly ash sorbent. After the modification with KMnO_4 the effects of pH, competing ions, the possibility of elution, and the effect of water volume were tested. As a suitable eluent 6 mol/L HCl was chosen, while the sorbent worked best at pH 6–8. The developed method is advantageous for minimizing the time required for separation, the volume of chemicals used, and the waste generated after separation.

Keywords Modification · Separation · Radium · 133-Ba · Fly ash

Introduction

Nowadays, over 20 radium isotopes are known, among them four can be found naturally [1]. The naturally occurring isotope ^{226}Ra is one of the most radiotoxic long-lived radionuclides present in the environment [2]. For this reason, national and international legislation requires its constant monitoring in the human environment, especially in drinking water. Therefore, for its determination, it is necessary to have reliable and accurate determination methods. There are a number of methods described in the literature for its determination, but it is somewhat common to use gamma spectrometry and/or radon emanation techniques for routine

determinations. However, these techniques have some drawbacks, which can significantly affect the reliability and accuracy of the determination, such as the emanation of radon from the measuring vessel during the measurement and the follow-up measurement in conditions of radiochemical disequilibrium [3]. In addition, in gamma spectrometric measurement some interference can appear (i.e., from ^{235}U using the line 186 keV). Other techniques, like thermal ionisation mass spectrometry, which has high analytical precision, requires extremely pure Ra load without presence of any Ba atoms. On the other hand, alpha-spectrometry in combination with simple and rapid radium isolation procedures can be advantageous over the mentioned techniques because measurements can be performed immediately after radium isolation from sample with significantly lower detection limits compared to other techniques [4]. Namely radium activity in the environmental samples is low so that almost all determination methods include preconcentration step before separation. It is well known that radium is inclined to the same behaviour as its chemically similar elements from the same group of the periodic table, particularly barium [5]. This fact Sill exploit in 1987, and proposed a method for the determination of ^{226}Ra that differed from other used techniques at that time. The method included microfiltration of co-precipitated $\text{Ba}(\text{Ra})\text{SO}_4$, using a non-radium tracer— ^{133}Ba for recovery determination [2].

In case of radium preconcentration, resins impregnated with manganese dioxide (MnO_2) can be used. It enables

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simple, rapid and efficient radium preconcentration from large volume liquid samples [6–8].

Fly ash, from coal burning, is grey coloured and contains many essential elements. The chemical composition of fly ash: silica SiO_2 (60–65%), alumina Al_2O_3 (25–30%), magnetite Fe_3O_4 and ferric oxide Fe_2O_3 (6–15%) allows its use for the synthesis of zeolite, alum and precipitated silica. Many of its physical and chemical properties make this material suitable for use as an adsorbent [9].

Limited literature data on the efficiency of radium separation using fly ash and the fact that MnO_2 is effective in supporting radium isolation motivated us to investigate the use of impregnated fly ash with potassium permanganate (KMnO_4) as sorbent for ^{226}Ra isolation. Therefore, the aim of this paper was to develop a cheap, easy to prepare, MnO_2 impregnated fly ash, to characterise it and to show that it can be used as a sorbent for efficient radium isolation. In this paper Ra was not used just Ba. Radium and barium have the same chemistry, so it is used for optimisation of new Ra determination methods as a non-isotopic tracer.

Materials and methods

Materials

Fly ash (under the commercial name MICROSILICA—SIOXID from OFZ, a.s., Istebné, Slovakia), potassium permanganate (KMnO_4 , Lachema, Czech Republic) and deionized water were used for the preparation of the modified fly ash sorbent. ^{133}Ba was used in the experiments as radioactive tracer. Hydrochloric acid (HCl , Slavus s.r.o., Slovak Republic) and sodium hydroxide (NaOH , Lachema, Czech Republic) were used to adjust the pH. Magnesium sulphate hexahydrate ($\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$, Slavus s.r.o. Slovak Republic) and calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, Slavus s.r.o., Slovak Republic) were applied to test the effect of competitive cations during adsorption. Hydrochloric acid (HCl , Slavus s.r.o., Slovak Republic) was used to eluate ^{226}Ra from the column. Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$, p.a., Slavus, Bratislava) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$; Slavus, p.a., Bratislava) were used for the preparation of samples for the alpha measurement.

