Pure and Sb-doped ZrO$_2$ for removal of IO$_3^-$ from radioactive waste solutions

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Abstract
Radioactive $^{129}\text{I}$ with a long half-life ($1.57 \times 10^7$ y) and high mobility is a serious radiohazard and one of the top risk radionuclides associated with its accidental and planned releases to nature. The complex speciation chemistry of iodine makes its removal a complicated task, and usually a single method is not able to remove all iodine species. Especially its oxidized form iodate (IO$_3^-$) lacks a selective and effective removal method. Here, the granular aggregates of hydrous zirconium oxides with and without antimony doping were tested for IO$_3^-$ removal and the effects of contact time, competing anions in different concentrations and pH were examined. The materials showed high selectivity for IO$_3^-$ ($K_d$ over up to 50,000 ml/g) in the presence of competing ions and relatively fast uptake kinetics (eq. < 1 h). However, B(OH)$_4^-$ and SO$_4^{2-}$, as competing ions, lowered the iodate uptake significantly in basic and acidic solution, respectively. The suitability of the materials for practical applications was tested in a series of column experiments where the materials showed remarkably high apparent capacity for the IO$_3^-$ uptake (3.2–3.5 mmol/g).

Graphic abstract

Keywords Iodate removal · $^{129}\text{I}$ · Zirconium oxide · Anion uptake · Decontamination

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Introduction

Iodine is a vital element for mammals as it is a critical component of hormones produced in a thyroid gland. The insufficient supply of iodine has several harmful health effects which are all together described as the iodine deficiency disorders (Zimmermann and Andersson 2012; Zimmermann and Boelaert 2015). In order to eliminate the adverse health effects of iodine deficiency, serious efforts have been put in action worldwide to supply the populations with the vital iodine (Andersson et al. 2010).

However, in addition to the stable isotope $^{127}\text{I}$, the thyroid gland absorbs the radioactive iodine isotopes generated by nuclear fission reaction. This increases the absorbed radiation dose of the gland which leads to an elevated risk of thyroid cancer. Iodine has several radioactive isotopes from which the short-lived isotopes, e.g. $^{131}\text{I}$ ($t_{\text{1/2}}=8$ d) or $^{133}\text{I}$ ($t_{\text{1/2}}=20.8$ h), pose an acute risk in the case of a nuclear accident, whereas the long-term significance comes from $^{129}\text{I}$ with an extremely long half-life ($1.57 \times 10^7$ y). Indeed, the nuclear accidents at Chernobyl and Fukushima released large amounts of $^{129}\text{I}$ to the environment (Aldahan et al. 2007; Hou et al. 2009, 2013). To minimize the internal dose of population, the authorities have set national or global guidance levels for the concentration of $^{129}\text{I}$ (WHO: 1 Bq/L (World Health Organization 2017); DWS in USA 0.04 Bq/L (Kaplan et al. 2014)) in drinking water. In the case of elevated concentrations, the purification of the water is required (Li et al. 2018).

Because of the potential radiation dose to populations, efficient treatment materials and methods are required for iodine containing wastes. Vast volumes of iodine waste waters are stored at various places worldwide, e.g. at the Hanford site (a former plutonium production site in Washington USA) because of the lack of a suitable treatment method (Zhang et al. 2013). The geosphere or the conventional synthetic materials used for the purification of other radioactive contaminants do not efficiently adsorb the different species of iodine (Li et al. 2018).

The complex chemistry of iodine makes the waste treatment difficult. Iodine has multiple stable redox states with different chemical and physical properties. For example, iodine ($I_2$) can occur as gas and iodide ($I^-$) and iodate ($IO_3^-$) are usually present as dissolved ions in solution. (Kaplan et al. 2014) $IO_3^-$ is the main species in aqueous solution and oxidizing conditions, whereas $I^-$ prevails in more reducing environments. Molecular iodine, $I_2$, is a major species only in low pH and over a narrow $E_h$ range (Moore et al. 2019). In addition to the inorganic species, iodine also reacts readily with organic compounds producing organo-iodine compounds with a wide range of chemical characteristics (Andersen et al. 2002). The diversity of iodine speciation and the fact that iodine can be present at several redox states simultaneously make a development of a universal iodine removal material hard or even impossible. Therefore, different removal strategies are required for the different iodine species.

