

## ORGANOKOVOVÁ SÍŤ UiO-66 PRO DEGRADACI ORGANOFOSFÁTŮ VE VODNÉM PROSTŘEDÍ

## METAL-ORGANIC FRAMEWORK UiO-66 FOR ORGANOPHOSPHATE DEGRADATION IN AQUEOUS ENVIRONMENT

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## Abstrakt

Porézní koordinační polymery, označované zkratkou MOF (Metal-Organic Frameworks), jsou nové a stále se rozvíjející typy materiálů se zajímavými vlastnostmi (např. vysoký měrný povrch, schopnost sorpce plynů, katalytická aktivita, apod.). Jedná se o krystalické, porézní materiály, které se skládají z kovových (oxo)klastů navzájem propojených organickými linkery (ligandy). MOFy na bázi Zr<sup>IV</sup> oxoklastů, [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>], jsou účinnými katalyzátory pro rozklad organofosfátových toxických sloučenin, zejména pesticidů a nervově paralytických bojových látek. Náš příspěvek je věnován využití UiO-66, který se skládá ze zmíněných Zr-klastů a kyseliny tereftalové, pro degradaci methyl-paraoxonu ve vodném prostředí. Nalezli jsme korelaci mezi rychlostí jeho degradace, počtem defektů ve struktuře UiO-66 a stabilitou UiO-66 ve vodném prostředí. Při pH vyšších než 7.0 roste rychlost degradace methyl-paraoxonu. Tento průběh souvisí s tvorbou nových katalytických center, jejichž vznik je spojen s rozkladem UiO-66.

**Klíčová slova:** Organokovová síť (MOF), organofosfáty, degradace

## Abstract

Porous coordination polymers, known as metal-organic frameworks (MOFs), are new and developing class of materials with advantageous properties (e.g., high surface area, sorption of gasses, catalytic activity, etc.). These crystalline porous materials are composed of metal (oxo)clusters, which are connected by organic linkers (ligands). The Zr-based MOFs of the UiO-66 family are among the most studied systems. MOFs containing Zr<sup>IV</sup> oxoclusters, [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>], are effective catalysts for the degradation of toxic organophosphates, mainly pesticides and chemical warfare agents. Here, we report on degradation of methyl-paraoxone by UiO-66 composed of the [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>] clusters linked together by terephthalic acid. We correlate the degradation rate of methyl-paraoxone with a number of defects in the structure and UiO-66 stability at aqueous medium. At the pH above 7.0, the degradation rate of methyl-paraoxone increases when compared with that at lower pHs. This behaviour is related to the formation of new catalytic centres, which is connected with the UiO-66 decomposition.

**Key words:** Metal-Organic Framework (MOF), organophosphate, degradation

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## 1. INTRODUCTION

Metal-organic frameworks (MOFs) are a subgroup of coordination polymers. Typical feature distinguishes them from coordination polymers is that MOFs are porous and crystalline materials consisting of metal cation or clusters linked together via organic ligands.<sup>1</sup> The metal clusters form nodes called secondary building units (SBUs). They contain usually few metal cations and other atoms such oxygen (oxoclusters). SBUs are coordinated with charge-compensating organic ligands called linkers and they are typically represented by polytopic carboxylic acids. This combination provides 2D or 3D crystalline structures with free space inside which is called cavities.<sup>1,2</sup> With respect to the choice of metals and linkers and their combinations variable MOFs structures with broad spectrum of the properties and functions can be prepared. Typical common property is a high surface area usually exceeding  $1000 \text{ m}^2 \text{ g}^{-1}$ .<sup>1,3</sup> Due to variable properties MOFs are potential candidates for gas sorption and separation,<sup>4,5</sup> catalysis,<sup>6</sup> medical applications,<sup>7</sup> and sensors.<sup>8</sup>

Despite the potential of MOFs, they have limited stability, especially in comparison with other materials such as zeolites. Recently, it was discovered zirconium-based MOF family with a high hydrothermal and chemical stability.<sup>9</sup> The most utilizing is UiO-66 which is composed of  $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$  SBUs as 12-connected nodes linked together by terephthalate linkers (Fig. 1).<sup>10</sup> The structure of UiO-66 is not perfect and contains a number of missing-linker or missing-cluster defects.<sup>11</sup> These defects provide the open-metal sites which can act as catalytic sites at hydrolytic reactions. However, the open-metal sites are occupied by compensating ligands such  $-\text{OH}$ , coordinated water, or most often by monocarboxylates used in the synthesis.<sup>12,13</sup> The compensating ligands can be easily substituted by organophosphate, i.e. pesticides or chemical warfare agents. The substitution leads to organophosphate hydrolytic degradation. For this reason, Zr-based MOFs are potential materials for organophosphate decontamination.<sup>13,14,15</sup>

