



Article Uptake of Radionuclides ⁶⁰Co, ¹³⁷Cs, and ⁹⁰Sr with α -Fe₂O₃ and Fe₃O₄ Particles from Aqueous Environment

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Abstract: In the paper, investigation results of the uptake efficiency of radionuclides 60 Co, 90 Sr, and 137 Cs dissolved in water onto iron oxides α -Fe₂O₃ and Fe₃O₄ are presented. It was found that sorption efficiency increased for higher pH values. Independent of the oxide nature, the uptake characteristics are the best toward 60 Co and the worst toward 137 Cs, forming the row as follows: 60 Co > 90 Sr > 137 Cs. The highest sorption ability at pH 9 was found for magnetite Fe₃O₄, which was 93%, 73%, and 26% toward 60 Co, 90 Sr, and 137 Cs, respectively, while the respective percentages for hematite α -Fe₂O₃ were 85%, 41%, and 18%. It was assumed that the main sorption mechanism was ion exchange. That may explain some decrease of the sorption efficiency in drinking water due to the interfering presence of magnesium and calcium cations. The obtained results indicated the feasibility of the tested sorbents and their merits, especially in terms of relatively high uptake coefficients, low costs, availability, and lack of toxicity.

Keywords: α-Fe₂O₃; Fe₃O₄; radionuclides; sorption; strontium; cesium; cobalt; drinking water

1. Introduction

The necessity of the ecological control of the aquatic environment in terms of radionuclides pollution level is closely connected with the activity of nuclear energetic complexes and especially their accidental failures. Special attention is paid to the consequences of catastrophic accidents at the Chernobyl nuclear plant in 1986, and at the Fukushima Dai-ichi Nuclear Power Plant in 2011, e.g., in papers [1,2]. According to the WHO Guidelines [3], the maximal acceptable total volumetric activity of β -radiators, i.e., $\Sigma\beta$ activity, should not exceed 1.0 Bq/dm³. The main portion of the total specific activity in the polluted waters belongs to the long-term radionuclides ¹³⁷Cs and ⁹⁰Sr. In the aquatic environments, these ones are present in the form of exchangeable radionuclides (cationic and water-soluble complex), as described by several authors [4,5]. Izrael et al. [6] emphasized that the radionuclides promoted their intensive migration in biosphere and threat to the human health. Gupta et al. [7] found that the radioactive strontium enters the human food chain by the consumption of plants, while according to Rauwel and Rauwel [8], after the consumption of contaminated game and fish, ¹³⁷Cs is introduced to the human body and emits radiations directly affecting the cell nucleus. Recent studies [9] demonstrated the transport of ¹³⁷Cs from nuclear reprocessing plants Sellafield and La Hague, as well as from Chernobyl accident to the Baltic Sea. Similarly, Kurikami et al. [10] suggested its transport from the forests to freshwater fish living in mountain streams in Fukushima. Cobalt belongs to the group of heavy metals, i.e., trace elements with elemental density above 4 ± 1 g/cm³. At dosages higher than the prescribed WHO limits, these substances are considered toxic to soil and



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). aqueous systems, as it was emphasized in [11]. Demir et al. [12] reported that observations of people accidentally exposed to a ⁶⁰Co source confirmed a significant unfavorable change induced by radiation in the oxidant/antioxidant status in their organisms. Therefore, many researchers emphasize the importance of cobalt removal from waters and soil [13,14].