The iodide decontamination has been successfully demonstrated with silver-containing materials. Activated carbons (Asmussen et al. 2016; Ho and Kraus 1981; Hoskins et al. 2002; Karanfil et al. 2005), zeolites (Asmussen et al. 2016; Faghidjan et al. 2002) and metal oxides with silver impregnation have been demonstrated to successfully remove the iodide, presumably by formation of scarcely soluble $\text{AgI}$ ($K_{\text{sp}} = 8.5 \times 10^{-17}$). In addition, hydroxalcites (Levitskaia et al. 2016) and organoclays (Bors et al. 2000) have shown significant capability of removing iodide. The iodate removal methods studied previously include hydroxypatites (Campayo et al. 2011; Coulon et al. 2014), sulphur-containing minerals (Strickert et al. 1980), hydroxalcites (Levitskaia et al. 2016; Liang and Li 2007; Toraishi et al. 2002), zero-valent and sulphur-modified iron (Lawter et al. 2018) and co-precipitation with calcite (Truex et al. 2017; Zhang et al. 2013). Despite the studies, the removal of iodate in the industrial scale still remains a difficult task and further studies as well as novel approaches are required.

Zirconium oxide (ZrO$_2$, also known as zirconia) and its doped (e.g. Y, Ca, Ce or Sb) derivatives have a versatile range of favourable properties like toughness, high physical and chemical stability, low solubility in water, and high ionic conductivity, which are utilized in a wide range of applications, including catalysts (Shao et al. 2010), gas sensors (Borhade et al. 2018), ceramics (Zhang et al. 2014) and fuel cells (Malolepszy et al. 2015).

ZrO$_2$ has different crystalline and non-crystalline structures: the three crystalline (monoclinic, tetragonal and cubic) and the amorphous phase are stable at low pressures. The stability and prevalence of the different structures depend on many factors like the concentration and nature of dopants, crystal size and synthesis conditions. (Graeve 2008) ZrO$_2$ is also known for both cation and anion-exchange properties (Singh and Tandon 1977; Veselý and Pekárek 1972). Antimony as dopant can affect the adsorption performance of ZrO$_2$ in many ways. It might be involved in redox reactions depending on the adsorbate element and the oxidation state (III or V) of antimony used as a dopant. Most importantly, the introduction of trivalent dopant ion, such as antimony, to the crystal structure of ZrO$_2$ creates crystal defects increasing the number of the oxygen vacancies (Graeve 2008). The latter could enhance the interaction of the material with oxygen-containing substances.

Indeed, pure and doped zirconium oxides have been widely studied for the decontamination of antimony (Lönrot et al. 2019; Paajanen et al. 2019), technetium (Lönrot et al. 2020), fluoride (Dou et al. 2012; He et al. 2014),...
phosphorus (Cui et al. 2012; Liu et al. 2008), arsenic (Cui et al. 2012; Zheng et al. 2011, 2012) and mercury (Mishra et al. 1996), for instance. Both pure and antimony-doped hydrous zirconium oxide have shown an excellent performance for the separation of different contaminant oxyanions, e.g. Sb and Tc (Lönnrot et al. 2019, 2020; Paajanen et al. 2019).

Iodine, similar to antimony and technetium, is present as an oxyanion in oxidizing conditions, but its adsorption properties on zirconium oxides have not been extensively studied. This study aims to fill that gap. The effect of the solution matrix (different competing ions in different concentrations, pH) and the uptake kinetics were studied by batch experiments. In addition, the application of the ZrO$_2$-based material in water treatment was demonstrated using $^{125}$I$O_3^−$ and $^{127}$I$O_3^−$ spiked simulant solution in dynamic column experiments.

The main laboratory experiments of this study were performed at the Radiochemistry unit at the Department of Chemistry, the Faculty of Science, the University of Helsinki, Finland, between the years 2019 and 2020. The synchrotron experiments were performed at BL22-CLÆSS beamline of the ALBA synchrotron light source, at Barcelona, Spain.

**Materials and methods**

**Chemicals**

All reagents were of analytical grade (Alfa Aesar, Sigma-Aldrich, Riedel de Haën) and used without further purification. The radioactive Na$^{125}$I tracer was purchased from PerkinElmer. Solutions were made by dissolving solids in grade 1 deionized water (18.2 MΩ cm at 25 °C, Milli-Q® Merck Millipore).

