# EQUILIBRIUM AND DYNAMICS OF WATER ADSORPTION ON A METAL-ORGANIC FRAMEWORK MOF-801

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# РАВНОВЕСИЕ И ДИНАМИКА АДСОРБЦИИ ПАРОВ ВОДЫ НА МЕТАЛЛОРГААНИЧЕСКОМ КАРКАСЕ MOF-801

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***Аннотация.*** *В работе представлены результаты исследования равновесия и динамики адсорбции паров воды на металлоорганическом каркасе MOF-801 с целью оценки потенциала его применения в системах адсорбционного охлаждения. Показано, что адсорбция воды на MOF-801 характеризуется S-образными изобарами IV типа по классификации ИЮПАК. В условиях типичного рабочего цикла адсорбционного холодильника (АХ) MOF-801 обменивает 0,21 г/г и может быть регенерирован при 80-85°С, что позволяет использовать источники низкотемпературной теплоты (солнечная энергия). Динамика адсорбции на гранулах MOF-801 в условиях рабочего цикла АХ происходит в режиме, при котором скорость процесса определяется отношением S/m площади поверхности теплопереноса S к массе адсорбента m. Эффективность и удельная мощность АХ с использованием пары «MOF-801–вода» достигают 0,67 и 2 кВт/кг соответственно, что представляет большой практический интерес.*

**Introduction.** Metal-organic frameworks (MOFs) are inorganic–organic hybrid compounds where the metal-oxygen units are bonded through organic linkers forming porous structure. Due to their high porosity, the extensive surface, and structural and chemical variability, MOFs present broad prospects for various applications, particularly for Adsorption Cooling (AC) [1]. The AC allows efficient utilization of renewable or waste thermal energy sources and can significantly minimize primary energy consumption and greenhouse gas emissions. Further implementation of AC significantly relates to developing the new efficient adsorbents. For this reason, MOFs have recently attracted research interest as the adsorbents for AC [3].

This work is aimed at the study of metal-organic framework MOF-801 as an adsorbent for AC. MOF-801 is microcrystalline porous compound whose structure consist of basic units of $Zr_6O_4(OH)_4(fumarate)_6$ [3]. Water adsorption equilibrium on MOF-801 is characterized by the step-wise isotherms, which are beneficial for AHT [2]. We present the results on the equilibrium and dynamics of water vapor adsorption on MOF-801 under operating conditions of a typical AC cycle. Based on the data obtained, the efficiency and the specific power of the chilling cycle employing the "MOF-801-water" working pair are evaluated.

**Materials and methods.** The sample of MOF-801 was synthesized by a solvothermal method following the procedure described in the literature [3].

**Results and discussion.** The structural characteristics of the MOF-801, determined by low temperature nitrogen adsorption, show that sample possess extensive surface with a specific area reaching $S_{sp}$ = 900 ± 20 $m^2$/g. Water vapor adsorption isobars for MOF-801, explored by thermogravimetric method, are step-wise curves showing a small water uptake at high temperature, followed by the abrupt water sorption in a narrow temperature range that depends on the vapor pressure (Fig. 1). The water uptake gradually increases to 0.4 g/g with a further decrease in temperature.

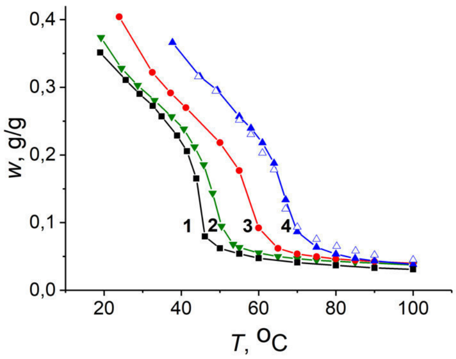


*Fig. 1. Isobars of water adsorption (solid symbols) and desorption (open symbols) on MOF-801 at vapor pressure P = 0.9 (1), 1.2 (2), 2.4 (3) and 4.3 (4) kPa*

The data on adsorption equilibrium allows the amount of water $\Delta w$ exchanged in the adsorption chilling cycle to be determined. At temperatures of evaporation $T_{ev}$ = 5°C, adsorption $T_{ads}$ = 30°C and regeneration $T_{des}$ = 80-85°C, $\Delta w$ = 0.20-0.21 g/g that exceeds the appropriate value for other adsorbents suggested for AHT (Fig.2).

