Chapter 8

Post-synthetic modification of zirconium terephthalate sorbents and their application for sorption of selected toxic elements from water

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1. Introduction

Metal-organic Framework (MOF) porous materials have been a subject of interest for about two decades. The discovered recipe for their synthesis consisting of a combination of highly tunable metal nodes and ditopic or multitopic ligands resulted in the exponential growth of new structures. At present, a wealth of material on synthesis, structural, and functional properties have been accumulated. It shows a potentially wide range of applications in the field of gas storage, separation of gaseous mixtures, catalysis, drug delivery, energy, and environment protection. The unique features of MOFs, such as large specific surface area, diversity of possible structures, and theoretical possibility of a design structure for specific applications make them suitable for industrial applications [1]. However, extensive application research is required before a potentially beneficial solution can be put into practice. The issue of economic efficiency and technical suitability should be resolved first.

In the framework of the PET-MOF-CLEANWATER project, the possibility of application of waste PET- derived terephthalic ligand for the synthesis of MOFs suitable for toxic elements removal from water are being explored. The aim of the project is to contribute to the resolution of

two issues. The first is to reduce the environmental impact of the growing amount of PET wastes. It aims to recover terephthalic acid from waste PET and reuse it for synthesis of mechanically and thermally stable porous MOF-type sorbents. The second one is to demonstrate the usefulness of the sorbents obtained in this way for the removal of toxic pollutants from water, for example, radionuclides and heavy metals.

Nuclear power is a mature technology that can make a vital contribution toward global low-carbon energy needs. The sustainable growth of nuclear energy to meet the needs of the future generations is heavily dependent on the practices followed currently in the management of nuclear waste. Recently, there has been growing interest in observing MOF applications for radionuclide waste immobilisation and storage. The high porosity, modularity, and synthetic diversity of metal-organic frameworks (MOFs) make them attractive candidate materials for selective sensing and sequestration of the radionuclides present in the nuclear wastes [2,3]. The results of these studies provide a promising alternative to sequestering nuclear wastes and open new ways for more efficient waste management to make nuclear power more feasible. In the present report, the results of our studies on the removal of technetium, ruthenium, and uranium radionuclides from water solution are presented. Additionally, we provide the data for the removal of mercury, classified by the World Health Organization (WHO) among the ten highly toxic heavy metal contaminants of water.

2. Material synthesis

In our study, we focused on structures built with terephthalic acid and zirconium. The reason for this choice is the chemical resistance in aqueous environments of MOFs constructed with metals of high valence. Moreover, the zirconium terephthalate UiO-66 structure is known for its tolerance for the structural defects of missing linker or missing site types. This makes it possible to functionalise the structure by incorporating a ligand possessing a functional group showing affinity to the metal to be adsorbed. Functionalisation may be carried out directly in the synthesis step or in the post-synthetic process.

Three different types of zirconium terephthalate UiO-66 type sorbents have been synthesised:

1. UiO-66_FA - synthesised according to literature procedure [4]. Briefly, 4 mM of zirconium chloride and 4 mM of terephthalic acid were dissolved in 100 ml of DMF. 50 eq of formic acid (FA) was added as a modulator to create the structure containing structural defects. The solution was refluxed at 120°C for 24 hours. Thereafter,

powdered material was recovered by filtration, washed in DMF and acetone, and dried at 120°C under vacuum. The XRD studies confirmed a synthesis of UiO-66 structure.

2. Zr_hcp – synthesised directly from PET flakes in acetic acid/ acetone mixture at temperature in the range of 160 –190°C. In each synthesis, 2.625 g of zirconium chloride and 1.875 g of PET flakes were added to 75 ml of acetone and 75 ml of formic acid solution. The mixture was processed in Berghof-300 pressurised reactor for 24 hours. The obtained material was porous (the specific surface area was 524.30 cm2/g) and identified as zirconium complex with hexagonal close packed structure (a=b = 14.71309 Å, c = 36.979496 Å)
3. Zr_PET – synthesised directly from PET flakes in acetic acid/ acetone mixed solvent at temperature as low as 120 °C. In typical synthesis 1g of PET and 1.611 g of zirconium oxychloride octahydrate were added to the solution of 20 ml acetone and 20 ml acetic acid. The resulting mixture was heated in sealed Pyrex bottle for five days on oil bath at temperature of 120°C. The obtained powder material was crystalline, but its structure is not known at present. We suppose that it is a zirconium complex with acetate and terephthalate ligands similar to zirconium complexes with terephthalate and acetic acid ligands described already [5,6]. It was also found that resulting material can be functionalised in a post-synthetic process in a solution containing monocarboxylic acid possessing an amino group. After functionalisation, this material acquires sorption capacity for pertechnetate anion. The thermogravimetric data for UiO-66_FA and Zr_hcp presented in Figure 1 confirm high temperature stability of these structures up to temperatures of around 500°C and their defective character. The number of lacking terephthalate linkers for UiO-66_FA structure was estimated as equal to 2.6.