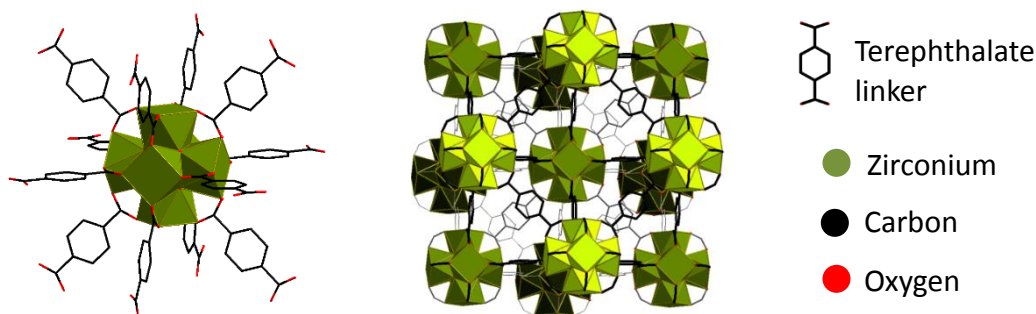


Figure 1: Zirconium based MOF UiO-66.  $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$  cluster occupied by 12 terephthalate linker (left). Ideal structure of the UiO-66 (right).

The catalytic activity of the UiO-66 depends on the number of the defects, which is limited by the stability. Here we report a method for the introducing new defects to UiO-66 structure and their effect on MOF stability and on the degradation rate of methyl-paraoxon (DMNP – dimethyl-4-nitrophenyl), a model molecule of organophosphates.

## 2. EXPERIMENTAL

Synthesis of UiO-66 was performed by solvothermal procedure using  $ZrCl_4$  and terephthalic acid in molar ratio 1:1 in DMF. As a modulator acetic acid was used.

The characterization of as-prepared UiO-66 was made by combination of the methods like powder X-ray diffraction (XRD),  $N_2$  adsorption isotherms at 77 K, scanning electron microscopy (SEM),  $^1H$  NMR, and thermal analysis (DTA/TGA). These methods were used also for the structure changes determination after the MOF treatment.

The quantification of the terephthalate linker leaching was performed by HPLC-DAD technique. The samples at different pH were taken during the acid-base titration of the UiO-66 using 0.1M NaOH. The HPLC was also used for the monitoring of DMNP degradation.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis and characterization of UiO-66

UiO-66 was prepared by the solvothermal synthesis with acetic acid as a modulator in 95 molar equivalents to terephthalic acid. The methods used for characterization, such as XRD,  $N_2$  adsorption isotherms at 77 K, SEM, NMR, and thermal analysis showed, that as-prepared UiO-66 is imperfect with defects in the structure.<sup>11</sup> The defects were occupied by monocarboxylates (formate, acetate).

### 3.2 Acid-base titration and evaluation of terephthalic acid release

As-prepared UiO-66 (50 mg in 50 ml in water) was titrated by 0.1M NaOH to evaluate its acid-base behavior. When the given pHs were reached the solid was separate by microfilteres and solution was analyzed by HPLC for quantification of released terephthalic acid and missing-linker defects formation. At given pH, the solid sample of treated UiO-66 was also collected to measurement of the structure preservation.

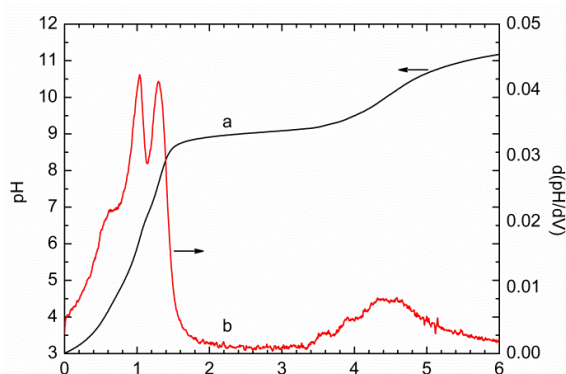


Figure 2: Acid base titration of the UiO-66 by the 0.1M NaOH. Titration curve (black) and its first derivation (red).