The test solutions used in the experiments consisted of simple solutions containing single competing anion prepared by dissolving appropriate amount of H$_3$BO$_3$ in the case of the borate, or sodium salts of the other corresponding anions (NaCl, NaNO$_3$, Na$_2$SO$_4$) in water. In addition to the simple solutions, also a more complex water simulant solution representing chloride containing process water (Table 1) was used in the batch experiments and in a single column experiment. The solution was prepared by dissolving Na, Ca or Mg salts of the anions and pH of the solution was finally adjusted to 7.0 with 1 M NaOH (Na$^+$ from this step is also included in the values described in Table 1).

**Synthesis of materials**

ZrO$_2$ with and without antimony doping was synthesized with a precipitation method. First, in the case of ZrO$_2$ 100 g of zirconium basic carbonate (Alfa Aesar) was carefully dissolved in 1 L of 6 M HNO$_3$ under vigorous stirring using a mechanical stirrer. In the case of Zr(Sb)O$_2$, 45 g of ZrCl$_4$ (Riedel de Häen) and 2 g of SbCl$_3$ (Sigma-Aldrich) were used as the starting materials and they were dissolved in 2 L of 3 M HCl.

Next, approximately 1200 ml of 6 M NH$_3$ solution was slowly added to both beakers until pH reached 7.8 and white precipitate was formed. The precipitate was let to settle for overnight, and white precipitate and clear supernatant were separated. The precipitate was washed with deionized water until the conductivity of the supernatant was less than 4.0 mS/cm. Finally, the supernatant was discarded, and the slurry was dried in an oven at 70 °C for three days. The dried sample was ground to fine powder and sieved to particle size 74–149 μm.

**Characterization**

The surface morphologies of the materials coated with 4 nm Au–Pd sputtering were examined using Hitachi S4800 FESEM (field-emission scanning electron microscopy). The crystallinity was studied with powder X-ray diffraction (XRD) in the Bragg–Brentano geometry using a Panalytical X’pert PW3710 MPD diffractometer, a PW3020 vertical goniometer and a Cu Kα radiation source ($\lambda = 1.54056$ Å, 40 kV and 40 mA).

Zeta potential of the materials was measured with Malvern Pananalytical Zetasizer Nano ZS. In these experiments, 20 mg of ZrO$_2$ or ZrSbO$_2$ ground fine powder and 10 ml of 10 mM NaNO$_3$ were mixed in a rotary mixer for 24 h before the measurement of the equilibrium pH and Zeta potential. Separate samples were prepared, and their pH was individually adjusted using diluted HCl or NaOH solutions.

**Measurement of iodate concentration**

Two different iodate probes were used in the experiments of this study: radioactive $^{125}$I$O_3^−$ and stable $^{127}$I$O_3^−$. In the case of experiments with radioactive $^{125}$I$O_3^−$ tracer, 5 ml of filtered solutions in polyethylene vials was measured with Wallac 1480 Wizard 3” automated NaI-scintillation γ-detector.

| Component | Concentration (mM) |
|-----------|-------------------|
| SO$_4^{2−}$| 2.8               |
| Cl$^−$    | 56.4              |
| NO$_3^{−}$| 6.6               |
| Na$^+$    | 58.7              |
| Ca$^{2+}$ | 1.2               |
| Mg$^{2+}$ | 3.3               |

Table 1 The composition of simulant process water solution used in some of the batch and column experiments
For the experiments with non-radioactive $^{127}$IO$_3^-$, 1 ml of filtered solution in a glass HPLC vial was analysed for iodide/iodate concentrations with an anion-exchange chromatography column (Dionex AS11 4 × 250 mm analytical column and AG11 4 × 50 mm guard column) attached to an Agilent 1260 Infinity quaternary pump and autosampler HPLC-system connected to an Agilent 7800 ICP-MS via direct connection between the column and ICP nebulizer. 50 mM sodium hydroxide (NaOH) was used as an eluent with a flow rate of 0.8 ml/min. The ICP-MS was driven in the no-gas mode. The dissolution of CO$_2$ from the ambient laboratory air was prevented by a constant Ar gas bubbling to the eluent container. The two main species of iodine I$^-$ and IO$_3^-$ were separated based on their retention times, first determined with standard solutions prepared from KI and KIO$_3$, and the concentrations were calculated from the chromatogram peak areas using external standards on the concentration range from 0 to 200 μg L$^{-1}$ for both iodine species. The stability of the instrument was followed using quality control (5 + 5 and 50 + 50 μg L$^{-1}$ of total iodine species. The stability of the instrument was followed using quality control (5 + 5 and 50 + 50 μg L$^{-1}$ of total iodine I$^-$ + IO$_3^-$) and blank samples. The retention times were 120 s for IO$_3^-$ and 360 s for I$^-$ and they remained stable during the analysis period. A limit of detection (LOD) for HPLC-ICP-MS system was 0.5 μg L$^{-1}$ and 0.2 μg L$^{-1}$ for I$^-$ and IO$_3^-$, respectively. A repeated injection method was used for LOD determination by measuring 8 replicates of 1 μg L$^{-1}$ of I$^-$ and IO$_3^-$ calibration standard and using a calculation procedure described in the literature (Wells et al. 2011).