Thus, it is urgent and important to improve the existing methods and to develop new ones in order to perform effective deactivation of radionuclide-polluted natural reservoirs and wastewaters. The simplest, most easily available, and effective methods are those based on the sorption phenomenon described in [15], since large volumes of water can be treated without affecting its chemical composition and adding new contaminations. The present study is focused on the uptake of ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs radionuclides. A wide range of materials has been proposed, so that a particular one may be chosen dependent on the removal effectiveness, chemical stability, expenses, regeneration ability, etc. described in details e.g., in [16,17]. Among numerous recent reports, it is worth mentioning the study of polyaniline/zirconium aluminate composite (PANI/ZAI) as a novel sorbent synthesized by the sol-gel hydrolysis method. According to Metwally et al. [18], its capacity was 140.3 mg/g for 60 Co, and the desorption percent was 95.4%. To form a new nanosorbent (NMn₃O₄-OA), manganese oxide nanoparticles were fabricated via combustion synthesis and later functionalization with olevl amine. The maximum capacities reported in [19], reached 100 mg/g for Co^{II}. In another study [20], the nanobentonite clay has been activated with H₂SO₄ to produce nanosorbent (A-NBent) with a maximal removal capacity of $125.27 \text{ mg/g for } {}^{60}\text{Co.}$

In the case of ¹³⁷Cs dissolved in surface water reservoir, an illite adsorbent was evaluated by Park et al. [21]. Other scientists analyzed bentonite upon thermal treatment performed at various temperatures, i.e., 150, 300, and 600 °C, considering their effect on the sorption of ¹³⁷Cs [22]. It came out that the heated forms had reduced selectivity for ¹³⁷Cs compared to the original bentonite, while B-150 and B-300 exhibited the best sorbent properties toward ¹³⁷Cs solved in salt media. Magnetic potassium–zinc hexacyanoferrate (II) was investigated by Puzyrnaya et al. [23] to determine its feasibility for the selective sorption of ¹³⁷Cs particles from water. Singh et al. [24] reported that sodium aluminosilicate has been synthesized by the solution route for use as a sorbent for ¹³⁷Cs radionuclides. Voronina et al. [25] studied the uptake of ¹³⁷Cs and ⁹⁰Sr radionuclides out of seawater under batch conditions. They used ferrocyanides based on hydrated titanium and zirconium dioxides (T-35, NPF-HTD), natural aluminosilicates, zirconium phosphate, and modified hydrated titanium dioxide, as well as manganese dioxide based on hydrated titanium dioxide. Nano-sized stannic silicomolybdate was synthesized and tested for the adsorption of ¹³⁷Cs, ⁹⁰Sr, too, as described in [26]. Sadeghi et al. [27] reported the successful synthesis of MnO₂ NPs-AgX zeolite composite via the impregnation method intended for the uptake of radioactive ⁹⁰Sr from drinking water. The As-obtained novel adsorbent demonstrated high capacity and potential in treatment during 8 h with the yield of 100%. Crystalline silicotitanates (CST) and onosodium titanates (MST) are among the most widely studied materials due to their decent strontium uptake characteristics at neutral and basic conditions, and in [28], it was demonstrated that a novel anionic-layered CP material [(CH3)2NH2][ZrCH2(PO3)2F] (SZ-4) was able to remove Sr²⁺ ions effectively over a very wide pH range, starting from highly acidic environments of pH1 and pH2.

Iron oxides, namely, goethite FeO(OH), maghemite γ -Fe₂O₃, hematite α -Fe₂O₃, and magnetite Fe₃O₄, can be considered promising materials for the uptake of heavy metal ions from aqueous solutions. Among their merits are low costs, availability, good sorption properties, possibility of modification, and lack of toxicity, which was confirmed by numerous studies, e.g., [29–33]. In particular, iron oxides are capable of removing copper, europium, and cerium from aqueous solutions in the range of pH from 5 to 9, reaching a yield of 95–97%. Odnovolova et al. [34] proved that the sorption capacity of α -Fe₂O₃ toward europium, cerium, and copper at pH 5 was 21.3, 9.2, and 15.7 mg/g, respectively, while that of Fe₃O₄ is 19.7, 7.5, and 11.6 mg/g, respectively. Similarly, it was reported that the sorption capacity of α -Fe₂O₃ and Fe₃O₄ toward cobalt was close to 18 mg/g [32]. Given the abovementioned needs of new sorbents and proven potential of the iron oxides, it was found reasonable to perform tests on their uptake of radioactive isotopes. In case of radionuclides, a sorption process will take place in the aqueous solution with very small concentration. Thus, the objective of the presented work was to assess the removal effectiveness of hematite α -Fe₂O₃ and magnetite Fe₃O₄ toward ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs.