For the functionalisation of the structures, different monocarboxylic (or dicarboxylic) acids possessing amino group or mercapto (-SH) group were applied.

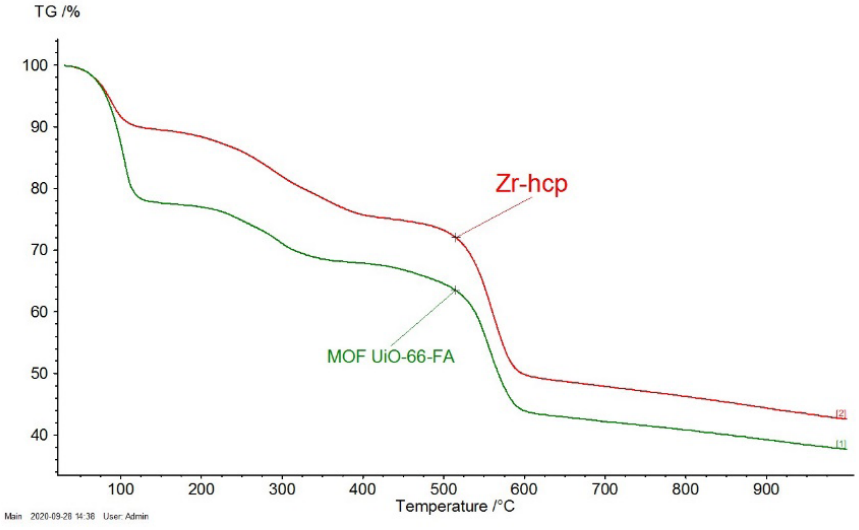

Figure 1: TGA data for defective Zr_hcp structure synthesised from PET waste flakes in acetone/acetic acid mixture and for defective UiO-66_FA sorbent synthesized with formic acid as modulator

3. Sorption of pertechnetate anion from water solution

^{99}Tc is long-lived isotope ($t_{1/2}$ = 213000 years) created in a reactor as a fission product of ^{235}U (6.18 % yield) and ^{239}Pu (6.21% yield). Ground state ^{99}Tc decays by beta emission (Emax — 292 keV), while the metastable isomer ^{99m}Tc ($t_{1/2}$ = 6.0 h) decays rapidly by emitting a gamma photon. Large quantities of technetium have been produced in the course of nuclear weapons research and are stored in underground tanks containing mixed radioactive waste awaiting reprocessing and subsequent disposal. Technetium (^{99}Tc) is an abundant fission product of particular concern in nuclear reprocessing and waste solidification technologies because of the high solubility and mobility of Tc (VII) pertechnetate (TcO_4^-), and the stable form of technetium in aerobic environments. Tc is volatile during waste vitrification. It can leach from vitrified glass, and greatly interfere with the separation of uranium and plutonium during the PUREX solvent extraction process, making it one of the most problematic radionuclides in the nuclear fuel cycle. Therefore, direct removal of pertechnetate anion from the solutions of used nuclear fuel is considered beneficial to make progress in the recovery of uranium and plutonium from nuclear wastes and as a means of eliminating ^{99}Tc discharge into the environment. It is possible to capture and remove TcO_4^- using a number of processes such as ion exchange, extraction, and precipitation [7,8]. Each of these processes

has its own advantages and disadvantages, but pertechnetate removal by ion exchange has received the most attention to date because of its ease of implementation, cost efficiency, and high ^{99}Tc recovery rate. MOF-type sorbents have an advantage over sorbents of other types due to their construction, which gives the possibility to shape the structure and size of pores and their physicochemical properties in a wide range. But relatively few materials have been tested directly for TcO_4^- ion exchange [9,10]. It is also worth mentioning that protonated zirconium complex with 2-amino-1,4-benzene dicarboxylic UiO-66_NH_2 has been found as an effective adsorbent for the removal from water perrhenate anion ReO_4^-, non-radioactive surrogate of pertechnetate, even in the presence of other competing anions [11].

