



Chapter 2

Synthesis of zirconium porous sorbents from waste PET flakes

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1. Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer synthesised by polycondensation of terephthalic acid and ethylene glycol monomers. Developed in 1942, it found its way into fiber production. The advances in polymer processing in the 1970s, in particular the development of injection stretch blow molding process, made the mass production of beverage bottles possible. Since then, PET polyester has been an excellent choice as a material in many industries. Factors such as its chemical resistance, strength-to-weight ratio, shatterproof properties, and low cost to product, make it an accessible solution for consumable product packaging [1].

The widespread use and high consumption of PET plastics, low biodegradability, and low recycling rates resulted in rapid increase in the volume of PET waste. Existing PET recycling technologies (chemical, mechanical, and incineration) have not been sufficiently applied in practice. Chemical PET depolymerisation to terephthalic acid for reuse

in PET production faces a price barrier due to the difficulty of delivering a product with the desired purity at a competitive price. The mechanical reprocessing of waste PET to pellets is limited to the low number of cycles due to the degradation of mechanical properties in subsequent cycles of recycling. The incineration of PET requires the removal of toxic gaseous pollutants and doesn't match the requirements of a circular economy. For these reasons, landfilling is at present a common practice for the PET waste management. This poses a serious threat to the environment in the long term due to the slow release of microplastic particles and toxic chemicals [3–5].

The development of new economically efficient ways to recycle PET waste is of paramount importance. Such a proposal is the concept of using waste PET as a linker source for the synthesis of porous metal-organic sorbents. It is worth noting that PET polymer contains a significant amount of terephthalic acid (86 wt %). This ligand is frequently used for the synthesis of valuable porous metal-organic framework materials (MOF), for example, UiO-66, MIL-53, MIL-101. MOFs are considered as materials with a broad spectrum of applications, for example, in the field of gas storage, gaseous mixture separations, heavy metal removal from solutions etc. The possibility of synthesis of selected MOFs using direct PET flakes or terephthalic ligand recycled from PET has already been demonstrated [6,7]. The review on the concept of PET recovery from PET bottles for reuse in MOFs synthesis has been recently published [8].

The aim of the PET-MOF-CLEANWATER project is to investigate the possibility of using PET waste for the synthesis of organometallic compounds of MOF type and to demonstrate the usefulness of such obtained sorbents for the removal of toxic elements from water. Two possibilities are explored in the course of the project. The first consists of recovering terephthalic acid using chemical methods of PET depolymerisation. The recovered terephthalic acid would then be used to synthesise MOF type sorbents. The zirconium terephthalate UiO-66 is mainly considered here due to its high chemical stability over a wide pH range and a high tolerance to structural defects that can be of the missing ligand or missing cluster type. The tolerance to defects is an important property as it ensures the stability of the structure during the process of its functionalisation. The functionalisation process is aimed at incorporating into the structure a functional group showing a chemical affinity for the metal to be adsorbed. The functionalisation process can be carried out at the synthesis stage or after its completion [9–11]. In the first case, a ligand containing a single coordinating group and a side functional group not participating in the coordination is added to the reaction mixture. In the second case, the structure building ligands are exchanged with another

ligand containing coordinating groups and the desired side functional group. Ligand exchange is carried out in solution after the completion of the primary synthesis.

The second possibility explored in the project is to synthesise sorbents directly from PET flakes using environmentally friendly solvents. The development of such a process would enable the simplification of the synthesis, saving of chemicals and, as a result, increase the economic efficiency of sorbents synthesis. An additional benefit would be the opportunity to reduce problematic PET waste and use the products made from it for environmental purposes.

The paper presents results of work carried out on:

- different PET depolymerisation methods and application of the recovered terephthalic acid for the synthesis of UiO-66 sorbents,
- synthesis of zirconium sorbents and zirconium sorbent precursors in acetic acid and acetone solutions directly from PET flakes,
- synthesis of UiO-66 sorbent in gamma-valerolactone solvent,
- functionalisation of sorbents applying modulated synthesis and post-synthetic ligand exchange methods, and
- evaluation of the suitability of the produced materials for mercury sorption from aqueous solutions.