2. Materials and Methods

2.1. Synthesis of Powders α -Fe₂O₃ and Fe₃O₄

The synthesis route of iron oxide micro- and nanopowders affects the final morphology of the particles [35]. The hematite powder α -Fe₂O₃ was obtained with the method described in detail in [36]. Namely, to the volume of 100 mL of FeCl₃ 0.1 M solution was added aqueous solution of ammonia (25% solution 266.8 g/L), reaching pH 10 or 11, and the obtained mixture was agitated with the magnetic stirrer during 15–20 min. The precipitate was filtered, then washed several times using distillated water, and finally calcinated at 450 °C during 4 h. Using the Brunauer–Emmett–Teller (BET) model, it was found that the obtained hematite powder α -Fe₂O₃ had a specific surface area (SSA) of 150 m²/g.

Similarly, the magnetite Fe₃O₄ particles were precipitated from aqueous solution with the method described in [36]. To the Erlenmeyer flask of 500 mL, 100 mL of FeCl₃ 0.2 M solution and 50 mL of FeSO₄ 0.2 M solution were added, so that the proportion $c(\text{Fe}^{3+}):c(\text{Fe}^{2+})$ was 2:1. The mixture was heated up to 80 °C with constant stirring, and then, an aqueous solution of ammonia was added with uninterrupted stirring, reaching pH 10 or 11. The obtained solution was mixed for further 30 min. After that, the precipitate was filtered, washed with distillated water until the ammonia smell disappeared, and then dried up on the air at room temperature during 48 h. The obtained magnetite powder Fe₃O₄ had a specific surface area (SSA) of 140 m²/g.

2.2. Sorption Tests

The sorption capacity of α -Fe₂O₃ and Fe₃O₄ toward radionuclides ¹³⁷Cs and ⁹⁰Sr was investigated with the limited volume method in the pH interval between 2 and 9 at a temperature of 293 K. In the experiments, model aqueous solutions of radionuclides with no carriers were used, as follows: ⁶⁰Co ($5.2 \cdot 10^7$ Bq/dm³), ¹³⁷Cs ($3.2 \cdot 10^7$ Bq/dm³), and ⁹⁰Sr ($1.8 \cdot 10^7$ Bq/dm³). These solutions were prepared on the basis of distillated water. Sorbent weights of 0.05 g were added to 10 mL of the solution containing radionuclides at known preset pH value. Based on the previous experience, a solid to liquid proportion of 1:200 was then mixed with ultrasonic, but the sorption experiments were performed without stirring or ultrasonic influence.

The time of equilibrium was derived from the sorption kinetics. Kinetic diagrams were built with the method of subsequent samples selection in the time interval from 0 up to τ_{∞} and the measurement of the radioactivity of dry residue from an aliquot of the solution. The τ_{∞} denotes the time of thermodynamic equilibrium in the solution–sorbent system. When two subsequent samples had constant radioactivity, it was seen as the proof of thermodynamic equilibrium in the system.

The radioactivity of the dry residue of the solution aliquot before and after the sorption equilibrium of ⁹⁰Sr was measured with a beta-spectrometer SEB-01-150 produced by PRE Atom Komplex Prylad (Kyiv, Ukraine), while that of ¹³⁷Cs and ⁶⁰Co was measured with an NRR 610 automatic alpha beta counter made by Tesla company (Prague, Czech Republic). The relative error of each measurement did not exceed 2%.

Quantitative characteristics of the interaction between sorbents and radionuclides was determined using sorption percentage coefficient K_s , %. It was calculated as follows:

$$K_s = \frac{I_0 - I_p}{I_0} \cdot 100\%,$$
 (1)

where I_0 and I_p denote initial and equilibrium radioactivity of the solution [pps], respectively.