We recently conducted a study on pertechnetate anion sorption from water for a number of sorbents synthesised using terephthalic acid linker derived from waste PET. The four different types of sorbents were synthesised. One of them is well-known MIL-101(Cr) synthesised according to the literature procedure [12]. The others were UiO-66_FA, Zr hcp and Zr_PET types described in the material synthesis section.

All the sorbents were functionalised in the post-synthetic process in order to introduce the amino group to the structure. For the MIL-101 structure, ethylenediamine was grafted to uncoordinated chromium sites created by dehydration at 150°C for 12 hours. For the three others, functionalisation with 2-aminobenzoic acid, glycine, and 3,5-diaminobenzoic acid was carried out in the post-synthetic ligand exchange process. The last step in the functionalisation consisted of protonating the incorporated amino group of the sorbent in the 4N HCl solution. As a result, cationic MOFs were obtained for which weakly bound chlorine anion can be exchanged in water solution for pertechnetate anion.

The sorption kinetics studies of the sorbents have been performed using the radiotracer method. The ^{99m}Tc isotope in the chemical form of pertechnetate anion has been used as a tracer. ^{99m}TcO4- was eluted from ^{99M}o/99mTc generator (POLATOM production) with 8 mL 0.9% NaCl water solution. The activity of ^{99m}TcO4- was at the level of 1 GBq. To each sample of 15 mg MOF in 10 mL of water 50 µL of ^{99m}TcO4- was added (around 6 MBq). The control samples without MOF sorbent were also prepared. All the samples were mixed for a predetermined time. After mixing, samples were centrifuged and 1 mL of supernatant was taken and its activity was measured with a gamma counter. By comparing the measured values with the activity of the control sample, the percentage of activity remaining in the solution was determined.

A high pertechnetate anion removal rate was found for the sorbents being studied. The results of the MIL-101(Cr) case are shown in Figure 2 and for modified UiO-66_FA in Figure 3. In the case of MIL-101(Cr), 92.1% removal efficiency, near saturation value (96.5%) has been achieved after 1 hour.

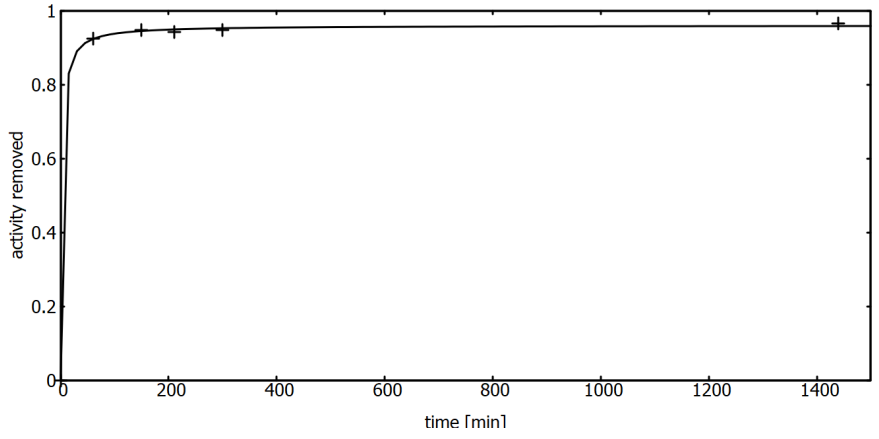

Figure 2: Kinetics of pertechnetate anion removal for MIL-101(Cr) type sorbent grafted with ethylenediamine and protonated in 4N HCl.