Radiometric analysis

^{133}Ba activity in solutions was determined using Gamma ORTEC HPGe 20,109 P detector with the data processing software Gamma Vision-32bit, f. EG&G ORTEC (6% of relative efficiency for ^{133}Ba determination). Calibration of the gamma detector was performed using certified gamma standards obtained from the Czech Metrology Institute. All applied counting geometries were calibrated by using

a certified standard. 20 mL scintillation vials were used for batch and column experiments, where from 5 to 15 mL of solutions were analysed. All data were obtained with a measurement error of 2% for the counting time of 3600 s. This measurement error does not reflect other error sources. The minimum detectable activity $\text{MDA} = 0,28 \text{ Bq}$ and it was calculated according to Currie [10].

Methods

As it is visible on Fig. 1 to develop the suitable conditions for radium separation from water samples, different experiments were carried out under column conditions described in Experimental conditions.

Preparation of the sorbent

The fly ash used in this work was purchased from the commercial company OFZ, a.s. (Slovak Republic) under the trade name MICROSILICA—SIOXID. Most particles have a diameter in the range of (10–300) μm . The material has the following guaranteed composition: min. 85% silica, max. 1% calcium oxide, max. 2% sulphates, max. 2% alkali content, max. 0.3% chlorides and the loss by annealing at 750 °C is maximally 4%.

The modification of the fly ash was done using a KMnO_4 solution [8, 11, 12]. The fly ash (10 g) was rinsed twice with deionized water to remove fine dust particles and drench in 0.5 L of 0.5 mol/L KMnO_4 for 2 h at 80 °C. The suspension was then cooled to room temperature and filtered through filter paper (Surface weight: 84 g/m^2 , retention range 8–12 μm , filtration time: 20 s). The modified fly

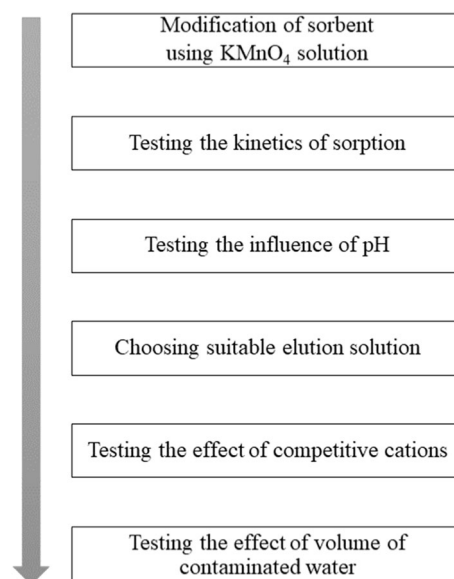


Fig. 1 Complete analytical procedure for determination of radium

ash was washed with deionized water and air dried at room temperature.

Kinetics of sorption

The radionuclide tracer ^{133}Ba was used to test the possibility of sorption on unmodified and modified fly ash [13]. The sorption experiments were carried out in 15 mL centrifugation tubes containing 0.5 g of fly ash (dry weight, unmodified and modified) and 10 mL of 0.1 mg/L Ba^{2+} carrier solution with ^{133}Ba tracer (70 Bq/L). The centrifugation tubes were shaken in a reciprocal shaker at room temperature for 1 min to 30 min. In total, 10 samples were prepared. The supernatants were collected using a centrifuge (Centrifuge Frontier™ FC5706 Mult, Ohaus GmbH, 4000 rpm for 5 min.) to separate the sorbent from a solution. The sorption rate was monitored by measuring ^{133}Ba in the solution after a certain contact time (by counting on HPGe detector).

Column experimental conditions

For all the experiments column filled with 0.5 g of modified sorbent (BV = 5 mL; column diameter 1 cm) and preconditioned with 2×20 mL of deionized water was used. Model solutions contained 0.5 mg/mL of Ba^{2+} carrier and were spiked with ^{133}Ba (70 Bq/L) and passed through the column at a flow rate of 0.4 mL/min. The effluents were collected into 20 mL vials and the activity of ^{133}Ba was measured by HPGe detector. All experiments were carried out two times. These conditions were used for all the experiments unless stated otherwise.