2.3. Measurement Apparatus

X-ray powder analysis was performed using Siemens D500 X-ray Diffractometer (XRD), with Cu sources and graphite-diffracted beam monochrometer. Full profile X-ray diagrams were converted in the angle range $10^{\circ} < 2\theta < 90^{\circ}$ with a step of 0.02 during 10 s at each point. The infrared spectra were obtained in tablets of potassium bromide with a Spectrum One FT-IR Spectrometer produced by PerkinElmer (Waltham, MA, USA). The sample was thoroughly ground with potassium bromide in a sample/KBr proportion of 1:100, after they were tableted under load 10 t/cm² during 1–2 min.

The morphology of the obtained powder surface was analyzed with a scanning electron microscope (SEM) JSM-6390LV made by Jeol Ltd. (Akishima, Tokyo, Japan) at accelerating voltage 10–20 kV. The samples were placed on the graphite bars of dimensions 5 mm and height 5 mm in form of alcohol suspension, which was later dried in air.

The SSA value of the synthesized powder was obtained with the method of gas thermal desorption with chromatographic detection, using gas mixture 10% of argon in helium. As a reference, alumina with SSA 4.2 and 52 m²/g were used.

3. Results and Discussion

3.1. Characteristics of the Sorbents

Figure 1 presents an XRD measurement of the synthesized iron oxides. In the diagrams, the reflections can be seen that correspond with the respective phases of hematite α -Fe₂O₃ (curve a) and magnetite Fe₃O₄ (curve b).



Figure 1. XRD of the synthesized powders α -Fe₂O₃ (**a**) and Fe₃O₄ (**b**).

Figure 2 presents the IR spectra of the synthesized iron oxides. In the spectra, intense absorption bands are seen in the range between 500 and 1000 cm⁻¹, with the peaks at 541 cm⁻¹ (curve *a*) and 565 cm⁻¹ (curve *b*). According to several reports [34,37], these peaks are attributed to the vibration of Fe–O bond in the iron oxides α -Fe₂O₃ and Fe₃O₄, respectively. Moreover, in the IR spectrum of the Fe₃O₄ powder represented by curve *b*, absorption bands with maxima at 1400, 1111, 1040, and 971 cm⁻¹ are registered, which can be attributed to the presence of SO₄²⁻. In turn, the absorption band with a maximum of 1400 cm⁻¹ can be attributed to the CO₃²⁻ ion vibrations, as it was in other studies, such as [38,39]. The presence of sulfate ions is caused by the application of iron sulfate as a precursor in the synthesis, while carbonate ions appeared as a consequence of the alkaline

solution carbonization process during particles precipitation. SEM images of the obtained particles are presented in Figure 3.



Figure 2. IR spectra of the synthesized powders α -Fe₂O₃ (**a**) and Fe₃O₄ (**b**).



Figure 3. SEM images of the synthesized particles α -Fe₂O₃ (**a**) and Fe₃O₄ (**b**).

The powder α -Fe₂O₃ seen in Figure 3a formed large, porous, shapeless agglomerates with dimensions of ca. 30 μ m, which were composed out of small spherical particles below 80 nm. The powder Fe₃O₄ appears also in form of porous agglomerates shown in Figure 3b, but their dimensions are much smaller, below 8 μ m. It consists of small spherical particles below 80 nm, too.

Synthesized iron oxides were used for further sorption characteristics assessment.

3.2. Effect of Sorption Time

Kinetic investigations were performed in order to determine the optimal time for radionuclides removal. In Figure 4, there are diagrams of the sorption coefficient dependent on the uptake time. From the experimental data, it can be concluded that the sorption coefficient in the time domain behaved similarly for both α -Fe₂O₃ and Fe₃O₄, and it did not depend on the removed radionuclide 60 Co, 90 Sr, and 137 Cs.