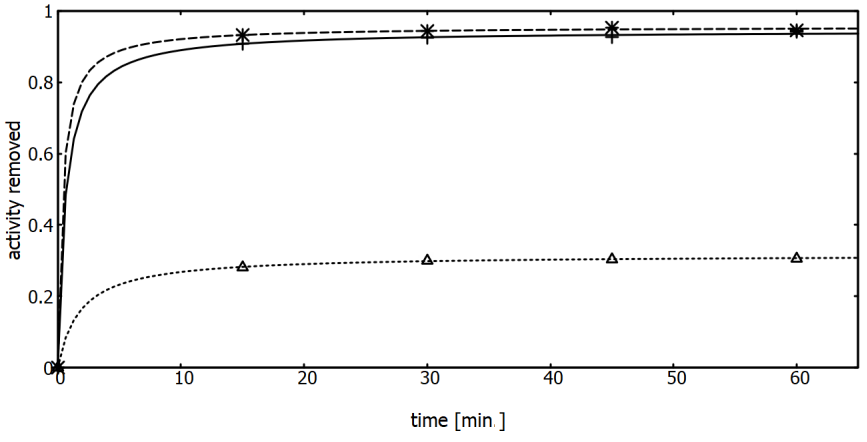

Figure 3: Kinetics of technetium anion removal from water for UIO-66_FA type sorbent modified in post-synthetic ligand exchange process with 2-aminobenzoic acid (solid line), glycine (dashed line) and 3,5-diaminobenzoic acid (dotted line).

The dependence of sorption capacity on solution pH was also investigated. The results showing the pH dependence of distribution coefficient for zirconium complex with 2-aminoterephthalic acid UiO-66_NH_2

and zirconium complex Zr_hcp, modified by post-synthetic ligand exchange process with 2-aminobenzoic acid are presented in Figure 4. The graph shows similar dependence on pH in the range of 2-9 pH for both sorbents. The values of the distribution coefficient for modified Zr_hcp solvent synthesised by a procedure developed during the project exceed those obtained for UiO-66_NH_2 synthesised from a commercial 2-aminoterephthalic ligand.

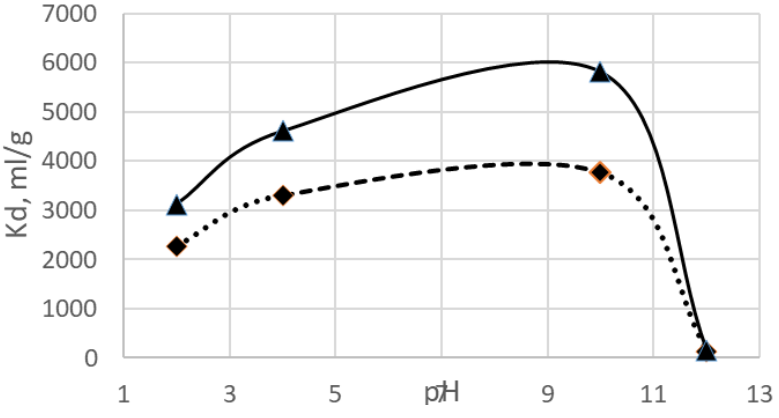

Figure 4: pH dependence of distribution coefficient for Zr_hcp (solid line) and UiO-66_NH2 sorbents (dotted line).

4. Sorption of uranyl ion from water solution

Uranium is a fissile material required for nuclear energy production. Hence, it is considered as a strategic material, and there is a strong interest in securing stable sources of uranium supply. Due to the limited natural resources of uranium, the possibility of obtaining uranium from seawater is often explored. Nuclear weapons research has resulted in the accumulation of large quantities of nuclear waste requiring reprocessing. The inadvertent release of radioactive materials into the environment poses potential severe threats to human health. Hence, the separation of uranium from water is becoming a topic of great interest from the point of view of both reasonable utilisation of uranium resources and environmental protection. The subject has been recently reviewed [13].

In our search for applications of MOFs built around terephthalate linker, we performed studies on the possibility of application of robust UiO-66 structure for sorption of uranyl ion from water. For this purpose, the functionalisation of the UiO-66 structure will be necessary. It will be aimed to incorporate within their structure a functional group sensitive to the uranium species to be adsorbed. To check this possibility, we

synthesised UiO-66 type structures using the modulation synthesis method and applied different modulators based on benzene and pyridine carboxylic acids having the amine group in different positions. The amino group free benzene acid was also included in the study. The ligands applied as modulators are shown in the Figure 5.