2. Synthesis of UiO-66 sorbents using terephthalic acid recovered by PET chemical depolymerisation

The general synthesis scheme is shown in Figure 1. In the first step, PET flakes cut out from light-blue coloured water bottles were depolymerised using alkaline or neutral hydrolysis methods. Four different variants of depolymerisation were used:

1. depolymerisation under reflux at 190 °C in a mixture of water and ethylene glycol. In typical synthesis 22 g PET, 8.7 g NaOH, 100 ml H₂O, 87 ml ethylene glycol were used (sample s1),
2. alkaline hydrolysis under reflux at 120 °C in 8M water solution of sodium hydroxide (sample s2),
3. alkaline depolymerisation in hydrothermal reactor at 170°C, 180 °C, and 190 °C. In typical synthesis 6 g PET, 8 g NaOH and 150 ml of water were used (sample s3), and
4. neutral hydrolysis in hydrothermal reactor in water at 200°C, typically 16 g PET were used (sample s4).

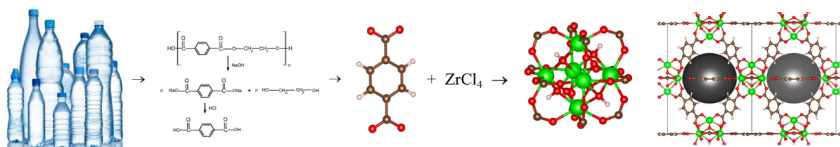


Figure 1: The scheme of the synthesis of UiO-66 sorbent using waste PET-derived terephthalic acid.

After the completion of the alkaline depolymerisation reaction, the resulting solution was diluted with water and subjected to filtration. Terephthalic acid was recovered from the filtrate by precipitation with sulfuric acid. The high efficiency around 95% was obtained except in the case of alkaline hydrolysis under reflux at 120°C. The NMR and X-ray diffraction spectra measured for the obtained materials confirmed their compliance with terephthalic acid offered commercially by Sigma-Aldrich.

In order to confirm the practical usefulness of the obtained depolymerisation products, UiO-66 sorbents were synthesised using recycled terephthalic acid. The synthesis of UiO-66 was carried out according to the procedures described in the literature. DMF was used as solvent and zirconium chloride as metal source. Synthesis was carried out at 120 °C on oil bath in Pyrex bottle. The diffraction spectra of the resulting products shown in Figure 2 confirmed an excellent agreement with that of the UiO-66 structure. The porous nature of synthesis products was confirmed by BET measurements. Values in the range of 1200 – 1300 m²/g were obtained for the specific surface area.

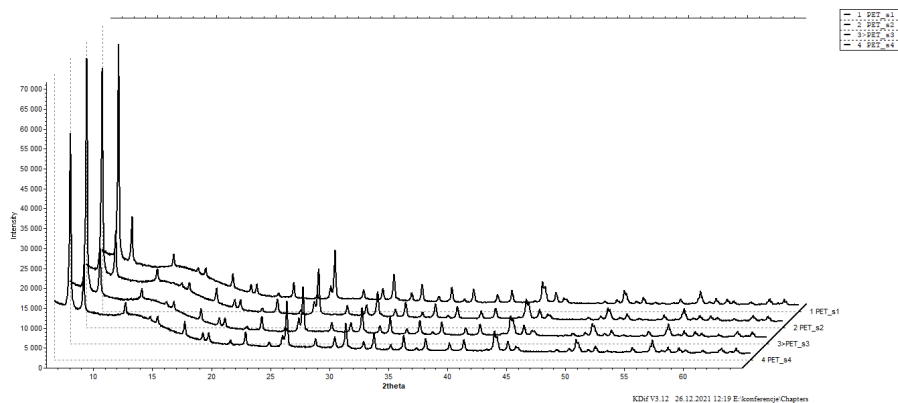


Figure 2: XRD diffraction spectra of the UiO-66 structure synthesised with terephthalic linker obtained by waste PET depolymerisation using different variants of this process (sample s1, s2, s3, s4).