Figure 4. Kinetic sorption diagrams of radionuclides ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs at pH 8: (a) with particles Fe₂O₃; (b) with Fe₃O₄.

The kinetic diagram may be divided on probation in three areas. The first area of 1 h can be considered as a rapid increase of the K_s , the second one between 1 and 2 h corresponds with its slow increase, and the third one above 3 h is in a stationary area, since it reveals practically no increase of K_s . The latter testifies that the equilibrium is reached.

It should be noted that the maximal sorbent coefficient was reached for ⁶⁰Co, while the next was for ⁹⁰Sr, and the minimal one was for ¹³⁷Cs. At the same time, Fe₃O₄ particles performed much higher sorption coefficients than hematite particles. In particular, the sorption ability K_s for Fe₃O₄ toward ⁶⁰Co reached 88%, while for α -Fe₂O₃ particles, it did not exceed 65%. Similarly, K_s for Fe₃O₄ toward ⁹⁰Sr reached 54%, while for α -Fe₂O₃ particles, it did not exceed 30%.

From the obtained results, it can be derived that the optimal time for the uptake in the above-mentioned conditions was ca. 1.5 h.

3.3. Effect of pH

Sorption effectiveness is dependent on the solution pH to a high degree. Figure 5 demonstrates the effect of pH on the sorption coefficient K_s during 1.5 h of the experiment. Independent of the nature of iron oxide, the sorption coefficient always gradually increases with the increase of solution pH. In the range of pH 2–5, sorption effectiveness is rather small, and its dependence on pH is weak, since K_s increased from 5–10% to 10–15%. A further pH increase up to 9 led to a substantial improvement of the sorption effectiveness. As in the case of kinetic investigations, the K_s coefficient is the highest for ⁶⁰Co, then for ⁹⁰Sr, and the lowest is for ¹³⁷Cs. The maximal sorption degree was obtained for pH 9, and respective values of the K_s coefficient for ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs with hematite particles were $K_{sCo} = 85\%$, $K_{sSr} = 41\%$, and $K_{sCs} = 18\%$, while with Fe₃O₄ particles, they were $K_{sCo} = 93\%$, $K_{sSr} = 73\%$, and $K_{sCs} = 26\%$. It is noteworthy that Fe₃O₄ particles performed much higher values of sorption coefficient compared to α -Fe₂O₃ particles.



Figure 5. Sorption coefficients K_s of ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs dependent on solution pH at temperature 293 K: (**a**) with particles Fe₂O₃; (**b**) with Fe₃O₄.

Low sorption effectiveness at pH below 5 may be caused by two factors. First, dependent on the pH, the surface of iron oxides may be loaded positively or negatively as a result of the following reactions:

surface FeOH +
$$H^+ \leftrightarrow$$
 surface FeOH²⁺, (2)

surface FeOH + OH⁻
$$\leftrightarrow$$
 surface FeO⁻ + H₂O. (3)

In the acid environments at low pH, iron oxide is loaded positively, which prevents cations uptake concurrent with H⁺ ions. Second, when the pH is below 5, the process of iron oxides dissolution may take place, inhibiting sorption of the radionuclides on the surface.

Increased sorption coefficient at higher pH values is attributed to the possibility of hydrocomplex formation by the metal cations. The relation between cation hydratation energy and sorption effectiveness can be traced, because the hydration energy of Sr²⁺ ions is $-\Delta H^0_{hydr} = 1412.46 \text{ kJ/mol}$, and that of Co²⁺ ions is $-\Delta H^0_{hydr} = 1780.68 \text{ kJ/mol}$, which is much higher than that of Cs⁺ ions $-\Delta H^0_{hydr} = 251.93 \text{ kJ/mol}$ reported in [36]. Hence, the higher the hydration energy, the higher the uptake effectiveness.