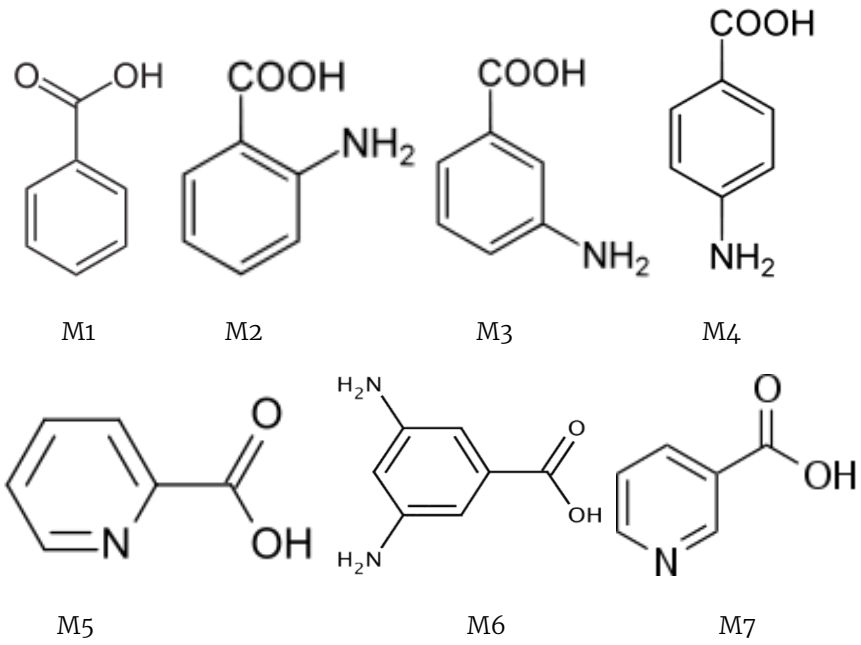

Figure 5: Structural schemes of modulators used in the study: M1 – benzoic acid, M-2 – 2-aminobenzoic acid, M3 – 3-aminobenzoic acid, M4 – 4-minobenzoic acid, M5 – 3,5-diaminobenoic acid, M6 – 2-pyridinecarboxylic acid, M7 – 3-pyridinecarboxylic acid.

For the synthesis, zirconium chloride, terephthalic acid and modulators in molar ratios of 1:1:10 were used. The synthesis was performed in eight-dram glass vials on an oil bath at a temperature of 120°C for 24 hours. Synthesised material was recovered by filtration, purified by washing in DMF and methanol, and finally dried in a dry box. For the screening of the best sorbents, 50 mg of each material was contacted with 10 mL of uranyl nitrate water solution with concentration of 200 mg U/L in plastic vials and shaken overnight. After that the sorbents were recovered by filtration using a track-etched membrane with a 0.4 µm pore diameter. The uranium to zirconium molar ratios on sorbent were determined by inductively coupled plasma mass spectrometry (ICP-MS) and are given in Table I.

The highest value was obtained for the case of a 3,5-diaminobenzoic acid modulator possessing two amino group on third and fifth positions in benzene ring. It is interesting to note that some adsorption of uranyl ion has been obtained also for UiO-66 structure not having amino group (modulator M1). Such effect has been reported already and was interpreted as the result of structural defects [14].

Table 1: The results of U/Zr molar ratio for different modulators.

Modulator	M1	M2	M3	M4	M5	M6	M7
U/Zr	0.089	0.000	0.195	0.207	0.327	0.132	0.024

The sorption isotherm for UiO-66 functionalised with 3,5-diaminbenzoic acid is shown in Figure 6. The best approximation has been obtained by applying the Langmuir model. The saturation value of sorption capacity has been determined as 240 mg U/g.