Influence of the pH change

To test the influence of pH on the sorption of the ^{133}Ba the modified fly ash sorbent was loaded onto the column. The pH of model samples was adjusted to various values in the interval from 1 to 10 with step 1 pH, using 0.1 mol/L hydrochloric acid (HCl) or 0.1 mol/L sodium hydroxide (NaOH). The adjusted model samples were loaded onto the column filled with the preconditioned modified sorbent. The effluents were collected into plastic vials and ^{133}Ba was measured using HPGe detector.

Effect of the elution solution

To test the influence of elution solution on the sorption of ^{133}Ba the model solution (pH = 6–7) was loaded onto the column. Barium was eluted from the column using different concentrations of HCl and HNO_3 , both in a range of 1 mol/L to 9 mol/L. The eluted sample was collected into a plastic vial and the ^{133}Ba activity was measured as described before.

Effect of competitive cations

The experiments to study the effect of competitive cations on the sorption of barium were carried out according to the above-mentioned column system conditions. In this case the model samples contained Na^+ , K^+ , Ca^{2+} , Mg^{2+} ions with different concentrations: Na^+ : 7 g/L–150 g/L, K^+ : 7 g/L–150 g/L, Ca^{2+} : 7 g/L–70 g/L, Mg^{2+} : 7 g/L–112 g/L. The model samples were loaded onto the columns and the effluent fractions were collected into plastic vials in which the activity of ^{133}Ba was measured as described.

Effect of volume of contaminated water

To study the effect of contaminated water on the sorption of ^{133}Ba , different volumes of model samples (1 L–50 L) were used. The model samples were loaded onto the big glass column (length 20 cm, diameter 3 cm) filled with 3 g of modified fly ash sorbent. The time frame for the separation depending on the volume was up to 5 days. We used an infusion set to continuously dose the sample onto the column. Barium was eluted from the column using 100 mL of 6 mol/L HCl and ^{133}Ba was measured as described.

Results and discussion

Emami [14] showed, that the charge of the silica surface in fly ash plays a significant role in the adsorption of radium as does the pH of the solution. Hence, the increase in pH leads to an increase in surface charge and consequently enables stronger binding of the cation on the surface. Therefore, it was assumed that radium can be separated using clean fly ash without any modification. However, obtained results showed that the unmodified sorbent has low sorption capacity for radium. In our previous paper was shown that sorption capacity of the fly ash can be increased after its treatment with suitable modifying agent [15] like manganese oxides, which show remarkable adsorbing abilities [8, 11, 12]. The treatment of fly ash with 0.5 mol/L KMnO_4 , resulted in capacity increase from 1.5 mg/L to 20 mg/L.

Kinetics of sorption

Sorption kinetics was examined by monitoring of barium sorption rate on modified sorbent as described in experimental part. From the results shown in Fig. 2, it can be seen that after 10 min percentage of barium sorption R has reached the maximum value and it can be assumed that the equilibrium has been reached. The sorption is faster in a first few minutes probably due to mostly non-occupied bind spots. In the later stages, the sorption is noticeably slower, since most of the free spots were already occupied,

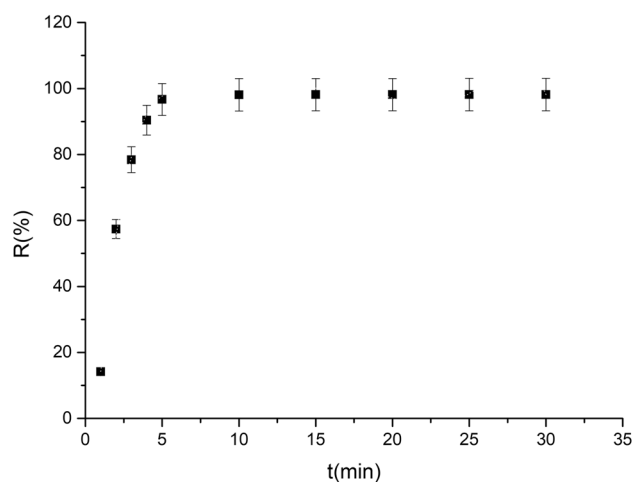


Fig. 2 Kinetics of barium sorption on modified fly ash sorbent (R —percentage of sorption, t —contact time of the sorbent and the model solution)

and there was a reduced amount of available free spots. This leads to the existence of a plateau area, where an equilibrium state is achieved between the two phases (liquid phase and solid sorbent) for the precise activity of ^{226}Ra (amount of Ra^{2+} ions) in the sorbate. This concept was also suggested by other authors [8, 16], while researching the sorption of Ba^{2+} (chemical equivalent of Ra^{2+} ions) on manganese dioxide and indicated that an equilibrium will be achieved in 30 min.