Moreover, high effectiveness of the tested sorbent toward ⁶⁰Co can be attributed to the predisposition of the Co²⁺ ions to form complex bounds with OH groups of weak coordination bonds. According to [40], the hydration shell Co²⁺ has weak deformation, which determines its stability. As a result, it can be expected that apart from ions exchange, there is a formation of the complex bonds of Co²⁺ ions with weak coordination bonds with OH groups of the sorbent.

It is noteworthy that ⁹⁰Sr uptake is close to the 80% value recently reported by [41] with a composite sorbents containing iron oxide in a polymer matrix after hydrothermal treatment at a temperature of 175 °C. However, in our study, the methodology is much less energy and time consuming.

3.4. Drinking Water Treatment

Drinking water components cannot constitute a threat to human health [42]. Elimination of the radionuclides from the natural environment and water is very important due to their harmful effects on living organisms [43]. To make assessment of the radionuclides uptake feasibility in real work conditions, the experiments were performed with the drinking water, pH 6.8. From the measurement results, the uptake coefficient K_s , % toward each radionuclide was calculated. The obtained values are collected in Table 1.

Sorbent	Sorption Coefficients toward Respective Radionuclide K_s , %			
	¹³⁷ Cs	⁹⁰ Sr	⁶⁰ Co	
α-Fe ₂ O ₃	8.7%	19.8%	51.4%	
Fe ₃ O ₄	18.7%	34.8%	71.6%	

Table 1. Sorption effectiveness of investigated sorbents applied in drinking water.

It is noteworthy that the overall trend in drinking water compared to model aqueous solutions is some decrease of the uptake efficiency. This phenomenon can be attributed to the fact that the radionuclides are present in solutions in sub-micron amounts. As a result, the removal takes place concurrently with the ion exchange with a dominant mechanism of secondary potential-forming sorption. Moreover, the presence of extrinsic ions in the drinking water has a further negative impact on the uptake process.

Table 2 presents the chemical composition of the drinking water before and after its treatment with sorbents. It can be seen that the calcium, magnesium, and hydrogen carbonate ions concentration is reduced due to adsorption on oxides.

Table 2. Chemical composition of the drinking water before and after its treatment with respective sorbents α -Fe₂O₃ and Fe₃O₄.

Indicators	Content before and after Treatment, mg/dm ³			
	Before	After α -Fe ₂ O ₃	After Fe ₃ O ₄	
Sodium (Na ⁺)	93.0	92.7	92.5	
Potassium (K ⁺)	13.0	12.3	12.0	
Magnesium (Mg ²⁺)	24.3	14.2	13.9	
Calcium (Ca ²⁺)	86.2	27.6	27.1	
Sulfates (SO ₄ ²⁻)	107.5	104.9	104.5	
Hydrogen carbonates (HCO ₃ ⁻)	293.0	157.1	147.0	
Chlorides (Cl ⁻)	160.0	156.0	156.0	

The hydration energy of the ions Ca^{2+} is 1577 J/mol, while for Mg^{2+} , it is 1908 J/mol [40]. Thus, calcium ions interfere with the process of cobalt and strontium ions removal.

4. Conclusions

The results of the uptake effectiveness of iron oxides α -Fe₂O₃ and Fe₃O₄ toward radionuclides ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs dissolved in water are very promising. It was found that the sorption efficiency increased with higher pH values. At any pH, the sorption activity of the tested radionuclides fitted to the row as follows: ⁶⁰Co > ⁹⁰Sr > ¹³⁷Cs. It was assumed that the dominant sorption mechanism of these elements on the iron oxides surface was ion exchange.

When applied for drinking water treatment, the tested sorbents had an insufficient decrease of the uptake effectiveness. It was attributed to the concurrent sorption of magnesium and calcium cations.

The results of investigations proved the feasibility of the iron oxides α -Fe₂O₃ and Fe₃O₄ as sorbents in water treatment plants. They may become an alternative because of their low costs, availability, modification flexibility, and lack of toxicity. From the perspective of green and sustainable manufacturing, the iron oxides appeared to be advantageous materials.

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