The speciation of iodine was confirmed with two methods depending on whether radioactive $^{125}$IO$_3^-$ or non-radioactive $^{127}$IO$_3^-$ was used. For experiments with non-radioactive iodine, commercial K$^{127}$IO$_3$ was used as the tracer without any treatment. In addition, the speciation was confirmed using HPLC-ICP-MS. However, because the radioactive tracer was in the form of Na$^{125}$I, the oxidation of iodide to iodate was needed. In order to obtain $^{125}$IO$_3^-$ solutions, an appropriate volume of NaOCl solution was added to obtain 2 × 10$^{-4}$ M NaOCl concentration in 10 mM NaOH and the solution was let stand for at least 24 h before use. The speciation of $^{125}$IO$_3^-$ was confirmed with repeated simple batch experiments done for tracer solutions where silver-impregnated activated carbon (Silcarbon Aktivkohle GmbH, Germany) was used to quantify the iodate fraction. The procedure has been previously validated for the alteration and separation of the oxidation states of iodine (Suorsa et al. 2020).

**Batch ion exchange experiments**

To assess the potential of zirconium oxides on iodate uptake, the combined effect of different competing ions in different pH’s and concentrations was studied with batch experiments. The sample preparation in all batch experiments was similar: 20 ± 1 mg of ground material was weighed to a polyethylene vial, 10 ml of appropriate test solution was pipetted, and pH was adjusted by adding appropriate volume of NaOH or HCl and finally either $^{125}$IO$_3^-$ or $^{127}$IO$_3^-$ was added as tracer. The samples were equilibrated for 24 ± 2 h and solid and liquid phases were separated by centrifuging (2100 G, 10 min) followed by filtering with a 0.2 μm filter (PVDF LC. Arcodioc, Gellman Sciences). The filtered solution was either put to a 10 mL polyethylene vial ($^{125}$I) or a glass HPLC vial ($^{127}$I). The equilibrium pH of remaining supernatant was measured using Ross combined electrode. The determination of iodine concentration was done with NaI-scintillation γ-detector ($^{125}$I) or HPLC-ICP-MS ($^{127}$I) depending on whether the radioactive or stable isotope of iodine was used in the particular experiment.

The effect of competing ions to iodate adsorption was tested by using 10 mM solutions of different anions (Cl$^-$, NO$_3^-$, B(OH)$_3^-$, SO$_4^{2-}$) as a function of pH in the range 3–10. The effect of concentration of ions was screened at single pH value using different concentrations (1, 10 and 100 mM). The experiments with single competing ion were separately done with the radioactive $^{125}$IO$_3^-$ and in addition, a pH series with simulant solution (see Table 1) containing several components was done with non-radioactive $^{127}$IO$_3^-$. The latter was done to assess the effect of a more complex matrix as well as the potential difference between $^{125}$IO$_3^-$ and $^{127}$IO$_3^-$ possibly caused by the concentration or speciation differences. The radioactivity of carrier-free $^{125}$I was between 100–250 Bq per 10 ml sample corresponding to concentrations on the scale ~ 10$^{-13}$ M. With non-radioactive $^{127}$I, the concentrations were 8 × 10$^{-7}$ M.

The distribution coefficients, $K_d$, in the batch experiments were calculated by Eq. 1:

$$K_d = \frac{c_i - c_f}{c_i} \times \frac{V}{m}$$  

(1)

where $c_i$ = initial concentration of iodate in the solution; $c_f$ = final concentration of iodate in the solution; $V$ = volume of solution in mL; and $m$ = mass of material in g.

The error calculations are represented in SI.