The sorbents obtained were functionalised with mercaptoacetic acid. The functionalisation was carried out by soaking the sorbent in 0.1 M mercaptoacetic acid solution in DMF or ethanol at 80°C for a few hours with continuous stirring. The sorption capacity tests were carried out in batch mode contacting 15 mg of sorbent with 10 ml of water mercury chloride solution with a concentration of 0.01M for 2 hours. The sorbent was then recovered by filtration on a track-etched membrane and used for structural and elemental content studies. The morphology of the sorbent was retained after functionalisation and after mercury sorption as shown in SEM image in Figure 3. The elemental content analysis by EDS method confirmed the successful mercaptoacetic acid ligand embedding in the sorbent and adsorption of the mercury on the sorbent. The average value of the molar ratio of sulphur to zirconium content after functionalisation was equal to 1.06 and mercury to zirconium molar ratio after sorption was 0.51.

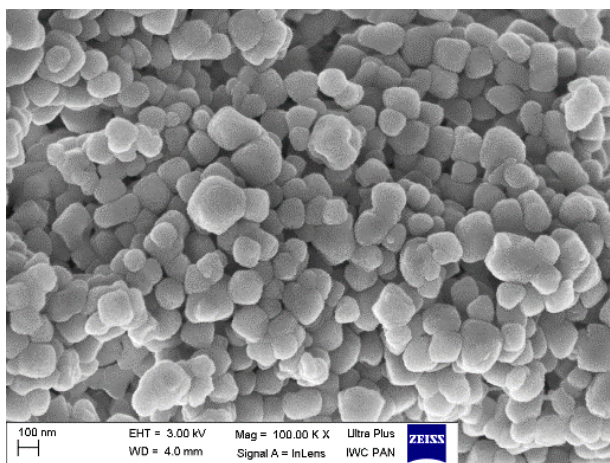


Figure 3: SEM image of sorbent (sample1) after functionalization with mercaptoacetic acid and mercury sorption.

For the quick determination of mercury accumulated on sorbent, we used the X-ray fluorescence spectroscopy. Fluorescence studies were performed on a home-made instrument equipped with a low-power rhodium X-ray tube operating at 40 kV. The ratio of areas under the $L\alpha$ line of mercury line and $K\alpha$ line of zirconium allows the determination of the relative content of mercury to zirconium. For the determination of absolute value of mercury to zirconium ratio calibration standards were prepared.

The X-ray fluorescence spectra of sorbent (sample s1) after mercury sorption is shown in Figure 4.

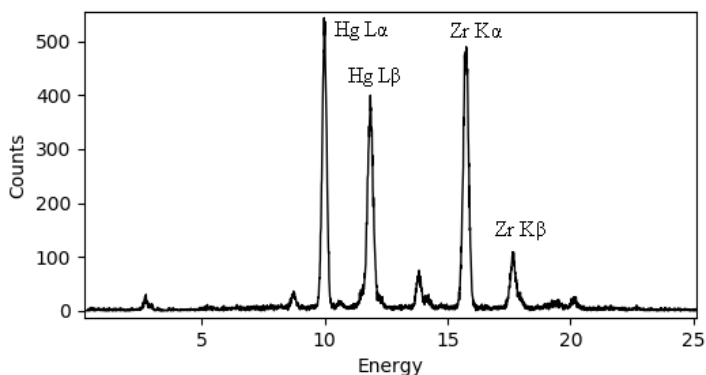


Figure 4: X-ray fluorescence spectrum of sorbent (sample s1) after mercury sorption. The intensities ratio of mercury L_{β} line to zirconium K_{α} line is equal to 0.906 (estimated molar ratio Hg/Zr = 1.17)