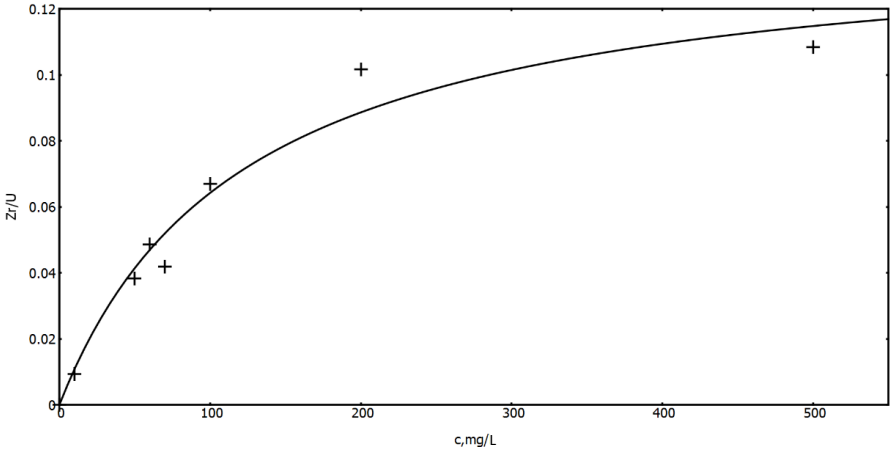

Figure 6: Sorption isotherm for the UiO-66 structure modified by modulated synthesis with 10 eq. of 3,5-diaminbenzoic acid modulator

5. Sorption of mercury from water solution

The World Health Organization (WHO) has listed mercury (Hg) as one of the ten pollutants of particular concern for public health. Mercury can be released from several sources such as electronics, paints, pharmaceuticals, paper and pulp, chloralkali, oil refinement, plastics, rubber processing, and manufacturing industries. Other significant (>10%) sources of Hg emission include coal and fossil fuel combustion (25%) and non-

ferrous metal production. Moreover, mercury compounds can persist and accumulate in the environment, causing severe toxicity to humans and animals, especially methyl-mercury. The fate of inorganic mercury ions in nature is its turning into methyl mercury due to the aerobic action of micro-organisms.

There are various methods of removing heavy metals from aqueous environment, which include reverse osmosis, chemical precipitation, ion exchange, coagulation, and adsorption. Adsorption is best suited for this purpose due to its simplicity and cost efficiency.

The high affinity of Hg-compounds to sulfhydryl (–SH) groups has been reported in numerous studies [15]. In the present report, we present the results of our studies on incorporating this group into zirconium UiO-66 MOF for converting them to effective mercury sorbent. Both known strategies for MOF functionalisation, modulated synthesis method and post-synthetic ligand exchange were utilised. For the modulated synthesis, mercaptoacetic acid (MAA) and mercaptosuccinic acid (MSA) were applied as modulators. Synthesis was conducted by refluxing the synthesis mixture containing zirconium chloride, terephthalic acid, and modulator dissolved in DMF solvent at 120°C for 24 hours. In the case of mercaptoacetic acid, five modulator concentrations equal to 10, 20, 50, 70, 90 and 100 eq of zirconium, respectively, were applied. The SEM images and XRD diffraction patterns confirmed crystallinity of synthesised materials (Figure 7, Figure 8). The successful incorporation of –SH group into UiO-66 structure has been confirmed by EDS analysis. The ratio of molar S/Zr content was determined as equal to 0.21 for the case of 10 eq MAA modulator content, 0.32 for the 50 eq and 0.32 for the case of 100 eq.

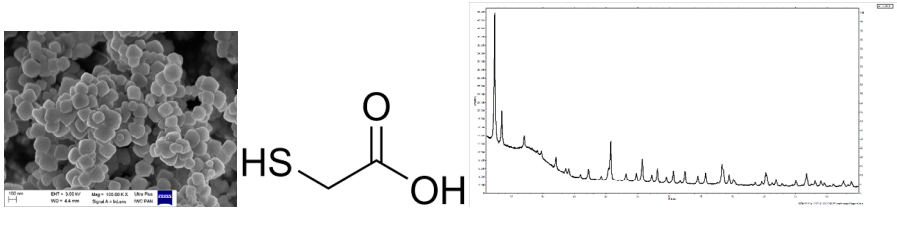

Figure 7: SEM image and diffraction pattern of UiO-66 modified with 50 eq. mercaptoacetic acid

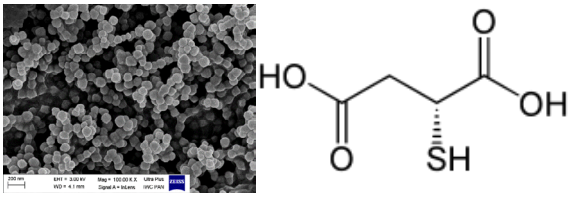

Figure 8: SEM image of UiO-66 type sorbent synthesizsd by modulation synthesis method at terephthalic acid/mercaptosucinic acid ratio equal to 3:1

The sorption capacity of the sorbents has been determined using radiotracer methods. The mercury ^{197}Hg isotope obtained by neutron flux activation of mercury nitrate of natural composition in the MARIA reactor in Świerk, Poland, has been used as radiotracer. The sorption studies were carried out on samples containing 15 mg of sorbent suspended in 10 mL of mercury chloride solution with varying concentrations of mercury of 0.5 to 10 mM and labelled with radioactive mercury isotope. The results of the study showing mass of mercury (in mg) accumulated on 15 mg of sorbent after two hours of contact are presented in Figure 9. The experimental data were approximated with Langmuir isotherm.