**Column experiments**

Dynamic column experiments were done to test the zirconium oxide materials iodate uptake properties in more practical set-up. Three sets of column experiments were done: first experiment with solution containing only 10 mM $^{127}$KIO$_3$ to see maximum apparent capacity, second experiment with 10 mM NaNO$_3$, 1 mM KIO$_3$ and $^{125}$IO$_3$ as tracer to see the effect of weakly competing anion and last experiment with more complex simulant solution (Table 1) demonstrating the uptake properties in more realistic conditions from the waste management.
point of view. Two first experiments were done for both ZrSbO$_2$ and ZrO$_2$, the last experiment only with ZrSbO$_2$.

Approximately 0.5 g (1 g in the case of third experiment with simulant solution) of the sieved material (74–149 μm) was loaded by pipetting with a small volume of 10 mM NaNO$_3$ to a low-pressure borosilicate glass column with a diameter of 0.7 cm and a porous polymer bed support at the bottom (Econo-Column®. Bio-Rad Laboratories, Inc.). Two different approaches were used for the probing of the breakthrough: non-radioactive $^{125}$I$_2$ tracer and radioactive $^{125}$I$^{-}$. The specifications of the individual column experiment sets are described in detail in Table 2.

$^{125}$I$_3$ or $^{127}$I$_3$ spiked simulant solution was pumped through the column bed (volume ~0.6 ml for the experiments 1 and 2, ~1.2 ml for column experiment 3 with simulant solution) with a flow rate of 10 bed volumes per hour. For the column experiment 1, only the total concentration of iodate and pH of effluent and eluent were measured, i.e. no individual fractions were collected. In the case of column experiments 1 and 2, the automated fraction collector was used to collect samples with the interval between one and two hours and samples were measured for iodate concentration and pH. In addition, the feed solutions were inspected regularly for iodate concentration and pH to make sure no changes in speciation, for example, had occurred before the contact with the materials.

The I K-edge XANES (X-ray absorption near edge structure) spectra of the IO$_3^-$ loaded ZrO$_2$ and ZrSbO$_2$ (from Column experiment 1) were measured at BL22-CLÆSS beamline (Simonelli et al. 2016) of the ALBA synchrotron light source, Barcelona, Spain. The loaded column beds were moved to separate vials and washed two times by mixing with 5 mL of deionized water, followed by centrifugation (2100 G, 10 min) and removal of supernatant. After the wash, the samples were dried in 70 °C for overnight. The samples and the reference materials were homogenized with a mortar and pestle, and approximately 50 mg of sample (less in the case of references) was mixed with 150 mg of cellulose and pressed into pellets. The samples were measured in transmission mode inside a He-cryostat. The collected spectra were analysed and merged with Athena software (Ravel and Newville 2005). The XANES spectra of the samples were compared with KIO$_3$, I$_2$ and KI as reference materials.

### Results and discussion

#### Characterization

The synthesized materials were examined using XRD for their crystallinity (Fig. 1a), SEM for their morphology (ZrSbO$_2$: Fig. 1b, see Supplementary Information (SI) Fig. 1 for ZrO$_2$) and electrophoretic light scattering for the isoelectric point (see SI Fig. 2). XRD of the zirconium oxide materials shows a broad peak located at $2\theta$ of 30° making the determination of the crystal structure impossible. For both materials, the XRD and SEM measurements indicate the large aggregates of poorly crystalline zirconia. This kind of a structure is optimal for practical column use due to the low flow resistance and fast adsorption on the edge surfaces.

Similar ZrO$_2$ syntheses in our previous studies yield materials with high surface area (Lönnrot et al. 2019).

The isoelectric points of the materials were determined by measuring Zeta potential in the pH range 4–10 (see SI Fig. 2) and the values are approximately 7.5 for both materials which agree with the published values in literature where the values of pH 3–8, usually around 7, have been reported (de Kretser and Scales 2008; Leong et al. 1995; Lönnrot et al. 2019; Schultz et al. 1993). The surface charge determines whether the anionic or cationic ions are attracted making it an important factor governing the uptake process.

#### Adsorption kinetics

The kinetics of iodate uptake was studied for both materials to see how fast uptake reaction proceeds to equilibrium (see SI for the graph). From the start, both materials showed a similar trend, and the adsorption reaches over 99.5% after 60 min. We suspect that reaction kinetics is fast because IO$_3^-$ does not have to diffuse inside the crystalline structure; instead, the adsorption occurs on the crystallite surfaces.