Varga [8] tested the radium sorption at two different pH values (6 and 8). He obtained significant difference between the adsorption at these two pH values and concluded that the primary parameter that affects the sorption is exactly the pH. At pH = 8 the equilibrium was reached under 30 min. In our case the kinetics were tested at pH (7–8), and the time required for complete sorption was less than 10 min. These results are in agreement with those of Varga [8]. Later it is shown that the optimum working pH range for our sorbent is between 6 and 9.

Effect of the elution solution

Barium preconcentration can be achieved by elution of ^{133}Ba using a suitable eluent. For the testing of the barium elution, two acids were used: HCl and HNO_3 . From the results shown in Fig. 3, it seems that hydrochloric acid is more suitable for the elution. Obtained results for barium yield showed that nitric acid gave lower yield compared with 6 mol/L HCl hydrochloric acid, (85 ± 11) % vs (97 ± 14) %. Therefore 6 mol/L concentration of HCl was used in the next experiments.

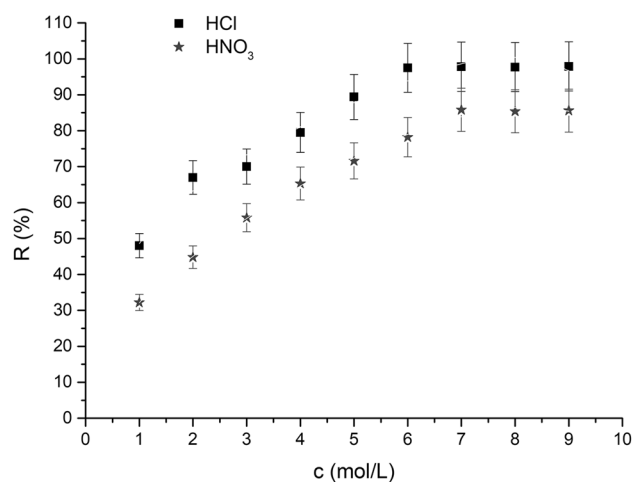


Fig. 3 Effect of the solution for elution on the chemical yield of ^{133}Ba (c —concentration of elution solutions, R —percentage of sorption)

Effect of competitive cations

Natural water contains a significant number of dissolved cations and anions which can compete with the Ra^{2+} ions and limits the sorbent sorption potential as well as capacity for barium therefore also radium. The influence of the concentration of other ions on the sorption of barium was examined. Na^+ and K^+ ions do not affect barium sorption. However, from the results shown in Fig. 4, it can be seen that the presence of Ca^{2+} ions can significantly reduce the sorption yield. Up to a concentration of 50 g/L it was above 90%, but above this concentration, the sorption yield decreased rapidly.

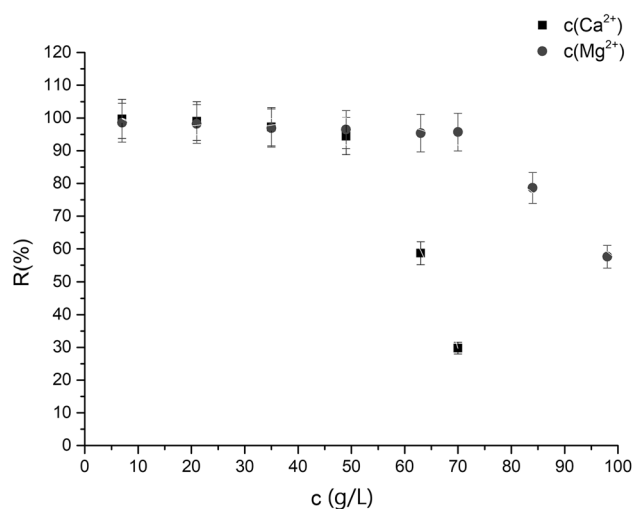


Fig. 4 Effect of competing ions (Ca^{2+} and Mg^{2+}) on the sorption in the modified fly ash sorbent (c —concentration of the competing ion, R —percentage of sorption)

Similar effect is caused by Mg^{2+} , the sorption yield was higher than 90% up to a concentration of 70 g/L but above this concentration it decreases rapidly.