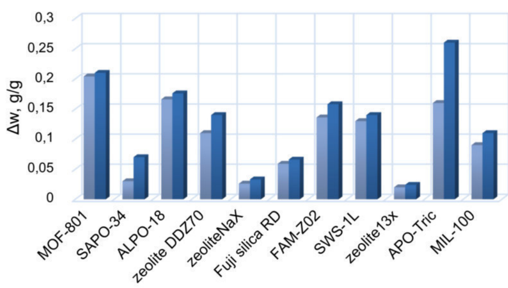


*Fig. 2. The amount $\Delta w$ of water exchanged in the chilling cycles at $T_{des}$ = 80 (light) and 85 (dark) $^oC$*

The dynamics of water adsorption on the loose grains of MOF-801 was studied by the Large Temperature Jump method [4] that imitates the operating conditions of the isobaric stages of the AC cycle. The initial parts of the dynamic curves of water adsorption and desorption match well with the exponential equations $\frac{\Delta w(t)}{\Delta w_{t\to\infty}} = 1 - e^{-\frac{t}{\tau_{ads}}}$ (Fig. 3), where $\Delta w_{t\to\infty}$ is the final uptake variation and $\tau$ is the characteristic time. The effects of the adsorption/desorption temperatures, adsorbent grain size $d_{gr}$, and number $N$ of the grain layers are explored. The growth of the uptake variation $\Delta w_{t\to\infty}$ from 0.18 ± 0.02 to 0.26 ± 0.02 g/g at adsorption temperature decreasing from 35 to 20 °C is observed. The increase in both grain size $d_{gr}$ at fixed $N$ and the layers number $N$ at fixed grain size $d_{gr}$ results in the deceleration of water ad-/desorption (Fig. 3). Water adsorption dynamics on loose grains of MOF-801 was shown to occur under so-called "grain size insensitive" mode when the adsorption rate is proportional to the $S/m$-ratio of the heat transfer surface $S$ to the adsorbent mass $m$. This indicates that the heat transfer between the adsorbent bed and the metal support is a factor which mainly dominates the sorption rate.

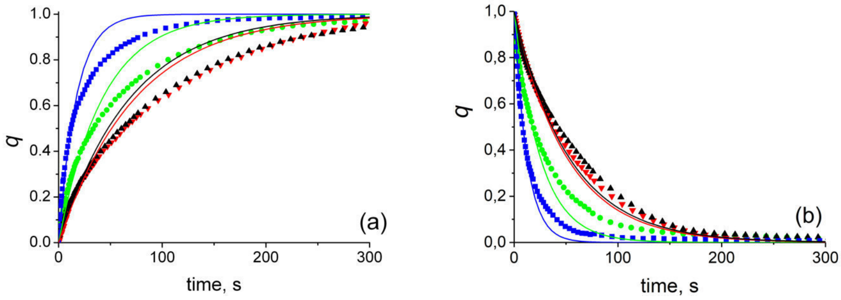


*Fig. 3. The kinetic curves of water adsorption (a) at $T_{ads}$ = 30 °C and desorption (b) at $T_{ads}$ = 85 °C. The grain size $d_{gr}$ = 0.2 – 0.25 (■), 0.4 – 0.5 (●), 0.4 – 0.5 (▲) and 0.8 – 0.9 (▼) mm, N = 1 (■, ●, ▼) and 2 (▲)*

Based on the data obtained, the Coefficient of Performance (COP) of the chilling cycle using the working pair "MOF-801-water" was evaluated as 0.67 at the desorption temperature $T_{des}$ = 85°C. The Specific Cooling Power SCP is estimated as 1-2 kW/kg at $S/m$ = 2.6 – 6 $m^2$/kg typical for advanced heat exchangers.

**Conclusion.** Taking into account the large amount of water exchanged on MOF-801 in the AC cycle, low desorption temperature and its good dynamic performance, "MOF-801 – water" working pair demonstrates a high potential for AC systems.

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