#### Effect of pH and competing ions on the adsorption

The effect of pH was studied in the range between 3 and 10 with a series of batch experiments done with different competing ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and B(OH)$_4^-$) in a concentration of 10 mM. The results are shown as a mean of

| Column experiment | Materials       | Solution                  | Feed pH | IO$_3^-$ probe | IO$_3^-$ analysis method |
|-------------------|-----------------|---------------------------|---------|----------------|------------------------|
| 1                 | ZrO$_2$ & ZrSbO$_2$ | 10 mM KIO$_3$            | 6.0     | $^{127}$I$_3^-$ | HPLC-ICP-MS            |
| 2                 | ZrO$_2$ & ZrSbO$_2$ | 10 mM NaNO$_3$ + 1 mM KIO$_3$ | 6.0     | $^{129}$I$_3^-$ | Nal-scintillation γ-detector |
| 3                 | ZrSbO$_2$       | Simulant solution (Table 1) + 4 μM KIO$_3$ | 7.0     | $^{127}$I$_3^-$ | HPLC-ICP-MS            |
parallel samples ($n=2$), the error bars represent the standard deviation of the parallel samples ($n=2$) and are included in the figure but are not showing for all of the data points as they are less than the size of the markers. Both ZrSbO$_2$ and ZrO$_2$ show a similar uptake trend for IO$_3^-$ as the function of pH (Fig. 2): the $K_d$ values are the highest at low pH (10,000 ml g$^{-1}$) and decrease as function of pH (100 ml g$^{-1}$). A clearly visible decrease in uptake is observed for all the ions at pH 8. This is most likely associated with the isoelectric point of ZrO$_2$ and ZrSbO$_2$ which lie within this range (see SI Fig. 2). Above this point, the surface charges of the materials turn negative causing the repulsion of negatively charged ions and inhibiting the adsorption process. From all the ions, SO$_4^{2-}$ has the most dramatic effect on IO$_3^-$ uptake. The uptake of IO$_3^-$ in SO$_4^{2-}$ solution was notably less at low pH compared with other competing ions. At low pH, the divalent charge of sulphate strongly affects the iodate uptake. At pH’s closer and above the isoelectric points, the differences in uptake are significantly smaller apart from borate that has changed its speciation from neutral B(OH)$_3$ to negatively charged B(OH)$_4^-$.

It is suggested that the uptake of iodate at high pH is other than traditional anion uptake (rather uptake to defect sites at the material surface). In addition, SO$_4^{2-}$ may react with the hydroxyl groups in zirconia causing the sulphonation of the surface (Chen et al. 1993; Deshmame and Adewuyi 2013). Compared with
SO$_4^{2-}$, the uptake of IO$_3^-$ is significantly higher in the case of NO$_3^-$ and Cl$^-$ as competing ions. In borate solution, the IO$_3^-$ uptake is at the same level with the latter at low pH ($< 6$), but at higher pH a significant drop in the IO$_3^-$ uptake was observed most likely due to the speciation change of borate. The anionic B(OH)$_4^-$ becomes thermodynamically stable above pH 7 and competes more with IO$_3^-$ compared with neutral B(OH)$_3$ which is the only species in low pH.

The effect of concentration (1–100 mM) of competing ions Cl$^-$, NO$_3^-$, SO$_4^{2-}$ was tested (Fig. 3) for both ZrO$_2$ and ZrSbO$_2$ but only at pH 4, where the IO$_3^-$ uptake should be rather optimal based on the pH effect studies conducted in this study (Fig. 2). Figure 3 represents the distribution coefficients calculated as a mean of the parallel samples ($n = 3$). The error bars representing the standard deviation of the parallel samples are included in the figure but are not showing as they are less than the size of the markers. At the tested conditions, the difference in Cl$^-$ and NO$_3^-$ concentrations did not show any effect on IO$_3^-$ uptake as the $K_d$'s remained high (> 10,000 ml/g) over the concentration range. In the case of borate, pH 8 was used because the anionic species of borate are not thermodynamically stable in pH 4. For B(OH)$_4^-$ at pH 8, the decrease of IO$_3^-$ uptake as the function of borate concentration is dramatic: 100-fold from 10 000 to 100 ml/g for ZrSbO$_2$ and even more in the case of ZrO$_2$. The adsorption behaviour of IO$_3^-$ in the presence of B(OH)$_4^-$ resembles the typical uni–uni ion exchange reaction, but it should be noted that pH values are close to the PZC and were measured with a pH electrode and therefore are not accurate enough for a precise determination of exchange reaction. Compared with borate, the rise of SO$_4^{2-}$ concentration affected the uptake less: $K_d$ values drop ten-fold from 10 000 ml/g at 1 mM to almost 1 000 ml/g at 100 mM. This does not agree with typical 1:2 ion exchange between SO$_4^{2-}$ and IO$_3^-$ and the role of other uptake processes, like surface complexation, has to be considered for IO$_3^-$ uptake besides ion exchange.