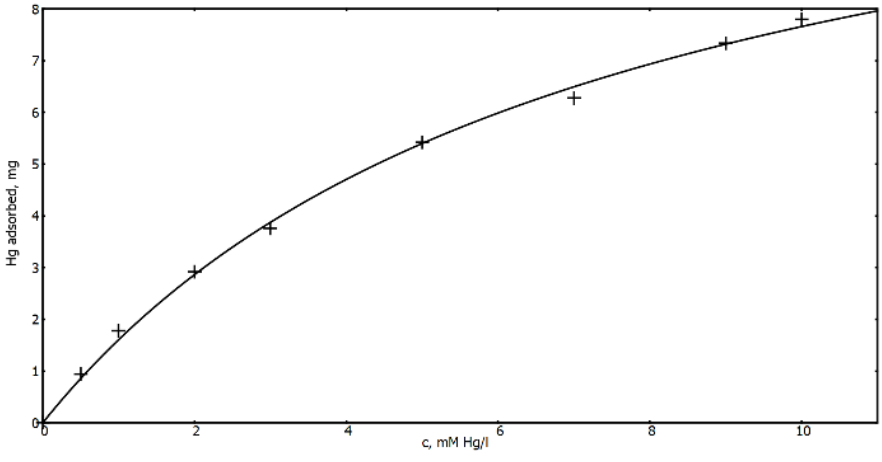

Figure 9: Sorption isotherm for UiO-66_FA synthesised by modulation synthesis method with 50 eq. MAA approximated with Langmuir model.

The functionalisation of zirconium structures in post-synthetic ligand exchange with mercaptosuccinic acid in DMF solvent has been found efficient for making them sensitive to mercury. Post-synthetic exchange has been carried out for UiO-66_FA and for Zr_PET structures. The kinetics properties of both sorbents have been determined using the

radiotracer method. The results are shown in Figure 10. The experimental data were approximated using the kinetic Elovitch model.

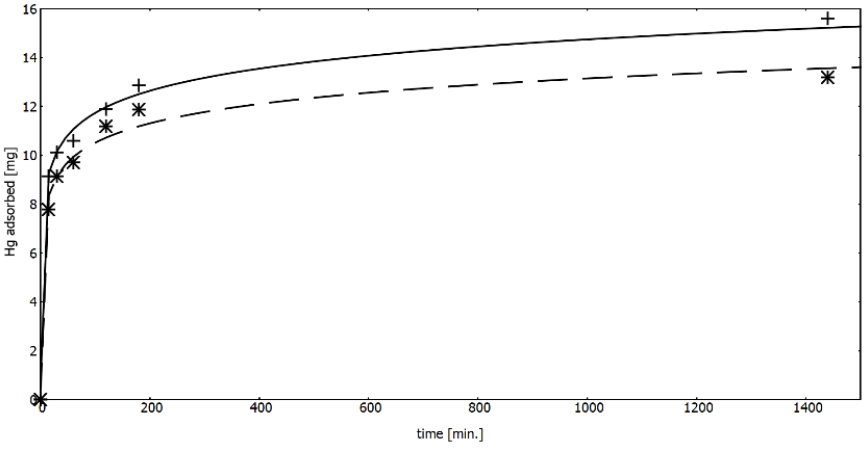

Figure 10: Kinetics of mercury adsorption on UiO-66_FA (solid line) and Zr_PET (dashed line) modified with mercaptosuccinic acid approximated with Elovich model.

