

## THE ORIGIN OF $^{99}\text{Tc}$ IN THE ENVIRONMENT AND ITS REMOVAL

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**Abstract:** *Technetium-99 ( $^{99}\text{Tc}$ ), as one of the important high-yield fission products, is a significant threat to the environment and human health. It is produced in large amounts by nuclear fission of  $^{235}\text{U}$  or  $^{239}\text{Pu}$  in nuclear reactions, though the quantity of Tc produced by the spontaneous fission of  $^{238}\text{U}$  or by decay of  $^{99}\text{Mo}$  in the nature which is very small.  $^{99}\text{Tc}$  in the environment originates from nuclear weapons tests, discharges from nuclear power plants, nuclear medicine and radiobiology. These activities generate large volumes of low and intermediate radioactive waste which can cause a significant impact on the environment if disposed without suitable treatment. Immobilization of  $^{99}\text{Tc}$  into a relatively small volume waste is vital for long term permanent disposal.*

*High mobility and long half-life of  $^{99}\text{Tc}$  considered to be one of the most important radionuclides in safety assessment of environmental radioactivity as well as nuclear waste management. Effective removal of radioactive technetium ( $^{99}\text{Tc}$ ) from contaminated water is of enormous importance from an environmental and public health perspective, yet many current methodologies are highly ineffective. This paper summarizes physico-chemical separation procedures emphasizing those that are the most used in practice.*

*Classic sorbents such as activated carbons, ion exchange resins as well, as new materials, such as metal-organic frameworks and graphene based membranes are described in the paper.*

**Keywords:** *Technetium-99, nuclear fission of  $^{235}\text{U}$  or  $^{239}\text{Pu}$ , nuclear weapons tests waste, sorption, activated carbon, synthetic resins, MOFs, graphene oxide membranes*

### 1. Tc isotopes: their appearances, characteristics and ways of synthesis procedures

#### 1.1. Radioisotope of Tc: its appearance in nature, types of isotopes, ways of synthesis

$^{99}\text{Tc}$ , a long-lived  $\beta$ -emitting radionuclide, with its half life of  $2.13 \times 10^5$  years, is the lightest element whose isotopes are all radioactive. There are 45 isotopes of Tc, ranging from  $^{85}\text{Tc}$  to  $^{117}\text{Tc}$ , that have been synthesized, and most of them are short-lived isotopes with half lives of less than 1 h. Among them most long lived are  $^{97}\text{Tc}$  ( $t_{1/2} = 2.6 \times 10^6$  y),  $^{98}\text{Tc}$  ( $t_{1/2} = 4.2 \times 10^6$  y) and  $^{99}\text{Tc}$  ( $t_{1/2} = 2.1 \times 10^5$  y). Relatively short half-life of technetium isotopes compared to the age of the Earth is responsible for its low presence in the environment, i.e. very small concentration of "natural" technetium exists in the nature [1]. Some authors mention that  $^{99}\text{Tc}$  can be produced in nature by spontaneous fission of  $^{238}\text{U}$  and neutron induced fission of  $^{235}\text{U}$  in the earth [2,3], but the quantity of  $^{99}\text{Tc}$  produced by spontaneous fission of  $^{238}\text{U}$  or by decay of  $^{99}\text{Mo}$  in the nature is very small [4]. Existence of "natural reactors" at Oklo in Gabon were described by several authors [5-9]. Such "reactors" can occur under the right geochemical conditions and if the geometry of the ore deposit is favourable. Natural fission can induce a nuclear chain reaction where  $^{99}\text{Tc}$  appears as one of the products [10].

Nearly all available technetium is produced by nuclear fission of  $^{235}\text{U}$  or  $^{239}\text{Pu}$  in nuclear reactors. Half-life of  $^{235}\text{U}$  is relatively shorter compared to  $^{238}\text{U}$  and proportion of  $^{235}\text{U}$  to  $^{238}\text{U}$  has become smaller over time and present-day quantity uranium is made up of only 0.72 percent  $^{235}\text{U}$  in the ore.

Small amounts of  $^{99}\text{Tc}$  that occur environmentally originate from the decay of the short-lived medical radioisotope  $^{99\text{m}}\text{Tc}$  (6.0058 h half-life), which decays by isomeric transition to technetium-99 [11]. Number of the longer-lived isotopes, such as  $^{95\text{m}}\text{Tc}$  and  $^{99\text{m}}\text{Tc}$ , have a plethora of research applications, especially in the medical field.

The greatest source of  $^{99}\text{Tc}$  is its artificial production by neutron-induced fission. The fission yield of  $^{99}\text{Tc}$  is 6.06 percent and one ton of  $^{235}\text{U}$ -enriched fuel (3% enrichment) will produce 1 kg of  $^{99}\text{Tc}$  at a typical burn up rate [12].  $^{99}\text{Tc}$  is produced in large amounts by nuclear fission of  $^{235}\text{U}$  or  $^{239}\text{Pu}$  in nuclear reactors in comparison to spontaneous fission of  $^{238}\text{U}$  in the Earth's crust or by decay of  $^{99}\text{Mo}$  in nature [13]. The fission of  $^{235}\text{U}$  produces a spectrum of fission products including  $^{99}\text{Mo}$ ,  $^{131}\text{I}$ , and  $^{133}\text{Xe}$ . These fission products are produced in the same proportions to each other whether highly enriched uranium or low enriched uranium targets are used. All these isotopes can be recovered when the targets are processed to obtain  $^{99}\text{Mo}$  [14].

Reprocessing of spent uranium fuel rods to recover  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and other fissile elements is the chief means by which Tc becomes part of the waste stream. Technetium has found its way into the environment over the last 40 years principally through the approved or accidental discharge of processing fluids [15].

$^{99}\text{Tc}$  can be also produced by thermal neutron induced fission of  $^{235}\text{U}$  with a relatively high accumulated fission yield of 6.1%, making  $^{99}\text{Tc}$  relatively high abundant among fission products [16, 17]. The decay of  $^{99}\text{Mo}$  is shown graphically on Figure 1.

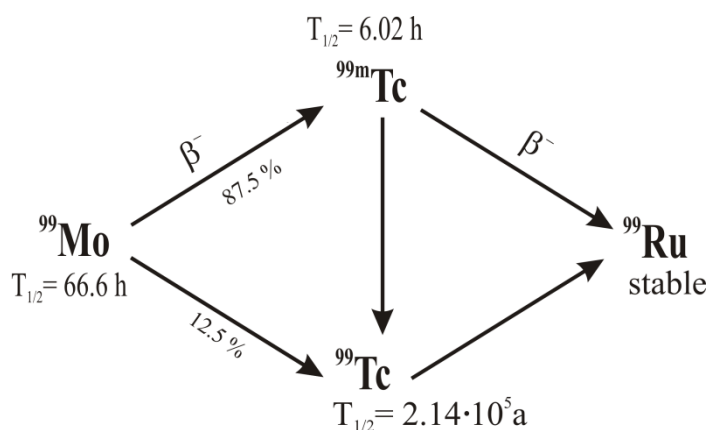
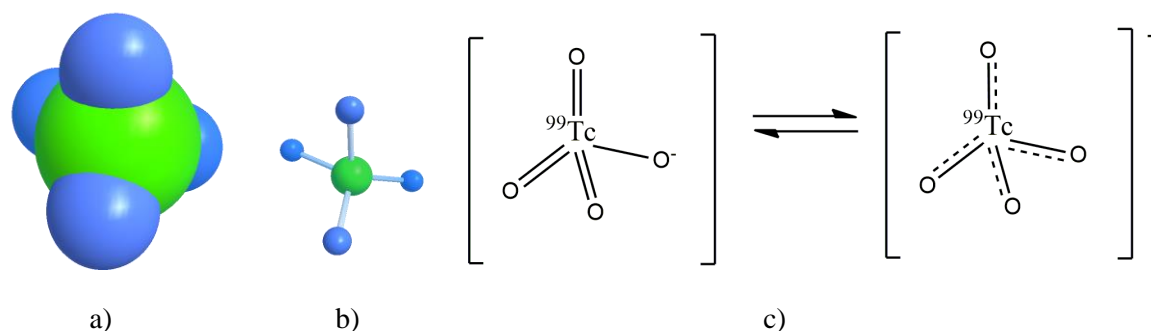


Figure 1. Decay scheme of  $^{99}\text{Mo}$

The predominant form of technetium is  $\text{Tc}_2\text{O}_7$ , which rapidly reacts with water vapor to form pertechnetic acid ( $\text{HTcO}_4$ ). Technetium sorbs onto particles in the atmosphere and settles through precipitation. The nuclear weapons industry is also responsible for increasing the amount of radioactive waste producing hundreds of tons of plutonium during the Cold War and the generation of over 300 million liters of hazardous liquid wastes among which hundreds of liters of  $^{99}\text{Tc}$  liquid waste [18-20].

Dissolution of U during reprocessing and fluorination to produce  $\text{U(VI)F}_6$  also produces fluoride complexes of Tc, such as  $\text{Tc(VI)F}_6$  and  $\text{Tc(VII)O}_3\text{F}$ , with the former more abundant than the latter. Although these species are volatile and potentially mobile to the atmosphere, most of the contamination caused by technetium fluorides is due to accidental release into water, where it hydrolyzes and disproportionates into Tc(IV) and Tc(VII). In localities where gaseous diffusion operations occurred, such as Paducah, Kentucky, and Oak Ridge, Tennessee, nearly 97.5 percent  $^{99}\text{Tc}$  was discharged to the environment through aqueous solution and only 2.5 percent by gaseous pathways [21].



**Figure 2.** Pertechnetate anion. Different views: space-filling model (a), stick and ball model (b), and structure view (c).

## 2. Technetium in the environment

Besides pertechnetate oxyanion ( $\text{TcO}_4^-$ ), the tanks with nuclear waste also contain other oxyanions of concern, such as chromate ( $\text{CrO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ), which can form spinels thus weakening the integrity of the vitrified waste glass and provoke leaching of the radioactive waste from the tanks used for disposal. After several incidents around the world, these radioactive materials entered the groundwaters and caused aquatic contamination. High toxicity, non-biodegradability, and mobility of oxyanions have become an urgent challenge that resulted in putting oxyanions in the Environmental Protection Agency, U.S. (EPA) priority pollutant list. Therefore, the importance of treatment of industrial wastewater containing oxyanions before their discharge into the water resources is of great importance to avoid detrimental effects on living organisms after exposure to higher concentrations of oxyanions.

Transport of radionuclides to the geosphere is generally controlled by their solubility and possible sorption onto surrounding materials. It is highly soluble in surface and near-surface environments. It is known that Tc is not sorbed on negatively charged surfaces such as layered silicate [22]. The retention of Tc in soils is enhanced however, by the presence of organic materials whereas the sorption of Tc in soils containing low amounts of organic materials is negligible [23, 24].

The most stable oxidation state of  $^{99}\text{Tc}$  under aerobic environments is the pertechnetate anion ( $\text{TcO}_4^-$ ) over a broad range of pH and Eh [25, 26]. Pertechnetate ( $\text{TcO}_4^-$ ) will not be significantly sorbed by anions colloids and suspended sediments and is therefore highly mobile under aerobic conditions. However, physical, chemical, and biological processes can strongly influence the fate of Tc [27].

In aqueous solutions technetium may exist in the valence states + 7, + 4, and 0 [28, 29]. Standard redox potentials of Tc species in aqueous solution are lower than the  $\text{O}_2/\text{H}_2\text{O}$  redox couple (1.23 V), thus, the spontaneous oxidation by air of Tc species in the intermediate oxidation states (i.e.,  $\text{Tc}^{\text{IV}}$  to  $\text{Tc}^{\text{VII}}$ ) is thermodynamically favorable [30]. In non-complexing media,  $\text{Tc}^{\text{V}}$  and  $\text{Tc}^{\text{VI}}$  are thermodynamically unstable and disproportionate to  $\text{Tc}^{\text{IV}}$  and  $\text{Tc}^{\text{VII}}$  species.

However, Tc(VII) is reducible to lower valence states by Zn, HCl, hydrazine, hydroxylamine, ascorbic acid, tin(II) chloride, and dilute sulfuric acid [31].

To avoid the usage of a radioactive element at high concentrations for laboratory testing and development, Tc can be replaced by studying non-radioactive rhenium ( $^{75}\text{Re}$ ), its chemical analogue [32].

### 2.1. Determination of $^{99}\text{Tc}$

Technetium is silvery-gray coloured metal which tarnishes slowly in moist air. It dissolves in  $\text{HNO}_3$ , aqua regia, and concentrated  $\text{H}_2\text{SO}_4$ , but is not soluble in any strength of HCl solution [40]. Chemical separation combined with radiometric and mass spectrometric measurement techniques, has been developed for the determination of  $^{99}\text{Tc}$  in different environmental samples [34]. Pre-treatment of solid samples consists of drying and ashing, alkali fusion, and combustion. Until then, water

samples are only filtered and acidified. Further treatment for both types of samples is the same and consists of pre-concentration by precipitation, evaporation, or ion exchange. After chemical separation like solvent extraction, ion exchange, or extraction chromatography, measurement of samples was provided by  $\beta$  counting or ICP-MS. Several new ion-selective electrodes for the electrochemical determination of  $^{99}\text{Tc}$  were recently presented [35-37].

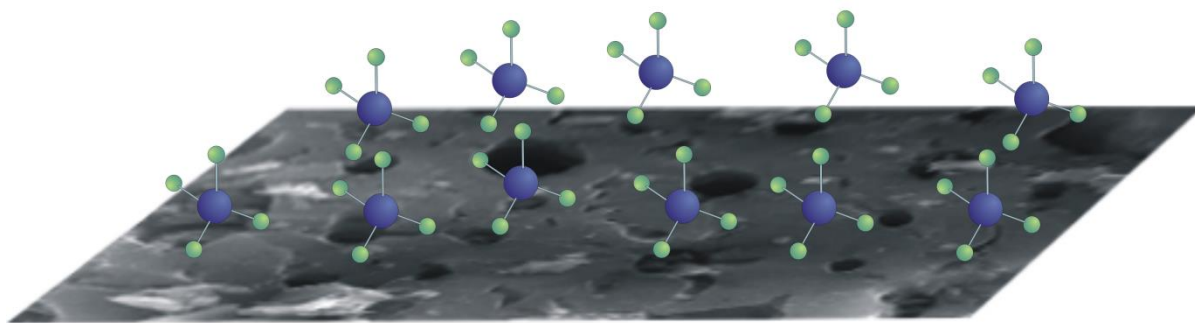
## 2.2. Removal of technetium

Removal of  $^{99}\text{Tc}$  from contaminated soil and groundwater is very difficult because of the influence of other anions presented in the environment. Sorption was and still is one of the most popular and widely used methods for removing heavy metals from the environment. Sorption of  $^{99}\text{Tc}$  on activated carbon was investigated [38-40], as well as various synthetic resins and sponges [41,42], elemental iron [43], magnetic iron sulphide material [44], organic polymers [45], chitin, chitosan [46-48] and commercial resins [49-50].

### 2.2.1. Organic materials for removal of pertechnetate

A simple and effective technology to remediate Tc (as  $\text{TcO}_4^-$ ) contaminated groundwaters was proposed by Gu et al. [51]. *Purchased granular activated carbon* was only washed with purified water (Milli-Q) by repeated decanting and sedimentation to remove fine carbon particles and then air dried and stored in a plastic bottle. Batch sorption of  $\text{TcO}_4^-$  on activated carbon was performed in various background electrolyte solutions including 0.01 M  $\text{CaCl}_2$ , 0.01 M  $\text{NaNO}_3$ , 0.01 M  $\text{Na}_2\text{SO}_4$ , Na-salicylate, and phthalate at pH - 6.5. The conclusion was that activated carbon adsorbs  $\text{TcO}_4^-$  selectively and effectively over a wide range of pH values and from various dilute electrolyte solutions.

Demir *et al.* [42] also used *activated carbon* as an adsorbent to remove  $^{99\text{m}}\text{TcO}_4^-$  from an aqueous solution. Although there is no explanation why  $^{99\text{m}}\text{Tc}$  was used instead of  $^{99}\text{Tc}$ , the assumption is that it is due to easier measurement of gamma radiation. They reported good adsorption capacity value obtained from the Langmuir isotherm model.



**Figure 3.** Schematic representation of the adsorption of pertechnetate anions on the modified carbon surface

Hexadecylpyridinium chloride monohydrate modified bentonite (HDPy-bent) was synthesized and used as an adsorbent to remove  $^{99}\text{TcO}_4^-$  [52]. The adsorption behaviours of  $\text{ReO}_4^-$  as an analogue for  $\text{TcO}_4^-$  were investigated as functions of contact time, solution pH, initial concentration, and competing anions using batch techniques. Research demonstrated that the HDPy-bent showed an excellent adsorption ability for  $\text{ReO}_4^-$  at the pH range of 2–11, fast adsorption kinetic (reaching equilibrium within 3 min at room temperature), and maintained desirable  $\text{ReO}_4^-$  adsorption in the presence of concomitant anions at an excessive concentration of 500 times ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ). As for the adsorption mechanism, the authors propose the anion exchange process at a low concentration of Re(VII) and precipitation reaction at a high concentration.



Chromatographic Experiments Flowsheet Feasibility Studies Using *ABEC Resins* for Removal of Pertechnetate from Nuclear Wastes was proposed by Bond *et al* [53]. The chromatogram in which  $^{99}\text{TcO}_4^-$  was loaded from 4.0 M NaOH was collected using a modified formulation of the gel-type resin ABEC G2. This material was prepared in a 110 L reactor using Me-PEG-2000, 2% divinylbenzene (DVB), and 10% vinyl benzyl chloride (VBC) in diglyme.

Some commercially available resins {Amberlite IRA-904 and IRA-900 (Rohm and Haas), Reillex HPQ (Lot 40404AD) from Reilly Industries, Inc., Indianapolis, IN; Purolite A-520E and A-850 from The Purolite Company, Bala Cynwyd, PA; and Sybron Ionac SR-6 and SR-7 from Sybron Chemicals, Inc., Birmingham}, were compared with laboratory synthesized resins based on divinylbenzene-cross-linked poly(vinylbenzyl) chloride in their efficiency for pertechnetate removal [54]. The authors reported that the 24-h *K<sub>d</sub>* for the synthesized bifunctional resins is the highest, being approximately twice the 24-h *K<sub>d</sub>* of any commercial resin and 50% better than any of the laboratory-prepared monofunctional resins.

Further,  $\text{ReO}_4^-$  and  $^{99}\text{TcO}_4^-$  removal from aqueous solutions using a *polyethylenimine-epichlorohydrin resin* was investigated in the absence and presence of background electrolyte (0.01 and 0.50 M NaCl) [55]. The investigated polyethylenimine-epichlorohydrin resin showed a strong tendency to remove significant amounts of perrhenate and pertechnetate ions (up to 4.9 mmol/g resin) from aqueous solutions in the absence and presence of competing ions ( $[\text{Cl}^-] \leq 0.5$  M) over a wide pH-range ( $2.3 \leq \text{pH} \leq 8.9$ ). The sorption of  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$  anions is pH and  $[\text{Cl}^-]$ -dependent, with the highest capacity and *R<sub>d</sub>* values observed for  $\text{pH} \leq 4.4$  and  $[\text{Cl}^-] \leq 0.01$  M.

A new anion exchanger with pyridine groups was prepared by grafting *2-vinyl pyridine* onto polypropylene nonwoven fabrics by pre-irradiation grafting technique, followed by quaternization of pyridine rings in grafted chains in reaction with bromoethane [56]. The results showed that the grafting yield increased with the monomer concentration and the conversion ratio of quaternization increased with time. The possibility of adsorption of perrhenate, as a nonradioactive analogue to pertechnetate, from an aqueous solution by an anion exchanger was investigated. The experiments performed at  $\text{pH} = 0.1-6$  showed that  $\text{pH} = 2.2$  was the optimal acidity for  $\text{ReO}_4^-$  adsorption and adsorption equilibrium was achieved in 30 min. The reaction enthalpy was  $-12.55$  kJ/mol, indicating that the adsorption process is exothermic. XPS tests indicated that the  $\text{ReO}_4^-$  uptake was a typical ion exchange between  $\text{Cl}^-$  anion exchanger and  $\text{ReO}_4^-$ .

Katayev *et al.* considered the possibility of using *organic molecules* that are used as radiopharmaceuticals to remove Tc [57]. The most effective way, according to them, to achieve strong binding in aqueous environments is to exploit Coulombic interactions. Using soft acids, such as low charge density cations, e.g., metal-based receptors, CTVs, polycations, phosphonium-based receptors or structures containing guanidinium sites is the best way of binding soft bases such as perrhenate and pertechnetate anions.

A class of *two-dimensional nanostructured anionic clays* named Layered double hydroxides (LDH) was also used for the removal harmful oxyanions such as arsenate, chromate, phosphate, pertechnetate, etc. from contaminated waters [58]. Calcined Mg-Al LDHs and uncalcined Mg-Al LDHs were the most used materials for the removal of pertechnetate and perrhenate oxyanions [59-62].

### 2.2.2. Inorganic materials for removal of pertechnetate

Also, different inorganic materials for selective separations have become abundant in the nuclear industry. Glassy, nanocrystalline *antimony-doped hydrous tin dioxide* was used for butch experiments and after 24 h achieved almost quantitative removal of Tc from solutions. The material obtained by alkali precipitated from an acidic metal chloride solution has good thermal stability and granular physical form that enables its use in a conventional column [63]. It shows excellent, almost quantitative, uptake properties for  $^{99}\text{Tc}$  radionuclide.

*Manganese oxide* nanoparticles loaded into activated carbon were presented as an improved method for pertechnetate sorption [64]. Composite was formed by co-precipitation by loading a nanoparticle into a modified activated carbon by different ratios.

$^{99}\text{Tc}$  radionuclide (activity 257.4 CPM/ml) was extracted from residual  $^{99\text{m}}\text{Tc}$  columns from the technetium generator used in nuclear medicine centers. Batch experiments were performed with 0.05

mg of sorbent which was added to 5 ml of radioactive waste solutions in a polypropylene centrifuge tube. The synthesized composite during a contact time of 60 minutes gave a higher adsorption efficiency of about 93% compared to nano manganese oxide and activated carbon whose efficiency was about 40%. Isotherms belonged to Freundlich model, the adsorption data followed the pseudo-second order model and the thermodynamic study indicated that the adsorption of nanocomposites was an exothermic and spontaneous process.

Low-cost adsorbents, *magnesium ferrite* ( $\text{MgFe}_2\text{O}_4$ ) nanoparticles were synthesized using three different types of fuels such as urea, oxalic acid, and citric acid via sol-gel auto-combustion method [65]. Batch experiments were carried out to examine the sorption of pertechnetate, from aqueous solution by the synthesized nano  $\text{MgFe}_2\text{O}_4$ . The results revealed that the  $\text{MgFe}_2\text{O}_4$  nanostructure has a high removal ability of  $^{99}\text{TcO}_4^-$  from aqueous solutions (98.84%). The adsorption data were in good agreement with Freundlich and pseudo second-order isotherm models. The adsorption process was a chemisorption reaction, additionally, the results of the thermodynamic parameters indicated that the adsorption of  $^{99}\text{TcO}_4^-$  on nanostructures was an exothermic and spontaneous process.

*Pyrite* nanoparticles were prepared by ball milling in the presence of ethanol resulting in pyrite nanoparticles capable for immobilization of  $\text{ReO}_4^-$  [66]. They offer much greater (>200 times) reduction reactivity for perrhenate than micron-scale particles due to the increased specific surface area and distortion of the crystalline lattice of the materials. The raw bulk pyrite was practically unreactive for perrhenate reduction. A much greater reduction rate and extent of  $\text{ReO}_4^-$  were observed under alkaline conditions. The favorable formation of composite ferrite and iron (hydro)xides under alkaline conditions plays important roles in the enhanced immobilization reactions. The column test data revealed that the pyrite nanoparticles may be used in a packed wall or permeable barrier configuration for in situ reductive immobilization of  $\text{ReO}_4^-$ . Compared to the loess soil, the water-leachable  $\text{ReO}_4^-$  was reduced by 44%.

*Cementitious waste technology* (CWT) has been considered for immobilizing pertechnetate,  $\text{Tc(VII)O}_4^-$ , in brine and alkaline waste solutions, as  $\text{Tc(IV)}$  oxides and/or sulfides with the use of reducing agents like slag [67]. Also, zero-valent iron (ZVI) was evaluated as a potential reducing agent in CWT as a function of pH using perrhenate,  $\text{Re(VII)O}_4^-$ , as an analogue for  $\text{Tc(VII)O}_4^-$ . Considering the thermodynamically favourable reduction of  $\text{Tc(VII)}$  over  $\text{Re(VII)}$ , ZVI might have the potential for improving the reduction capacity of the current CWT. The results of this study provide insight towards the use of ZVI particles in cementitious waste technology to immobilize  $^{99}\text{Tc}$ .

Generally, much of the  $^{99}\text{Tc}$  at SRS is cast into a *cementitious low-level waste form*, referred to as “saltstone”, whereas at the Hanford site, both the high and low-level fractions will be immobilized into a borosilicate glass waste form a process known as vitrification [68]. Technology for *vitrification* of low-activity waste – primarily  $^{99}\text{Tc}$  was described by Kathryn *et al* [69]. Tc removal via reductive precipitation with stannous chloride to examine the potential for diverting this stream to an alternate disposition path was investigated.

*Nanoscale zero-valent iron* (NZVI) supported on layered double hydroxide (LDH) was a composite applied for the reductive immobilization of  $\text{Re(VII)}$  [70]. The synergistic effect can be seen in the fact that LDH could promote a complete reduction of  $\text{Re(VII)}$  into  $\text{Re(IV)}$  by NZVI, while sorption and reduction occurred simultaneously on bare NZVI. As a scavenger for the coexisting anions, sparingly soluble products and pH buffering of LDH improve the reactivity of NZVI. The authors assumed that the immobilization performance of NZVI/LDH will provide a promising strategy for the decontamination of  $\text{Tc(VII)}$  from groundwater.

Li and Wang focused on a remediation strategy for the reduction of pertechnetate ( $\text{TcO}_4^-$ ) by nanoscale *zero-valent iron* particles supported on graphene [71]. The results demonstrated that NZVI/rGOs could efficiently remove Re from the aqueous solution, with enhanced reactivity, improved kinetics (50 min to reach equilibrium), and excellent removal capacity (85.77 mg/g). Mechanisms of Re immobilization by NZVI/rGOs included adsorption and reduction, which are significant to the prediction and estimation of the effectiveness of reductive  $\text{TcO}_4^-$  by NZVI/rGOs in the natural environment.

### 2.2.3. Metal-organic frameworks (MOFs) as inorganic-organic hybrid porous crystalline materials for removal of pertechnetate

*Metal-organic frameworks* (MOF) are compounds of metal ions and organic molecules that form structured frameworks [72]. These advanced materials can be compared with sponges with unique abilities – being able to take-up, hold, and release molecules from their pores. With a highly ordered framework of pores, metal-organic frameworks exhibit the largest surface areas per gram (about 7000 m<sup>2</sup>/g of MOF material). Banerjee with co-workers reported ReO<sub>4</sub><sup>-</sup> exchange properties of a protonated amino-functionalized MOF, UiO-66-NH<sub>3</sub><sup>+</sup>, in an aqueous solution in the presence of other competing anions [73]. The material has an uptake capacity of 159 mg/g, which is significantly higher than that of traditional inorganic materials such as layered double hydroxides.

A three-dimensional water-stable cationic *MOF* pillared by a neutral ligand and with Ni(II) metal nodes has been synthesized employing a rational design approach [74]. Owing to the ordered arrangement of the uncoordinated tetrahedral sulfate (SO<sub>4</sub><sup>2-</sup>) ions in the channels, the compound has been employed for aqueous-phase ion exchange applications. The compound exhibits rapid and colorimetric aqueous-phase capture of environmentally toxic oxoanions (with similar geometries) in a selective manner. This system is the first example of a MOF-based system that absorbs both dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) and permanganate (MnO<sub>4</sub><sup>-</sup>) ions, with the latter acting as a model for the radioactive contaminant pertechnetate (TcO<sub>4</sub><sup>-</sup>). MOF containing free SO<sub>4</sub><sup>2-</sup> ions is an unusual example of a MOF-based dual adsorbent for permanganate ions and the environmental pollutant dichromate, with the former acting as a model for the radioactive contaminant pertechnetate (TcO<sub>4</sub><sup>-</sup>). In comparison with other MOF-like systems, this compound exhibits a moderately high uptake capacity of about 166 mg g<sup>-1</sup> for Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions.

Three-dimensional cationic *metal-organic framework material*, SCU-100, was used by Sheng, *et al.* for removing TcO<sub>4</sub><sup>-</sup> [75]. Initial anion exchange studies show that SCU-100 can both quantitatively and rapidly remove TcO<sub>4</sub><sup>-</sup> from water within 30 min. The exchange capacity for the surrogate ReO<sub>4</sub><sup>-</sup> reaches up to 541 mg/g and the distribution coefficient K<sub>d</sub> is up to 1.9×10<sup>5</sup> mL/g, which is significantly higher than all previously tested inorganic anion sorbent materials. More importantly, SCU-100 can selectively capture TcO<sub>4</sub><sup>-</sup> in presence of large excess of competitive anions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>). The sorption mechanism showed that the sorbed ReO<sub>4</sub><sup>-</sup> anion is able to selectively coordinate to the open Ag<sup>+</sup> 36 sites, forming Ag-O-Re bonds and a series of hydrogen bonds.

An efficient and cost-effective way for the removal of radioactive pertechnetate anions from nuclear waste was proposed by Banerjee *et al* [76]. A series of functionalized hierarchical porous frameworks were evaluated for their perhenate removal capacity in the presence of other competing anions. Functionalized PAF-1, namely PAF-1-F showed the best uptake performance, with 97% ReO<sub>4</sub><sup>-</sup> removal within the first 24 h. Such performance is significantly better than other reported materials including traditional inorganic materials and protonated UiO-66-NH<sub>2</sub>.