There are many articles in which researchers use fly ash in different forms or with different modifications as sorbent for barium separation. In one of them [17], fly ash was used for the removal of environmental pollutants. For the removal of barium, the mixture of 25 kg of sand and 2 kg of zeolite was used. The most interesting thing about the samples that came from the coal mine was their high content of different salts, up to 110 g/L. One hundred and twenty litres of salt water were tested. The water sample contained 49 700 mg/L Na^+ , 4 410 mg/L Mg^{2+} and 2 970 mg/L Ca^{2+} . Other ions were present just in a negligible amount. When comparing the results with the modified fly ash used in this work, it is clear that the limits of the fly ash were much higher than the values determined in the coal mine water.

Influence of the pH change

The reason for studying the sorption of ^{226}Ra (^{133}Ba) on $KMnO_4$ as a function of pH is, that the pH of the solutions can change the surface charge of oxides/hydroxides of metals. To adjust the pH value of the solutions, usually NaOH and HCl are used. The pH of the solutions can change in different ways, as has already been shown with environmental waters. Therefore, Koulouris [16] tested the adjustment of pH in distilled water enriched with ^{226}Ra (^{133}Ba) using NaOH, Na_2CO_3 , and also HCl. According to the results, the use of different solutions to adjust the pH did not have any influence on the sorption.

In case of natural waters with pH from 7.5 to 8.5 and higher, a quantitative pre-concentration can be achieved without adjusting the pH, although absorption for radium is highly sensitive to pH. This factor should be considered when optimizing sample preparation step, as mentioned in Varga [8].

Varga [8] confirmed, that $KMnO_4$ modified sorbents show a higher ability to bind radium from alkaline solutions, mainly from solutions with $pH > 8.0$. $KMnO_4$ modified AG 1-X4 anion exchange sorbent showed similar sorption properties at different pH values as different $KMnO_4$ modified sorbents [12, 18]. Koulouris [16] determined a wide spectrum of pH (3.6–12.0) while using MnO_2 modified sorbents with particle size (0.60–1.20) mm. With values of $pH < 3.6$, he observed a rapid decrease in sorption. Because the plateau of the curve goes below 5.5, the author suggested that ion exchange might not be the main sorption process. This statement was also supported by kinetics testing, which gave an enthalpy change value of -20.0 kJ/mol, significantly higher than the ion exchange process or the physical sorption process.

In our experiments, it was found that the sorption on the modified fly ash sorbent was limited until $pH = 4.7$ as are shown in Fig. 5. However, over $pH = 5$, the sorption yield was more than 90%. At $pH > 9$, the sorption yields decreased rapidly. The minimum value of pH, where the sorption yield was greater than 90%, is 5.

Effect of volume

The ability to separate radium directly from large volumes of water samples with minimal pre-treatment would lead to a significant reduction in process time in comparison to other alternative separation techniques. The resulting high capacity for samples would be advantageous in some applications, including routine monitoring of drinking water samples and compliance testing of outlets with regulatory goals [19]. The experiments were carried out under column conditions, where 1 g of modified fly ash sorbent was used as a sorption material. The water samples containing ^{133}Ba tracer radionuclide, had volumes of 5 L, 10 L, 20 L, 30 L, 40 L, and 50 L and were loaded into the column. It was found that the sorption yield was higher than 92% at volumes from 5 to 30 L. A significant decrease in the sorption yield of ^{133}Ba was observed after applying 40 L of water. All results are shown in Fig. 6.

Chalupnik et al. [20] a synthetic zeolite-type NaP1 sorbent in their work used, which was created from fly ash. For column experiments, a mixture of zeolite, sand, and gravel was used. Different types of water samples were tested: drinking water, barium containing water and two types of mine water. The barium removal efficiency from water exceeded 90% for all the water samples, except the water containing barium. In that case, after overloading the filter

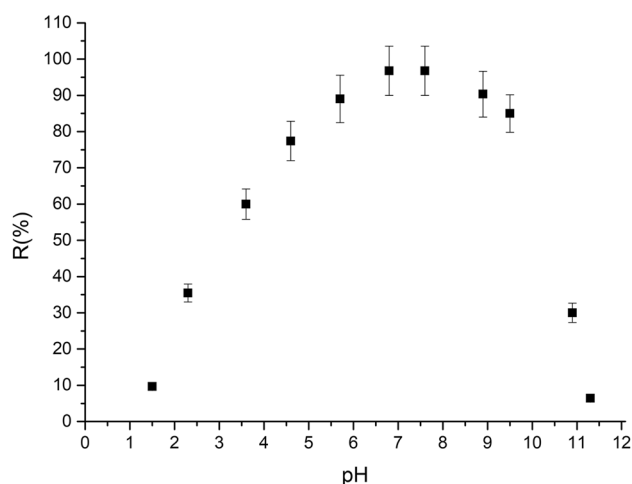


Fig. 5 Effect of the pH of the model samples on the sorption of barium on the modified fly ash sorbent (R —percentage of sorption, pH —pH value of model solutions)

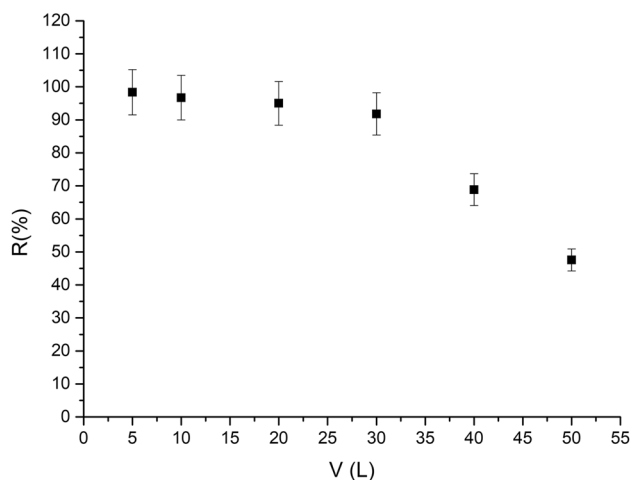


Fig. 6 Effect of sample volume on the sorption of ^{226}Ra (V —volume of contaminated water applied, R —percentage of sorption)

bed, the efficiency decreased significantly. During these experiments, leaching from the column of the very fine particles of zeolites was the biggest problem. According to the authors, this method must meet many specific requirements of the mining industry, since underground mine waste water can clog filters very effectively.

It seems that the application of zeolite materials together with fly ash for the construction of passive barriers will be a suitable solution to this problem. This material must be properly disposed because of the increased radioactivity in mine waters. To prevent any further radiation of miners, reuse is not expected. Because of this reason, any kind of application of ion exchangers, nanofibers, or polymers is excluded in the mining industry, mainly due to costs.

After the examination of results, it is visible that synthetic zeolites, and therefore fly ash, are suitable for the removal of barium and therefore radium from different contaminated waters. Moreover, it is suitable for single use, mainly because of its low cost and availability. From the results, it is clear that the method used in this paper is applicable only for samples with a volume less than 30 L per 1 g of modified fly ash sorbent.

Conclusion

The research carried out in this work was focused on the preparation of a sorbent for the separation and determination of ^{226}Ra . The goal was to modify the fly ash using KMnO_4 solution, in order to obtain higher capacity, to reduce the use of chemicals and to make the separation process easier, even for larger sample volumes. When testing the influence of volume of the model samples, it was found that a significant

reduction in ^{133}Ba sorption yield was observed when up to 40 L of contaminated water was used.

The developed and optimized method for the determination of ^{226}Ra on modified fly ash is characterized by high capacity. Compared to other types of sorbents, this sorbent is affordable and cost effective. Another advantage of fly ash is that it does not have to be manufactured, but is a by-product of burning coal, and it is available worldwide. Fly ash is considered waste material. During the laboratory application itself, where chromatographic columns are used, it was easy to work with fly ash and the column did not clog even with larger volumes of water samples. The method developed has the advantage of minimizing the time required for separation, the volume of chemicals used, and the waste generated after separation. It could be used for the determination of ^{226}Ra in samples of natural and mineral waters.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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