6. Sorption of ruthenium

Ruthenium isotopes ^{101}Ru (5.17%), ^{103}Ru (3.03%), and ^{106}Ru (0.4%) are produced in a reactor as a fission product of ^{235}U. During the process of uranium and plutonium recovery by extraction, (PUREX) high-level liquid waste is produced (HLLW). HLLW contains a significant amount of platinum group metals (PGM) such as palladium, ruthenium, and rhodium. It was estimated that one ton of HLLW of spent nuclear fuel from a light water reactor (LWR) contains around 4 kg of PGMs. The estimated content of fission- generated PGMs varies depending on the nature of fuel, burn up, cooling time etc, but significantly covers the amount obtained naturally [16]. It has been suggested that PUREX raffinate can be used as a source of the ruthenium and palladium capable of meeting growing industrial demands.

Ruthenium is one of extremely troublesome radionuclide in reprocessing process of the spent nuclear fuel and most difficult to remove because of a large fission yield, relatively long half-live (Ru-106 $T_{1/2}$ =369d.) and complex chemistry (oxidations states from 0 to +8 and tendency to formation of large number of complexes). The volatility of the ruthenium oxide RuO_4 presents a technical problem for the vitrification of nuclear wastes [17]. Due to the volatile nature of ruthenium tetroxide, it gets deposited in the process pipelines and stacks. Moreover, ruthenium

(along with other platinum group metals) tends to form a separate phase in the vitrification process and hence, deteriorate the stability of a vitrified product. Attempts have been made over the years to separate radio-ruthenium from radioactive feeds, including the acidic high -level liquid waste (HLLW) as well as the alkaline low-level liquid waste (LLLW) or intermediate level liquid wastes (ILLW). Solvent extraction, precipitation, ion-exchange, etc. are some of the commonly employed techniques for the separation of radio-ruthenium from radioactive feeds.

In the present report, the preliminary results on MOF application for ruthenium removal from water using Zr_hcp sorbent synthesised in the course of this work are presented. The pH dependence of distribution coefficient on pH water solution of ruthenium chloride is shown in Figure 11. In the studies 50 mg of sorbent were administered to 10 mL of ruthenium chloride solution with a concentration of ruthenium 5 µg/g.

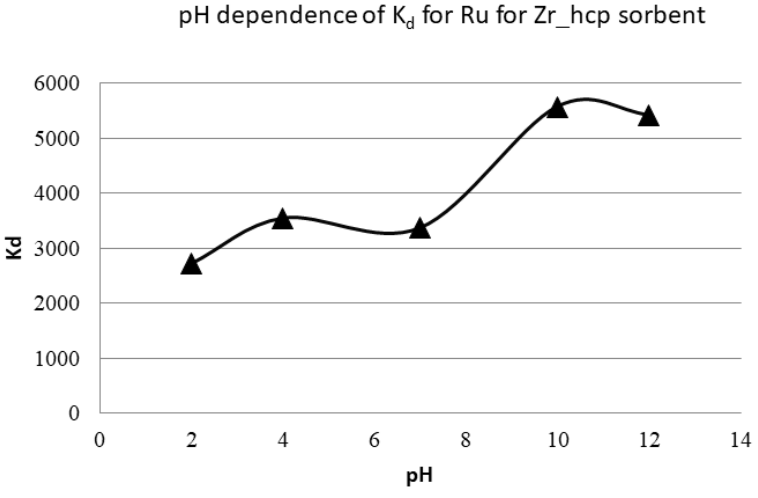

Figure 11: pH dependence of distribution coefficient for ruthenium ion sorption from water solution.

7. Conclusions

UiO-66 type MOF is a chemically resistant porous structure that can serve as a starting material for sorbents synthesis for selected radionuclides and heavy metals removal from water. For this purpose, it is necessary to carry out the functionalisation of relatively chemically inert UiO-66 to introduce into their structure a ligand containing a side functional group showing affinity to the metal which is to be adsorbed. PET waste material

can be used for the UiO-66 sorbent synthesis using a two-steps or one-step procedure. In the two-steps procedure, PET should be depolymerised to recover terephthalic acid, which will then be used to synthesise the final product. In a one-step synthesis, zirconium terephthalate sorbents can be synthesised directly from PET flakes. The examples of application of zirconium terephthalate structures synthesised by one pot method for sorption of radionuclides relevant to nuclear technologies as well for sorption of mercury were presented.

However, further research is needed to optimise the synthesis and functionalisation process of UiO-66 sorbents and to adapt their rheological properties to industrial requirements.

8. Acknowledgments

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