As the IO$_3^-$ adsorption is unaffected by increasing ionic strength in the case of NO$_3^-$ or Cl$^-$, it would indicate that the adsorption is not, at least solely, due the ion exchange. The rising SO$_4^{2-}$ and B(OH)$_4^-$ concentrations have a strong effect on IO$_3^-$ adsorption which would indicate that they are competing for the same sites with the latter at the corresponding conditions.

**Column experiments**

The series of column experiments were performed to assess the suitability of ZrO$_2$ and ZrSbO$_2$ in a more practical column set-up. Three sets of column experiments were done (Table 3): first experiment with solution containing only NaNO$_3$ at pH 4, NaCl at pH 4, Na$_2$SO$_4$ at pH 8, H$_3$BO$_3$ at pH 4, NaNO$_3$ at pH 4, NaCl at pH 4, Na$_2$SO$_4$ at pH 8, H$_3$BO$_3$ at pH 4.

![Fig. 3](image_url) The distribution coefficient ($K_d$) of IO$_3^-$ for Zr(Sb)O$_2$ (a) and pure ZrO$_2$ (b) as concentration 1–100 mM of different competing ions.
10 mM $^{127}$KIO$_3$ (to see maximum apparent capacity), second experiment with 10 mM NaNO$_3$, 1 mM KIO$_3$ traced with $^{125}$I$_3$ (as an iodate tracer for accurate and simple measurements) and third experiment with more complex simulant solution (Table 1), demonstrating the performance under more realistic conditions.

In simple KIO$_3$ solution, both materials showed similar apparent capacities for iodate: ZrSbO$_2$ (3.5 mmol/g) performed slightly more efficiently compared with ZrO$_2$ (3.2 mmol/g). The feed pH was 6.0 and final pH 4.7 and 4.3 for ZrSbO$_2$ and ZrO$_2$, respectively. The HPLC-ICP-MS (See SI for the example chromatograms) analysis did not show any changes in iodine oxidation state as only IO$_3^-$ was observed in the eluent and no I$^-$ or other iodine species were detected in effluent. In addition, the measured iodine K-edge XANES spectra of both ZrO$_2$ and ZrSbO$_2$ (Fig. 4) show the features characteristic to iodate, confirming that no redox changes occurred during the adsorption and iodine adsorbed to the materials as iodate.

In 10 mM NaNO$_3$ solution, the IO$_3^-$ uptake performance was reduced for both materials. Like in the first set of column experiments, ZrSbO$_2$ (0.64 mmol/g) performed more efficiently compared with ZrO$_2$ (0.58 mmol/g). The breakthrough curves of IO$_3^-$ in these experiments are presented in Fig. 5. The breakthrough curve shows highly symmetrical shape for ZrSbO$_2$ and the breakthrough started at approximately 500 BV’s. For ZrO$_2$, the breakthrough started at earlier stage after approximately 300 BV’s. The complete breakthrough was achieved at the same stage for both materials at 700 BV’s. The pH evolutions of the eluents were similar for both materials (Fig. 6). pH raised steadily from initial 2.5 to 4.0. At the same point when the actual breakthrough started (600 BV’s), pH rose fast to 5.0. In general, the pH was slightly lower in the case of ZrSbO$_2$ compared with ZrO$_2$ at the corresponding points of the experiment.

The performance of ZrSbO$_2$, which showed higher apparent capacity for IO$_3^-$ in previous experiments, was also tested in a more complex solution (Table 1) to better assess its suitability for real applications (Fig. 7). The breakthrough of IO$_3^-$ appeared after 1250 BV’s, and the complete breakthrough was achieved at 2500 BV’s. The apparent capacity in these conditions seems to be dramatically lower (approximately 5 μmol/g) compared with simpler solution in the previous column experiments. Most probably, this is because of the competition of other ions, especially divalent sulphate, which was also observed in the batch experiments. A steep rise in pH occurred at the same time with the breakthrough.

