CONFERENCE PROCEEDING

Scalable, High-Yield, and Green Synthesis Method of MOF-303 for Atmospheric Water Harvesting: A Literature Review

Nadia Camilla Darmawan[1]

[1]MAN 2 Kota Malang, 65113, Kota Malang, Jawa Timur, Indonesia

Corresponding author: nadar9028@gmail.com

ABSTRACT

In order to address the global issue of water scarcity, alternative methods of acquiring water from non-traditional sources are urgently required. Harvesting fresh water from the air through atmospheric water harvesting (AWH) serves as a promising solution. Metal-organic frameworks (MOFs), particularly MOF-303, have attained distinctive attention as the most favourable material for AWH due to their unique structure, namely, tunability, high-porosity, and capability of adsorbing water at low relative humidity and then mildly heated for the release of concentrated water vapors. This literature review aims to identify the results of a scalable, high-yield, and green synthesis of MOF-303 using a reflux-based method. Results of the review of 10 selected journals indicate that the method results in a remarkably high reaction yield of approximately >90%, with the results exhibiting outstanding characteristic qualities and water uptake capacities. Using water instead of any other toxic organic solvents in the synthesis makes this method harmless to the environment and human health. It allows for a cost-effective high-scale synthesis of up to 3.5 kg of MOF-303 per batch, making it highly functional for commercial production.

Keywords: *Atmospheric Water Harvesting, Metal Organic Framework, MOF-303, Reflux*

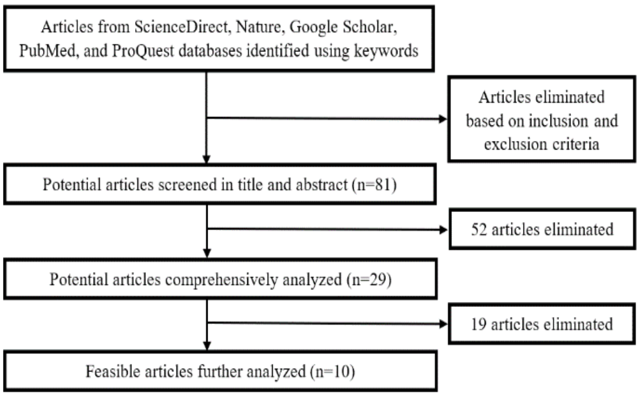
INTRODUCTION

Water scarcity is a prominent issue being faced globally, inducing exponential demand for alternative methods of acquiring water from non-traditional sources. In this case, atmospheric water harvesting (AWH) provides a procedure for obtaining vast amounts of water from the air under omnipresent accessibility. The highly porous material Metal-organic Frameworks (MOFs), particularly MOF-303 (Al(OH)(PZDC)), has been identified as an extremely suitable type of MOF for AWH, as it possesses the capability of capturing water at low relative humidity (RH) and releasing it under slight heating.

Various synthesis methods have been utilized in the production of MOF-303, some of which are reflux-based methods, resulting in a variety of synthesis outcomes. This study aims to comprehensively reveal the expected results of the reflux-based method for MOF-303 synthesis and aspects of it in terms of green and scale-up production. This study contributes to providing a universal outline regarding the effectiveness of the reflux-based synthesis, encouraging insights into scale-up synthesis methods to achieve commercial availability of MOF-303 for atmospheric water harvesting as a concrete approach to tackling water crisis globally.

MATERIALS AND METHODS

This study was conducted through a literature review with a descriptive qualitative approach. The review was conducted using databases obtained through Science Direct, Nature, Google Scholar, PubMed, and ProQuest by using appropriate keywords such as "MOF", "MOF-303", "Synthesis", "Reflux", and "Water Harvesting". Inclusion criteria employed to guide literature selection involve articles with titles, abstracts, accessible full text, and published in the last 5 years (2018-2023). Exclusion criteria involve articles showing abstracts only, not accessible in full text, and review journals.



Graph 1. Literature review selection process

RESULTS AND DISCUSSION

Out of the 29 journals that were selected from the database, 10 research journals were obtained with a feasible category to be involved in further analysis in this literature review. MOF-303 is a highly porous aluminium-based type of MOF with a reticular formula of Al (OH)(PZDC) (Gropp, et al., 2020), and uses 1H-pyrazole-3,5-dicarboxylate (PZDC) as the ligand unit (Fathieh, et al., 2018). The aluminium oxide rodlike secondary building units, joined with aligned $PZDC^{2-}$ linkers, create pores lined by an alternating pattern of hydrophilic and hydrophobic pockets, providing the *xhh* topology (Hanikel, et al., 2019) (Cong, et al., 2021). This creates an environment in which water sorption results in an unusual sorption isotherm at low vapor pressures labeled "S" which reduces its water-uptake capacity (Fig. 1A, red segment). As the pore gets filled with more water molecules, an exponential water uptake is achieved within a narrow RH range (Fig. 1A, yellow segment). Subsequent water adsorption continues to fill the pores entirely, covering a wider RH range (Fig. 1A, blue segment) (Hanikel, et al., 2021). Based on this review, MOF-303 synthesized using various reflux-based methods show excellent reaction yield characterizations.

Table 1. