Characterization of Sn-Apatites and $^{99m}TcO_4^-$ anions removal from aqueous solutions

Andrea Hamárová, Oľga Rosskopfová

Comenius University, Faculty of Natural Sciences, Department of Nuclear Chemistry, Ilkovičova 6, Mlynská dolina, 842 15 Bratislava, Slovenská republika
hamarova17@uniba.sk

Abstract: Apatite is a natural mineral from the group of phosphate minerals. It originates primarily in rocks and converted limestones. It is also one of the few minerals produced and used by microeconomic systems. Due to its low solubility in water and high sorption capacity, apatite is a suitable sorbent for heavy metals and radionuclides removal from aqueous radioactive waste. Increasing amount of radioactive waste (RAW) has a negative impact on human health as well as on the environment. Production of RAW is constantly increasing because of the use of nuclear energy as well as by the development of nuclear medicine.

The aim of this work was to study the effect of pH and various anions on the sorption of pertechnetate anions from aqueous solution to Sn-Apatite. Sn-Apatite samples used in the experiment were prepared by the wet precipitation method and adsorption of ^{99m}Tc was monitored by the radioisotope indication method. Sorption experiments were performed using the batch method. It was found that the sorption percentage was higher than 90 % in all Sn-Apatite samples and the dissociation constant, K_D, indicated high affinity of pertechnetate anions to the solid Sn-Apatite particles. The presence of competing anions did not significantly influence the ability of Sn-Apatite materials to adsorb $^{99m}TcO_4^-$ from aqueous solutions.

Key words: apatite, stannous ion, pertechnetate ion, sorption, aqueous solutions

Introduction

Increase in liquid or solid radioactive waste (RAW) has negative impact on human health as well as on the environment. Production of this waste constantly increases because of the use of nuclear energy and also due to the development of nuclear medicine.

Apatite is a natural mineral which belongs to phosphate minerals formed in rocks and converted limestones. Apatite is one of the few minerals produced and used in microelectronic systems and it is a suitable sorbent for the removal of heavy metals and radionuclides from liquid waste thanks to its special properties such as high chemical stability, low solubility in water, high specific surface area, high sorption capacity and buffering properties. Apatite can be prepared by various methods such as the precipitation method, hydrothermal synthesis, microwave synthesis, sol-gel method, microemulsion method, emulsion method, solid state method, spray-drying method, etc. (Rosskopfová et al., 2010; Hamárová, 2016). The most common method used to prepare synthetic apatite is the wet precipitation method in which cations and anions react in an aqueous medium to form an insoluble substance — clots (Rosskopfová et al., 2010).

Synthetic apatite consists of particles differing in their morphology, crystallinity, porosity, specific surface area and size. Apatites form large monocrystals but they may also have the size of nanoparticles. All properties of synthetic apatite depend on its use (Viswanath et. al, 2008).

Tin belongs to heavy metals and is most stable in the oxidation stages II and IV. Stannous ions belong to the strongest reducing agents. Sn ions are used as reducing agents in ^{99m}Tc chemistry. Sn (II) reduces ^{99m}Tc (VII) to ^{99m}Tc (IV) while being oxidized from oxidation stage II to IV. Sn (II) also interacts well with complex ligands such as OH^-, F^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}.

In addition, these ions react with halogens, Se, Te, HNO_3, etc. (Technical Reports Series No. 466., 2008). Dangerous radionuclides for the environment are mainly long-range radionuclides and radionuclides with long half-life. These radionuclides are often referred to as *millennial radionuclides*. Critical radionuclides include also ^{99}Tc, which is produced for example by bombarding Mo with deuterons (Pivarčiová et al., 2016). Technetium is a major component of nuclear waste because of its high fission yield (6 %) and relatively high half-life. Determination of ^{99}Tc in environmental and technological specimens is a very challenging task. It is mainly determined in RAW, corrosive products, processed uranium fuel and environmental samples (Paučová, 2013). It enters to the environment also in form of the ^{99m}Tc isotope. Technetium is used in nuclear medicine — PET, SPECT, etc., which are imaging techniques used to diagnose brain, thyroid,

heart, lung, bone diseases. It is used mainly for its high ability to bind to biologically active molecules (Zolle, 2007).

In this work, sorption properties of Sn-Apatites sorbents were studied together with the influence of pH and competing anions on $^{99m}TcO_4^-$ sorption on Sn-Apatite; point zero charge (pHpzc) of the studied molecules was also determined.

Material and Methods

Chemicals

All used chemicals were of p.a. purity and obtained from Lachema n.p., Czech Republic and Slavus s.r.o., Slovak Republic. The ^{99m}Tc radioisotope was obtained from an $^{99}Mo/^{99m}Tc$ DRYTEC generator (2.5—100 GBq), GE Healtcare, @ 1200 GMT.

Preparation of Sn-Apatites (ApA–ApE) by reaction of SnCl₂ with H₃PO₄, Na₂HPO₄ and K₂HPO₄

Sn-Apatites were prepared by mixing stannous chloride with phosphoric acid resp. sodium or potassium phosphate (Table 1). Calculated amounts of $SnCl_2 \cdot 2H_2O$ were added to H_3PO_4, Na_2HPO_4 resp. K_2HPO_4 to maintain the Sn/P ratio of 1.67. Solutions of H_3PO_4, K_2HPO_4 resp. Na_2HPO_4 were added to the $SnCl_2$ solution using a flow pump at the flow rate of 5 ml·min⁻¹. pH of the stannous chloride solution was adjusted to 8.5—9 with sodium hydroxide resp. potassium hydroxide solution. The apatite samples were precipitated at 85 °C and the apatite-clots were filtered and washed with distilled water. Sorbents were dried at 70 °C for 6 hours. Finally, the samples were homogenized to fine powders. Each Sn-Apatite sample was prepared under aerobic conditions.

Adsorption experiments

Adsorption of technetium-99m to Sn-Apatite was determined by the radioindication method. ^{99m}Tc in the form of $^{99m}TcO_4^-$ was used as a radioisotope indicator. Sorption experiments were performed by a batch method in plastic plugs with stoppers. Ratio of the solid and liquid phases was 1:100. To 20 mg of the sample, 2 ml of the aqueous phase were added. Both phases were mixed for 60 minutes on a Multi

Bio RS-24 laboratory extractor at 35 rpm. After the adsorption, the samples were centrifuged for 10 minutes at 6000 rpm in a Hettich EBA 20 type centrifuge.

Then, aliquot volumes of the supernatants were taken for the measurements, which were performed on a 1470 Wizard, Perkin Elmer automated gamma computer. The relative measurement errors were <5 %. pH values were measured before and after the sorption using a WTW 720 inoLab pH meter.

The effect of pH on technetium adsorption was studied on ApA—ApE samples. The aqueous phases — distilled water, were labelled with radioactive $^{99m}TcO_4^-$ and the pH was adjusted to the desired values from 4 to 7 with 0.1 mol·dm⁻³ HCl resp. 0.1 mol·dm⁻³ NaOH.

The effect of competing anions on $^{99m}TcO_4^-$ adsorption on ApA—ApE samples was also studied. The aqueous phases were prepared from distilled water and NaClO₄, NaNO₃ or Na₂SO₄. Concentrations of anions in the solutions were in the range of $1 \cdot 10^{-1} - 1 \cdot 10^{-5}$ mol·dm⁻³. All solutions were labelled with $^{99m}TcO_4^-$.

Adsorption properties of Sn-Apatites were calculated applying the equations distribution coefficient, K_D [ml·g⁻¹] (eq. 1), and sorption percentage, R [%] (eq. 2).

$$K_D = \frac{c_0 - c_{eq}}{c_{eq}} \times \frac{V}{m} = \frac{a_0 - a}{a} \times \frac{V}{m} = \frac{n_0 - n}{n} \times \frac{V}{m} \quad (1)$$

$$R = \frac{100 \times K_D}{K_D + (\frac{V}{m})} \quad (2)$$

where c_0 is the initial concentration [mol·dm⁻³], c_{eq} is equilibrium concentration [mol·dm⁻³], V is volume of the aqueous phase [ml], m is mass of the sorbent [g], a_0 is volume activity of the initial solution [Bq·ml⁻¹] and a is equilibrium volume activity of the solution [Bq·ml⁻¹].

Methodology of pH_{pzc}

Point zero charges (pH_{pzc}) for ApA—ApE samples were determined by acid-base titration. Hydrochloric acid solutions with the initial pH of 3, pH 4 and pH 5 were prepared using 0.1 mol·dm⁻³ HCl.

Tab. 1. Used reagents; pH-adjustment solutions and color of the precipitated sorbent ApA—ApE.

samples		reactants		pH-adjusting solutions	apatite-color
	A	$SnCl_2 \cdot 2H_2O$	H_3PO_4	0,1 mol·dm⁻³ NaOH	pale-yellow
	B	$SnCl_2 \cdot 2H_2O$	H_3PO_4	1 mol·dm⁻³ NaOH	pale-yellow
Ap	**C**	$SnCl_2 \cdot 2H_2O$	Na_2HPO_4	1 mol·dm⁻³ NaOH	pale-yellow
	D	$SnCl_2 \cdot 2H_2O$	H_3PO_4	1 mol·dm⁻³ KOH	dark-grey
	E	$SnCl_2 \cdot 2H_2O$	K_2HPO_4	1 mol·dm⁻³ KOH	dark-grey

Sn-Apatite samples were added to the solutions and were titrated with 0.1 mol·dm⁻³ NaOH. pH was measured by the WTW 720 pH meter inoLab with pH semi-micro gel electrodes. The pH$_{pzc}$ values were determined from surface charge calculations applying equation (eq. 3).

$$\sigma = \frac{\Delta V \times 96500 \times c \times 0.001}{m \times S}; \ [C \cdot m^{-2}] \qquad (3)$$

where V is volume; $\Delta V = V_{sample} - V_{blank}$; [ml], 96500 [C·mol⁻¹] is the elementary charge of 1 mol of particles, *c* is titrant concentration; [mol·dm⁻³], 0.001 is constant, *m* is sample weight; [g], and *S* is the surface size; [m²·g⁻¹].

Results and Discussion

Harding et al. and Genesan reported that point zero charge (pzc) for hydroxyapatite is at pH 7.3. (Harding et al., 2005; Genesan, 2008). Skartsila and Spanos determined the pzc values for HA by potentiometric titration at pH 6.3 (Skartsila et al., 20017). The results of Rosskopfova show pH values determined in the range from 6.1 to 8.6 (Rosskopfová et al., 2010).

Table 2 shows point zero charge of the Sn-Apatite samples determined by acid-base titration and specific surface area (S$_{BET}$). Values of pH$_{pzc}$ of the Sn-Apatite samples in a solution of HCl with pH 3 were in range of 6.5−9.25; at pH 4, pH$_{pzc}$ values were in the range of 5.37−9.82 and at pH 5, in the range of 5.55−8.62 (Tab. 2; Fig. 1). Table 2 shows the most similar pH$_{pzc}$ values at pH 5 as reported by Rosskopfová et al. (2010).

pH of the solution is a very important parameter because it affects the adsorption processes. Upon a pH change, ionization of functional groups on the surface of apatite can occur and the solution
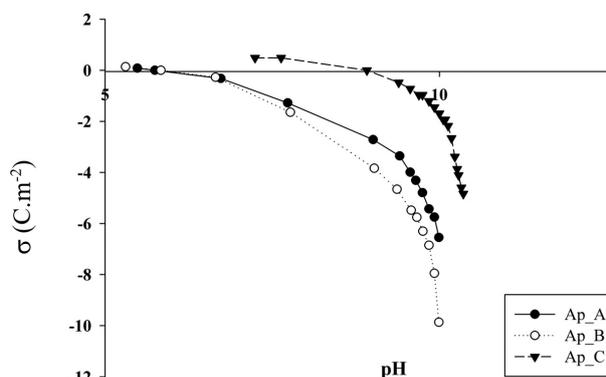
Fig. 1. Dependence of the surface charge, σ, at pH 5 for apatite samples: ApA, ApB and ApC.

Tab. 2. pH values for point zero charge (pH$_{pzc}$) of ApA−ApE at pH 3, pH 4 and pH 5.

samples		pH3	pH4	pH5
		σ = 0 C·m⁻²		
		pH$_{pzc}$	pH$_{pzc}$	pH$_{pzc}$
Ap4	A	6.15	5.99	5.55
	B	6.67	5.37	5.62
	C	9.25	9.82	8.62

composition can also change. At low initial pH values, protonization of the negatively charged P-O groups occurs and thus the pH increases. If the pH values are high, the apatite surface is deprotonated; H⁺ protons are released into the solution causing the drop of pH to lower levels. Conversely, negatively charged particles and neutral particles are predominant in alkaline environment (Technical Reports Series No. 466., 2008).

The effect of pH on pertechnetate ions sorption on ApA−ApE was determined. Sorption of ⁹⁹ᵐTcO₄⁻ was studied at pH 4, 5, 6 and 7. Figure 2 shows that
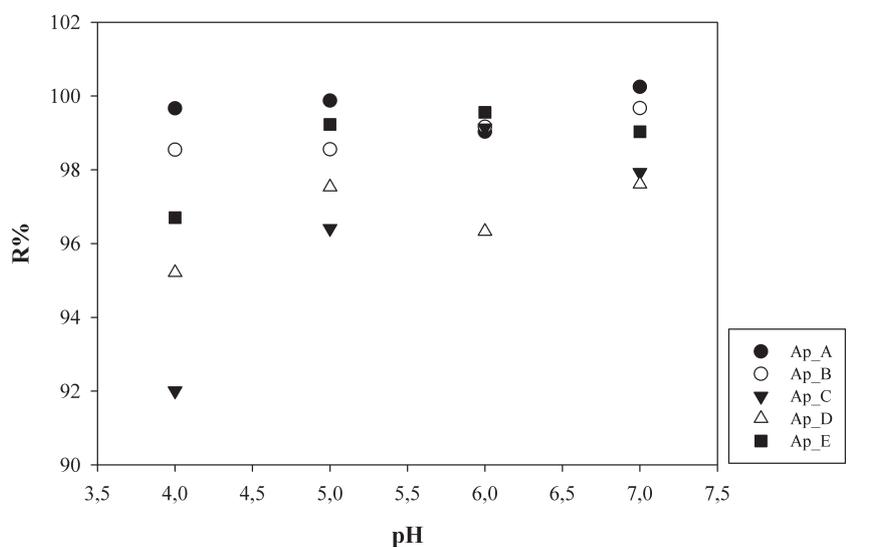
Fig. 2. Dependence of sorption percentage, *R* %, on pH for pertechnetate anion adsorption on ApA−ApE.

the sorption of $^{99m}TcO_4^-$ in all samples was higher than 92 % at all four pH values. Measurement errors were <5 %.

The presence of sulfate anions with the concentration of $1 \cdot 10^{-2}$ mol·dm^{-3} did not affect the sorption of $^{99m}TcO_4^-$ on Sn-Apatite. Sorption percentage for pertechnetate was in the range from 93.5 % to 99.7 % (Tab. 3). In general, sorption percentage decreases with the increasing concentration of sulfate ions in the order: ApE > ApA ≈ ApC ≈ ApD > ApB (Fig. 3). pH values before and after sorption of pertechnetate ranged from 5.5 to 6.5.
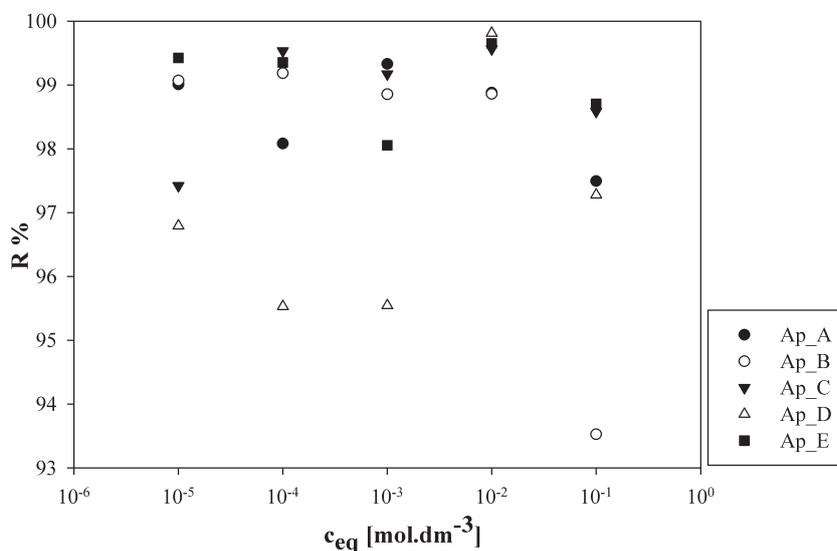
Fig. 3. Dependence of sorption percentage, R %, on SO_4^{2-} anions concentration, c_{eq}, for $^{99m}TcO_4^-$ sorption on ApA—ApE.

Tab. 3. Distribution constant, K_D, and sorption percentage, R %, for ApA—ApE samples in solution containing SO_4^{2-} ions.

c_{eq} [mol·dm^{-3}]	Ap_A		Ap_B		Ap_C		Ap_D		Ap_E	
	K_D	R %	K_D	R %	K_D	R %	K_D	R %	K_D	R %
$1 \cdot 10^{-1}$	3894	97.50	144	93.53	6959	98.58	3575	97.28	7622	98.70
$1 \cdot 10^{-2}$	88364	98.88	8681	98.86	22860	99.56	52816	99.81	28539	99.65
$1 \cdot 10^{-3}$	148514	99.33	8638	98.86	11959	99.17	2144	95.54	5039	98.05
$1 \cdot 10^{-4}$	51134	98.08	12169	99.18	21326	99.53	2137	95.53	15343	99.35
$1 \cdot 10^{-5}$	10003	99.01	10624	99.07	3778	97.42	3018	96.79	17288	99.42
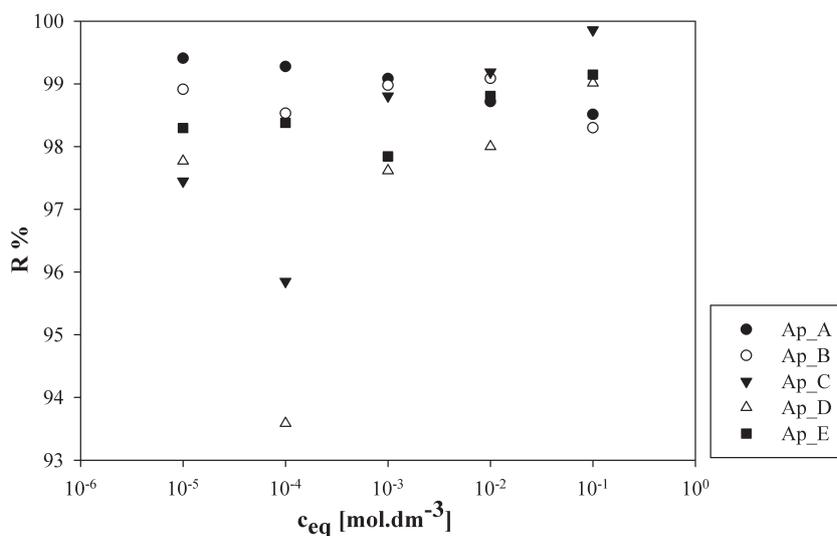
Fig. 4. Dependence of R % on c_{eq} of ClO_4^- anions for $^{99m}TcO_4^-$ sorption on ApA—ApE.

Tab. 4. Distribution constant, K_D, and sorption percentage, R %, for ApA—ApE samples in solution containing ClO_4^- ions.

c_{eq} [mol·dm^{-3}]	Ap_A		Ap_B		Ap_C		Ap_D		Ap_E	
	K_D	R %	K_D	R %	K_D	R %	K_D	R %	K_D	R %
$1 \cdot 10^{-1}$	6630	98.51	5783	98.30	70601	99.86	10039	99.01	11624	99.15
$1 \cdot 10^{-2}$	7697	98.72	10853	99.09	12198	99.19	4901	98.00	8289	98.81
$1 \cdot 10^{-3}$	10824	99.08	9677	98.98	8271	98.81	4095	97.62	4539	97.84
$1 \cdot 10^{-4}$	13701	99.28	6709	98.53	2310	95.85	1460	93.59	6066	98.38
$1 \cdot 10^{-5}$	16818	99.41	9095	98.91	3819	97.45	4380	97.77	5771	98.30
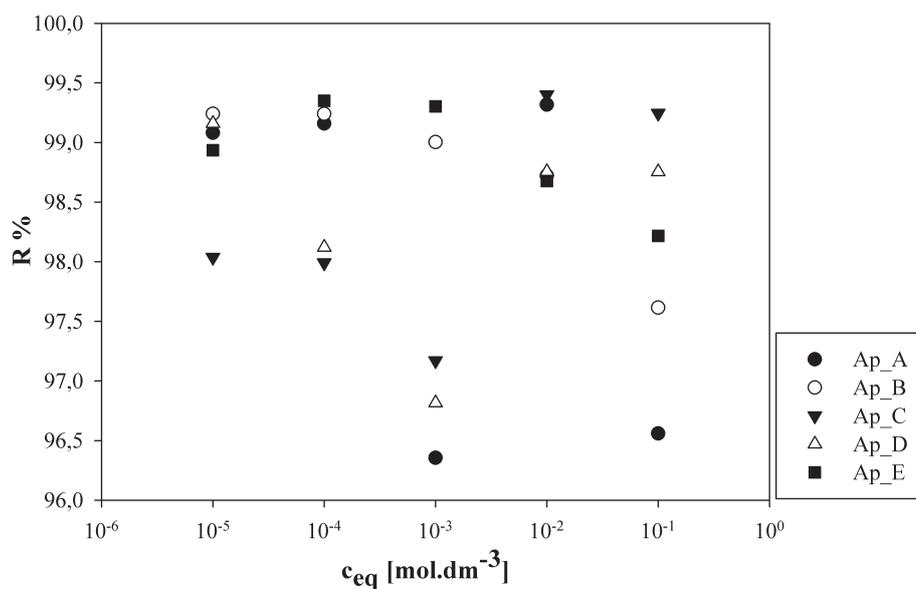
Fig. 5. Dependence of R % on c_{eq} of NO_3^- anions for $^{99m}TcO_4^-$ sorption on ApA—ApE.

Tab. 5. Distribution constant, K_D, and sorption percentage, R %, for ApA—ApE samples in solution containing NO_3^- ions.

c_{eq} [mol·dm^{-3}]	Ap_A		Ap_B		Ap_C		Ap_D		Ap_E	
	K_D	R %	K_D	R %	K_D	R %	K_D	R %	K_D	R %
$1 \cdot 10^{-1}$	2806	96.56	4092	97.61	13157	99.25	7924	98.75	5508	98.22
$1 \cdot 10^{-2}$	14557	99.32	7723	98.72	16552	99.40	7936	9876	7454	98.68
$1 \cdot 10^{-3}$	2644	96.36	9941	99.00	3433	97.17	3041	96.82	14234	99.30
$1 \cdot 10^{-4}$	11802	99.16	13077	99.24	4877	97.99	5222	98.12	15282	99.35
$1 \cdot 10^{-5}$	10784	99.08	13077	99.24	4995	98.04	11794	99.16	9287	98.93

Figure 4 shows pertechnetate sorption on ApA—ApE, where competing perchlorate anions were used. At all concentrations, $1 \cdot 10^{-5}$—$1 \cdot 10^{-1}$ mol·dm^{-3}, the sorption percentage, R %, was in the range of 93.5—100 %; which means taht perchlorate anions have no effect on pertechnetate sorption on Sn-Apatite sorbents (Tab. 4). pH values before and after sorption of pertechnetate ranged from 5.5 to 6.5.

In case of nitrate anions presence, the sorption percentage was in the range from 96.3 % to 99.6 % for all types of apatite-sorbents. The graph shows

that sorption percentage, R %, was not lower in the presence of higher concentrations of competing anions in the solution (Fig. 5). At all NO^{3-} anions concentrations, values of R % ranged from 95.3 % to 99.7 % (Tab. 5). pH values before and after sorption of pertechnetate ranged from 5.5 to 6.5.

Conclusion

The effect of pH on pertechnetate ions sorption on Sn-Apatite sorbents was studied as well as that of competing anions on $^{99m}TcO_4^-$ sorption on Sn-

Apatite. Point zero charge (pH_{pzc}) was determined for the studied substances. The best values of pH_{pzc} of 5.5—8.62 were determined at pH 5. Results showed that sorption percentage, R %, was higher than 92 % at all pH values studied (Fig. 2). Also, the effect of competing ions on $^{99m}TcO_4^-$ anions sorption on potentially usable Sn-Apatites in waste water was determined. Competing anions which are usually present in waste water were chosen for this experiment: ClO_4^- ions are products of drinking water chlorination; NO_3^- ions are present in sewage water and SO_4^{2-} ions are present in acid-rain water. It was found that the competing anions contained in the solution at a concentration of $1 \cdot 10^{-5}$ mol $\cdot$ dm^{-3} to $1 \cdot 10^{-1}$ mol $\cdot$ dm^{-3} have almost no effect on pertechnetate sorption on Sn-Apatites. Sorption percentage was in all cases above 93.5 %. These anions have no effect on the chemical reaction between Sn (II) ions and TcO_4^- anions in the solution. Lower values of pertechnetate R % in aqueous solutions with NO_3^- ions after the sorption are due to the interaction of competing anions and free stannous cations in apatite samples, which prevents effective oxidation-reduction reaction between Sn (II) and Tc (VII). In the conclusion, Sn-Apatite sorbents have suitable properties for potential use in radionuclides or heavy metals removal from water solutions.

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