3. **Synthesis of zirconium sorbents directly from PET flakes**

Dimethylformamide (DMF), commonly used solvent for MOF synthesis, is considered toxic and harmful for the environment. Developing a method of synthesis using a different solvent is paramount for larger than laboratory-scale applications. The synthesis of zirconium MOF with hexagonal structure using direct waste PET in formic acid and acetone mixture has been reported in [12]. Our research indicates the possibility of solvothermal synthesis of porous zirconium structure directly from PET flakes in a pressure reactor in acetic acid and acetone mixture at temperatures in the range 160 – 190°C. In typical synthesis 1 g of PET (5 mM) flakes, 1.15 g of $ZrCl_4$ (5 mM), 75 ml of acetic acid and 75 ml of acetone were used. The X-ray diffraction spectrum of material obtained, measured on PETRA III/P02.1 line of DESY (Hamburg) synchrotron at $\lambda = 0.20735 \text{ \AA}$ is shown in Figure 5. The spectrum obtained agrees well with the X-ray diffraction spectrum of zirconium complex with terephthalic acid, possessing hexagonal close-packed structure with parameters $a=b=14.71731 \text{ \AA}$, $c=36.9794 \text{ \AA}$, $\gamma=120^\circ$ already reported in the literature. The structural building unit for this structure containing 12 zirconium atom clusters which can be interpreted as fused two octahedral clusters known from UiO-66 structure, is presented in Figure 6. The obtained structure was porous and BET measurements gave the value of $524.30 \text{ m}^2/\text{g}$ for the specific surface area. We also found that the structure has sorption properties for ruthenium from water solution and after functionalisation with mercaptoacetic acid or mercaptosuccinic acid also for mercury (see Table I)

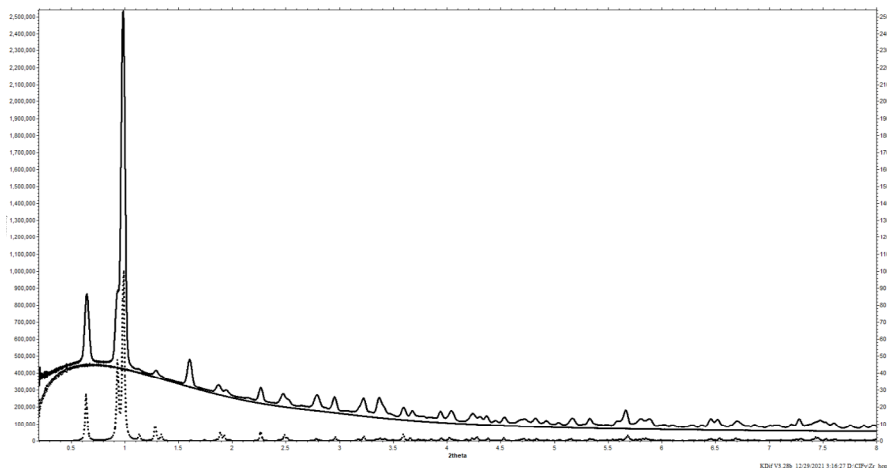


Figure 5: XRD diffraction spectra of Zr hcp structure measured at PETRAIII/ P02.1 synchrotron line in Hamburg at $\lambda = 0.20735\text{\AA}$ (upper), empty capillary (middle) and XRD spectrum calculated for Zr_hcp structure (dotted line)

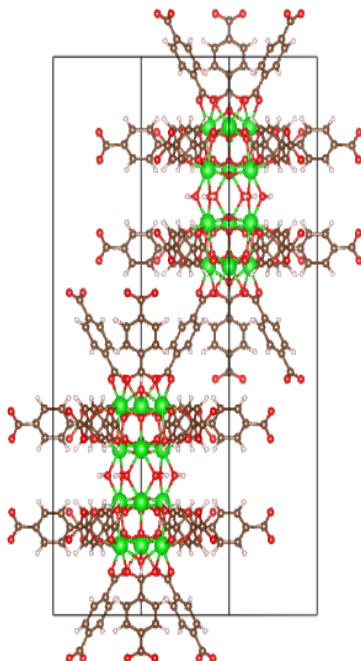


Figure 6: A view of the unit cell of zirconium hcp structure, (zirconium – green, oxygen – red, carbon – gray).

Continuing the research on the search for new synthesis methods, we found that it is possible to convert PET to fine powder at a low temperature of 120°C in acetic acid/ acetone solution and also in acetic acid solution alone in the presence of zirconium ions. In typical synthesis 1g of PET flakes, 1,61 g of $ZrOCl_2 \cdot 8H_2O$, 40 ml of acetic acid or 20 ml of acetic acid and 20 ml of acetone were used. The synthesis was done on an oil bath in Pyrex 100 ml bottles. The crystalline nature of the material obtained was confirmed by X-ray diffraction studies (Figure 7) and SEM microscopic examinations (Figure 8).

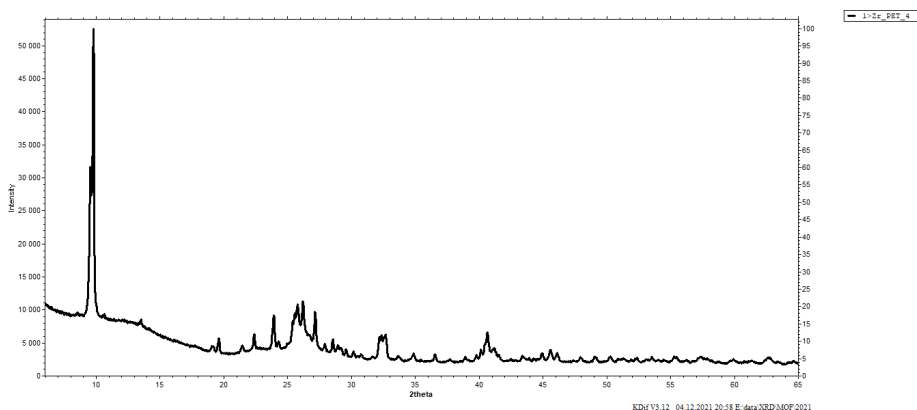


Figure.7: XRD spectrum of material synthesized directly from PET flakes at 120°C in acetic acid/acetone mixture.

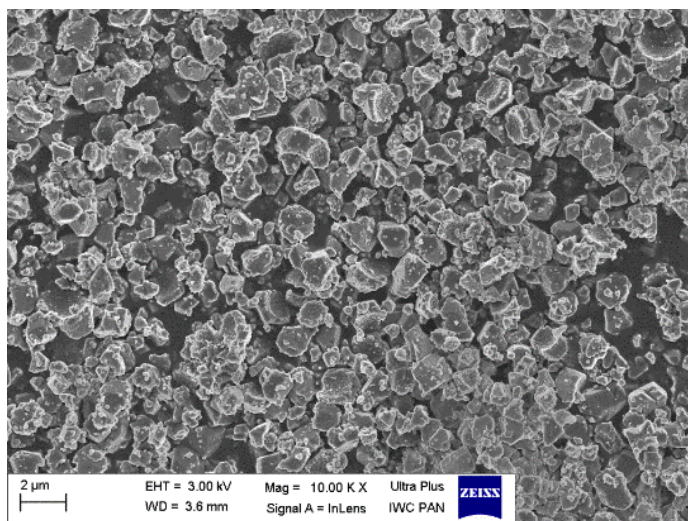


Figure 8: SEM image of material obtained from PET flakes in acetic acid/acetone mixture at 120°C.

The crystal structure of the material obtained is currently being investigated. It is worth noting that in the observed spectrum, the reflections belonging to PET or terephthalic acid are not visible. We suppose that the resulting material can be zirconium complex with mixed, terephthalic acid, and acetic acid ligands. Such complexes synthesised from zirconium chloride and terephthalic acid in acetic acid have been reported recently [13–14]. We have also found that the material synthesised may serve as a precursor for the synthesis of mercury sorbent. We performed functionalisation of this material using five different ligands (mercaptosuccinic acid, mercaptoacetic acid, L-cysteine, EDTA and thiosalicylic acid) in ethanol or DMF at 60°C. The relative intensities of mercury to zirconium measured by X-ray fluorescence method are presented in Table I.

Table 1: The results of an evaluation of the sorption capacity of the materials synthesised at different temperatures and after functionalisation.

Ligand	$I_{\text{Hg}}/I_{\text{Zr}}$
Synthesised in acetic acid/acetone mixture at different temperatures	
170°C, mercaptoacetic acid	0.336
180°C, mercaptoacetic acid	0.294
Synthesised at temperature 120°C and functionalised with	
Mercaptosuccinic acid	0.103
Mercaptoacetic acid	0.136
L-cysteine	0.481
EDTA	0.086
Thiosalicylic acid	0.224

The functionalised sorbent shows fast kinetics. The results of the sorption kinetics study for sorbent synthesised at 120°C and functionalised with mercaptosuccinic acid are shown in Figure 9. The data of activity remaining in the solution were obtained by the radiotracer method using mercury ^{107}Hg isotope. A good approximation to experimental data was achieved using the second-order kinetics model.

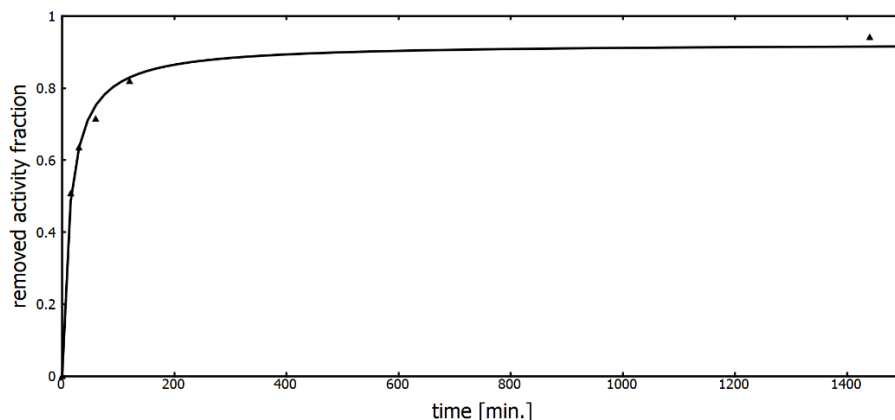


Figure 9: The time dependence of mercury activity removal from water solution for sorbent synthesised at 120°C using waste PET flakes and functionalised with mercaptosuccinic acid.

4. Synthesis of UiO-66 sorbent in GVL (gamma-valerolactone)

Gamma-valerolactone is a colourless liquid boiling at 230°C. It is obtained from levulinic acid and is considered an environmentally friendly solvent. Structural scheme of gamma-valerolactone is shown in Figure 10.

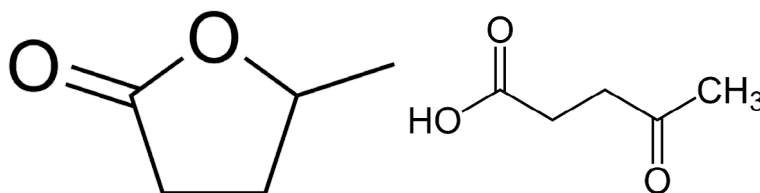


Figure 10: Structural scheme of gamma-valerolactone (left) and levulinic acid (right)

The synthesis of UiO-66 structure was performed in a Pyrex bottle at 120°C in 25 ml GVL using 5.4 mM $ZrOCl_2 \cdot 8H_2O$, 5.4 mM of terephthalic acid and 6 ml of formic acid used as modulator. The mass of the obtained product was equal to 0.81 g (0.54 efficiency). The SEM picture of the product showing regular crystals is presented in Figure 11.

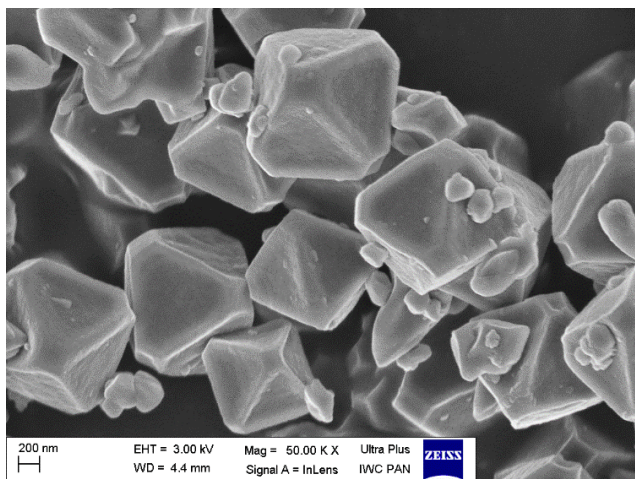


Figure 11: SEM picture of UiO-66 synthesised in gamma-valerolactone.

The sorbent was functionalised in a post-synthetic process with mercaptosuccinic acid and sorption kinetic of modified sorbent was studied using the radiotracer method. 10 ml of 0.01M water solution of mercury chloride was contacted with 15 mg of sorbents and activities remaining in the solution were measured at different times. The results showing the amount of mercury activity accumulated on sorbent are presented in Figure 12. The best fitting was obtained using the Elovich kinetics model, which assumes that the rate of adsorption of solute decreases exponentially as the amount of adsorbed solute increases.

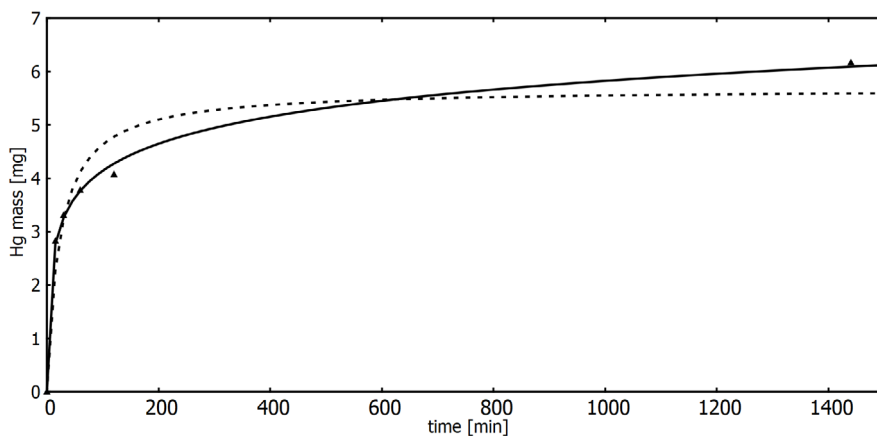


Figure 12: Time dependence of mercury activity accumulated on sorbent. Solid line – Elovich model, dashed line – second order kinetic model.

5. Conclusions

A synthesis of valuable UiO-66 type sorbents for toxic elements removal from water using waste PET as a linker source is possible. In the course of the project, different methods of PET waste utilisation for the synthesis of UiO-66 -based sorbents and their functionalisation were tested. The two routes seem to be possible for large-scale environmentally friendly synthesis. The first, one is based on depolymerisation of waste PET using chemical methods and on the usage of recovered terephthalic acid for UiO-66 synthesis using the environmentally friendly solvent, for example, GVL. The second one is based on the direct synthesis of sorbents from PET waste flakes. The acetic acid/acetone mixture at different ratios can be used for that purpose in the presence of zirconium salt. It has been shown that the decomposition of PET flakes to fine powder is possible in pure acetic acid at temperature as low as 120°C in the presence of zirconium salts. The resulting powder can serve as the precursor which can be converted to a usable sorbent after functionalisation. However, additional research studies are necessary to find optimal reaction parameters and determine phase purity of resulting material and efficiency of the process.

The understanding of the sorption mechanisms, especially their dependence on structural and morphological parameters of the sorbent is important for the development of practical applications.

Synchrotron- based methods for the study of nanomaterials like total scattering and pair distribution function (PDF) determination and high-resolution powder diffraction (HRPD) may be helpful to explore these possibilities.

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