The protonated version of an ultrastable *zirconium-based metal-organic framework* of the chemically robust MOF UiO-66-NH<sub>2</sub> can adsorb perhenate (ReO<sub>4</sub><sup>-</sup>) anions, a nonradioactive surrogate for TcO<sub>4</sub><sup>-</sup>, from water even in the presence of other common anions aqueous medium even in the presence of other competing anions [77]. The material has an uptake capacity of 159 mg/g, which is significantly higher than that of traditional inorganic materials such as layered double hydroxides.

Hydrolytically stable and radiation-resistant cationic metal-organic framework, SCU-101, that has extremely fast removal kinetics, exceptional distribution coefficient, and high sorption capacity towards TcO<sub>4</sub><sup>-</sup> was reported by Zhu *et al.* [78] This material can selectively remove TcO<sub>4</sub><sup>-</sup> in the presence of large excesses of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, as even 6000 times of SO<sub>4</sub><sup>2-</sup> in excess does not significantly affect the sorption of TcO<sub>4</sub><sup>-</sup>.

### 3. Conclusion

It can be concluded that measurable amounts of <sup>99</sup>Tc in the environment can be found after the nuclear reaction of <sup>235</sup>U or <sup>239</sup>Pu fission, whether they originate from nuclear reactors or nuclear explosions. Particle accelerators, such as linear accelerators or cyclotrons, although they provide the

possibility of different ways to obtain  $^{99}\text{Tc}$ , they produce insignificant amounts of this isotope. Here was also mentioned the existence of “natural reactors”, where  $^{99}\text{Tc}$  is produced by spontaneous fission of  $^{238}\text{U}$ .

In the environment,  $^{99}\text{Tc}$  is presented as oxyanion ( $\text{TcO}_4^-$ ) because solubility drastically decreased by the reduction of Tc(VII) to Tc(IV), where Tc(IV) exists in the sparingly soluble form of  $\text{MO}_2 \cdot n\text{H}_2\text{O}$ . Many authors used perrhenate ( $\text{ReO}_4^-$ ) anions, a nonradioactive surrogate for  $\text{TcO}_4^-$ , to avoid the complication of directly working with radioactive elements. Technetium and rhenium both belong to the VIIB subgroup, share the same configuration of extra-nuclear electrons, have similar chemistry, and are commonly present as oxyanions ( $\text{MO}_4^-$ ) in aqueous solutions.

The abundant literature that describes the removal of  $^{99}\text{Tc}$  from water and soil gives a good basis for practical actions if it is necessary to carry out the cleaning of contaminated environment and soil. The most popular and widely used method for removing heavy metals from the environment was sorption on activated carbons and synthetic resins. Most of the carbons and synthetic resins are of commercial origin and have been used by researchers with minimal preparation. More recent studies have included elemental iron, iron sulphide material, organic polymers, chitin, and chitosan. Results of sorption on different materials ranged from 90 to 99%, but the selectivity was weak. The adsorption data in most sorption experiments were in good agreement with Freundlich and Pseudo second order isotherm models. The results of the thermodynamic parameters (where there are) indicated that the adsorption of  $^{99}\text{TcO}_4^-$  on nanostructures of different origins, whether organic or inorganic or MOFs, was an exothermic and spontaneous process. Cementitious waste technology and vitrification were proposed methods for the permanent disposal of radioactive materials.

Recent works attempt to unravel the mechanism of  $^{99}\text{TcO}_4^- / \text{ReO}_4^-$  sorption and determine the position of the adsorbed oxyanions within the sorbents. Comparing sorbents according to their efficiency is very unreliable because the experiments were performed in different conditions. All experiments were carried out at room temperature, but their duration was different. Most of them were batch experiments (without automation), which varied in duration, from a few hours to the whole day, to establish a steady-state equilibrium. The working procedures were simple: samples suspensions usually were shaken, then centrifuged in order to separate the solutions from the remains. Results of sorption on different materials ranged from 90 to 99%. The influence of other anions presented in the environment makes the separation of  $^{99}\text{Tc}$  much more difficult and only a few works included the separation in addition to chlorides, nitrates, sulfates, etc.

The various materials that have been described give us different options for efficient collection and concentration of radioactive  $^{99}\text{Tc}$  that could eventually be removed and safely disposed.

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