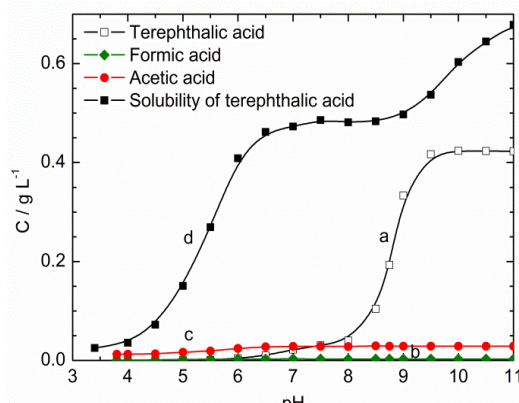


Figure 3: Concentrations of terephthalic (a), acetic (b), and formic (c) acids leached at different pHs from 50 mg of UiO-66 in 50 mL of water compared with the corresponding immediate solubility of terephthalic acid.

The natural pH of as-prepared UiO-66 in water is 3.8. The titration curve can be divided into three regions (Fig 2). The first region is characterized by fast pH increase from pH 3.8 to 8.5. The second region is connected with the gradual increasing between pHs 8.5-9.5. And finally, the last region of a rapid pH increase between pH 9.5 to 11.0. Three equivalence points were observed at pH 6.2, 7.9, and 10.1.

At the given pHs the samples were taken to the HPLC analysis of released terephthalic acid (Fig. 3). UiO-66 is stable to the pH 5.0 when no terephthalic acid was detected. Between the pHs 5.5-8.0 there was observed slight releasing of terephthalic acid to the solution from 1.1 to 40.3 mg L<sup>-1</sup>. Next region is related with a stable part resulting from the titration curves, and it is connected with a rapid releasing of the linker with the higher pH. This behavior was observed at pHs 8.5-9.5 when the concentration of terephthalic acid was 104-420 mg L<sup>-1</sup>. The last region above pH 9.5 was without any additional linker release and its concentration was stable on value 420 mg L<sup>-1</sup>. Theoretical calculation showed that 420 mg L<sup>-1</sup> of released linker is indicating total decomposition of MOF. This hypothesis was confirmed by the analytical method for solids (XRD, N<sub>2</sub> adsorption isotherms) which showed total loss of the crystallinity and surface area.

### 3.3 Catalytic activity of UiO-66 at different pHs

In order to correlate the amount of the released linker with catalytic activity of UiO-66, we investigated the degradation of DMNP to 4-NP at pHs between 3.8 and 11.0 (Fig. 4 and Table 1). The reaction follows first-order kinetics and therefore can be characterized by corresponding rate constants and half-times. The self-degradation of DMNP was evaluated in the absence of UiO-66. As expected, DMNP is stable in the broad range of pHs with only a subtle conversion of approximately 3 % at pH 11.0 after 60 min of the reaction.

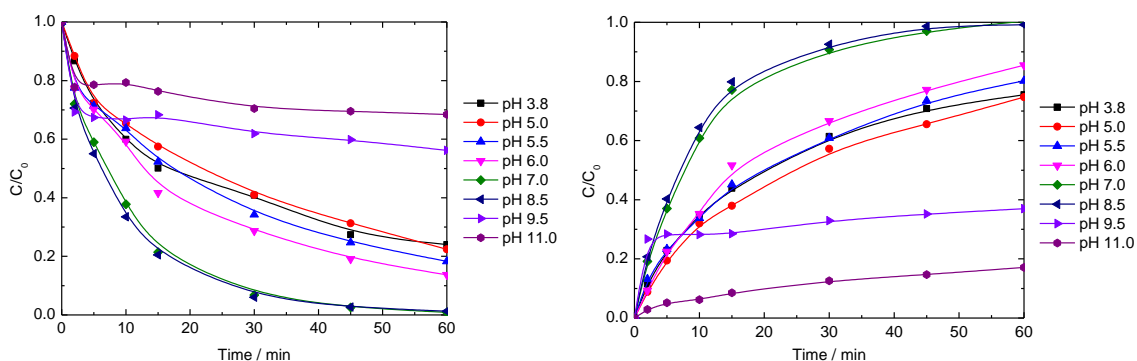


Figure 4: Degradation of DMNP (left) and formation kinetics of 4-NP (right) at different pHs.

The degradation curves can be divided to three groups providing similar behavior. In acidic environment (pH 3.8-6.0) the degradation rate is relatively slow (half-time 23 to 18 min for 4-NP formation) with slight acceleration with the higher pH. Conversion of DMNP to the 4-NP was from 76 to 81 % after 1 hour for pH 3.8 to pH 6.0, respectively. The reactions running at close to neutral pH (7.0-8.5) are very fast with half-time 7 min and 100% conversion. The last reactions are connected with deceleration and almost stopping the reaction. This behavior was observed at pH higher than 9.5, especially in case of pH 11 when the total conversion was 17% only.

Table 1: Degradation of DMNP catalyzed by UiO-66 at different pHs.<sup>a</sup>

pH	Conversion / %	$k_{\text{DMNP}} / \text{min}^{-1}$	$\tau_{1/2 \text{ DMNP}} / \text{min}$	$k_{4\text{-NP}} / \text{min}^{-1}$	$\tau_{1/2 4\text{-NP}} / \text{min}$
3.8	76	0.035	20	0.032	22
5.0	75	0.032	22	0.030	23
5.5	80	0.039	20	0.034	18
6.0	81	0.049	14	0.039	18
7.0	100	0.105	7	0.094	7
8.5	100	0.116	6	0.104	7
9.5	37	n.a.	n.a.	n.a.	n.a.
11.0	17	n.a.	n.a.	n.a.	n.a.

<sup>a</sup>Conversion of DMNP after 60 min of the reaction;  $k_{\text{DMNP}}$  and  $\tau_{1/2 \text{ DMNP}}$  are the first-order rate constant and half-time of DMNP degradation, respectively;  $k_{4\text{-NP}}$  and  $\tau_{1/2 4\text{-NP}}$  are the first-order rate constant and half-time of 4-NP formation, respectively.

The catalytic conversion of DMNP to 4-NP strongly depends on the pH and on the amount of leached terephthalic acid from UiO-66 structure. When the pH increased from 3.8 to 6.0 the half-time of 4-NP formation was very similar with insignificant decrease from 22 to 18 min. This correspond with the stability of UiO-66 indicating no (or only trace) terephthalic acid release. At this pH range, the reaction rate is given only by the defects presented naturally in UiO-66 structure from the synthesis.

However, when the pH was higher (7.0-8.5) the conversion speed was faster with half-time 7 min. The reason is simple – in this pH range, it was observed rapid and tremendous leaching of terephthalate linker from UiO-66. The releasing of terephthalic acid is connected with opening of the metal sites which are responsible for DMNP degradation. For this reason the UiO-66 provide best degradation speed for DMNP, however for the price of UiO-66 changes caused by terephthalic acid leaching. Moreover, at this pH range UiO-66 still keeping its structure which was determined by XRD and surface area measurement.

The last part is focused on the pH higher than 8.5. As was mentioned before, UiO-66 loss its crystallinity at the pH higher than 9.5. The determination of the leached terephthalic acid by the HPLC confirmed UiO-66 is totally decomposed. This observation is well correlate with the degradation kinetics of DMNP. During these pHs the degradation of the DMNP almost stopped shortly after the beginning. This was caused by total decomposition of UiO-66 which was transformed to the amorphous zirconium oxide/hydroxide species. The transformation is connected with the deactivation of the catalyzing open metal sites.

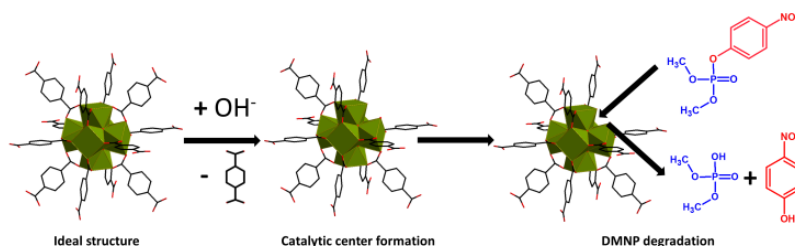


Figure 5: Formation of open-metal sites at Zr(IV) SBUs of UiO-66 after the release of terephthalate linkers. These sites act as catalytic centers of DMNP degradation.

#### 4. CONCLUSION

We summarize the results obtained from detailed HPLC study as follows: i) A number of the -OH<sub>2</sub> and -OH ligands in unsaturated coordination sites of as-prepared UiO-66 is limited as these sites are verifiably occupied by modulator anions including formates generated in situ from DMF during the synthesis. ii) The release of the terephthalate linkers and monocarboxylate ligands during the titration evidently creates new linker defects (i.e., unsaturated coordination sites), not originally present in the structure (Figure 5). This behaviour indicates that the titration experiments change the number of linker defects since these defects are continually formed. iii) Characterization methods generally used for quantification of MOF stabilities (SEM, XRD, and adsorption studies) are not conclusive. The subtle changes to the structure indicated by released structural components have to be analysed by sensitive techniques such as HPLC. iv) New catalytic sites towards the dimethyl-4-nitrophenyl phosphate degradation are formed after the release of the linker or other compensating monocarboxylate ligands - the more massive release without the disruption of the structure, the higher catalytic activity of UiO-66. These results point to the dynamic nature of Zr-based MOFs where coordination/de-coordination of ligands can occur at mild conditions and can significantly alter the resulting MOF properties.

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#### References

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- <sup>1</sup> Ch. Janiak, J. K. Vieth. MOFs, MILs and More: Concepts, Properties and Applications for Porous Coordination Networks (PCNs). *New J. Chem.*, 2010, 34, 2366-2388.
  - <sup>2</sup> D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe. Secondary Building Units, Nets and Bonding in the Chemistry of Metal-Organic Frameworks. *Chem. Soc. Rev.*, 2009, 38, 1257-1283.
  - <sup>3</sup> O. K. Farha, I. Eryazici, N. Jeong, et al. Metal-organic Framework materials with ultrahigh surface areas: Is the sky the limit? *J. Am. Chem. Soc.*, 2012, 134, 15016-15021.
  - <sup>4</sup> J. R. Li, J. Sculley, H. C. Zhou. Metal-Organic Frameworks for Separations. *Chem. Rev.*, 2012, 112, 869-932.
  - <sup>5</sup> Y. He, W. Zhou, G. Qian, B. Chen. Methane Storage in Metal-Organic Frameworks. *Chem. Soc. Rev.*, 2014, 43, 5657-5678.
  - <sup>6</sup> A. Corma, H. García, F. X. Llabrés i Xamena. Engineering Metal Organic Frameworks for Heterogeneous Catalysis. *Chem. Rev.*, 2010, 110, 4606-4655.
  - <sup>7</sup> D. Bůžek, J. Zelenka, P. Ulbrich, et al. Nanoscaled porphyrinic metal-organic frameworks: photosensitizer delivery systems for photodynamic therapy. *J. Mat. Chem. B.*, 2017, 5, 1815-1821.
  - <sup>8</sup> L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp. Metal-Organic Framework Materials as Chemical Sensors. *Chem. Rev.*, 2012, 112, 1105-1125.

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- <sup>9</sup> S. Yuan, J.-S. Qin, Ch. T. Lollar, H.-C. Zhou. Stable Metal-Organic Frameworks with Group 4 Metals: Current Status and Trends. *ACS Cent. Sci.*, 2018, 4, 440-450.
- <sup>10</sup> J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.*, 2008, 130, 13850-13851.
- <sup>11</sup> G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye, K. P. Lillerud, K. P. Defect Engineering: Tuning the Porosity and Composition of the Metal–Organic Framework UiO-66 via Modulated Synthesis. *Chem. Mater.*, 2016, 28, 3749-3761.
- <sup>12</sup> M. Taddei, R. J. Wakeham, A. Koutsianos, E. Andreoli, A. R. Barron. Post-synthetic ligand Exchange in zirconium-based metal-organic frameworks: beware of the defects! *Angew. Chem. Int. Ed.*, Accepted manuscript.
- <sup>13</sup> M. J. Katz, R. Klet, S. Y. Moon, J. Mondloch, J. T. Hupp, O. K. Farha. One step backward is two steps forward: Enhancing the hydrolysis rate of UiO-66 by decreasing [OH<sup>-</sup>]. *ACS Catalysis*. 2015, 5, 4637-4642.
- <sup>14</sup> S. Y. Moon, Y. Liu, J. T. Hupp, O. K. Farha. Instantaneous Hydrolysis of Nerve-Agent Simulants with a Six-Connected Zirconium-Based Metal–Organic Framework. *Angew. Chem. Int. Ed.*, 2015, 54, 6795 –6799.
- <sup>15</sup> G. W. Peterson, S. Y. Moon, G. W. Wagner, M. G. Hall, J. B. DeCoste, J. T. Hupp, O. K. Farha. Tailoring the Pore Size and Functionality of UiO-Type Metal–Organic Frameworks for Optimal Nerve Agent Destruction. *Inorg. Chem.*, 2015, 54, 9684-9686.