Altogether, the column experiments demonstrate that the IO$_3^-$ apparent adsorption capacity is lowered from the ideal conditions due to competing anions. However, even at complex solution (Fig. 7) with a high excess of other ions (SO$_4^{2-}$ and Cl$^-$ to IO$_3^-$ ratios 700 and 14,000, respectively) a selective removal of IO$_3^-$ is achieved. The lower uptake in the column experiments with higher ionic strength can

### Table 3

The column experiments performed within the study

| Material | Solution                | Feed pH | Apparent IO$_3^-$ capacity (mmol/g) |
|----------|-------------------------|---------|-------------------------------------|
| ZrO$_2$  | 10 mM KIO$_3$           | 6.0     | 3.18 ± 0.09                         |
| ZrO$_2$  | 10 mM NaNO$_3$ + 1 mM KIO$_3$ | 6.0     | 0.58 ± 0.01                         |
| ZrSbO$_2$| 10 mM KIO$_3$           | 6.0     | 3.49 ± 0.17                         |
| ZrSbO$_2$| 10 mM NaNO$_3$ + 1 mM KIO$_3$ | 6.0     | 0.64 ± 0.01                         |
| ZrSbO$_2$| Simulant solution (see Table 1) | 7.0     | 0.0047 ± 0.0001                     |

Fig. 4 Normalized I K-edge XANES spectra of the reference samples and zirconium materials loaded with IO$_3^-$ (ZrO$_2$: 3.2 mmol/g; ZrSbO$_2$: 3.49 mmol/g)

Fig. 5 Breakthrough of IO$_3^-$ for ZrSbO$_2$ (black) and ZrO$_2$ (red) columns as the function of effluent volume in bed volumes. The error bars are not showing as they remain hidden behind the symbols.
be explained by the presence of two different adsorption sites for IO₃⁻ on the zirconium oxide materials with different adsorption mechanisms. This is supported by the results of the batch experiments (“Effect of pH and competing ions on the adsorption”) as the rising concentrations of Cl⁻ and NO₃⁻ do not affect the IO₃⁻ uptake at all, whereas higher SO₄²⁻ concentrations reduce it strongly. It is suggested that at ideal conditions without competing anions, IO₃⁻ is adsorbed to both selective and non-selective sites at the zirconium oxide materials. The introduction of NO₃⁻ or Cl⁻ lowers the removal performance because then IO₃⁻ is adsorbed mostly or only at the selective sites. In the presence of both Cl⁻ and SO₄²⁻, the IO₃⁻ uptake is furthermore decreased because the selective sites are shared between IO₃⁻ and SO₄²⁻. Like suggested by the batch experiment results, SO₄²⁻ seems to compete for the IO₃⁻ selective sites indicating a similar adsorption mechanism. However, more detailed experiments are needed to verify the exact mechanism behind the adsorption of IO₃⁻ to the zirconium oxide materials.

Conclusion

This study altogether demonstrates the potential of zirconia-based materials on the selective removal of radioactive IO₃⁻ which currently is an unresolved task. The ZrO₂ and Sb-doped ZrO₂ exhibited the high apparent capacities of 3.2–3.5 mmol/g for IO₃⁻ in ideal conditions. More importantly, the materials showed high selectivity to IO₃⁻ as the uptake performance of the materials was unaffected by the large excess of competing NO₃⁻ or Cl⁻ ions (in batch). However, SO₄²⁻ and B(OH)₄⁻ lowered the iodate adsorption significantly in acidic and basic conditions, respectively. In addition, the apparent capacity was reduced from the ideal situation in more complex solutions due to the competition of the other anions from which the most important is SO₄²⁻. This is most likely explained by its divalent charge and sulfonation of the material surface, which is a known phenomenon and observed in catalysis applications with zirconia. Although the apparent capacity was lowered significantly from the ideal in the presence of competing anions, the zirconia materials show potential for the remediation of radioactive wastes where the contaminants are often in trace concentration levels and the most important factor regarding the performance is the selectivity of the materials.

The pure and Sb-doped ZrO₂ performed both efficiently in IO₃⁻ removal, but the latter showed approximately 10% higher apparent capacity. It is likely that antimony disturbs the formation of ZrO₂ structure and produces more defects to the structure that are typically active adsorption sites for IO₃⁻ uptake. However, the exact role of antimony and the detailed uptake mechanism of IO₃⁻ require further investigation on the structure at the sorption site (preferably synchrotron-based XAS measurements) in order to optimize the removal performance of the materials. Consequently, competent zirconia adsorbent materials suitable for direct disposal could be developed for the present and forthcoming radioactive IO₃⁻ waste, which at the moment, lacks a specific removal method.

Supplementary Information

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Data availability The additional data are contained in supplementary material.

Declarations

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

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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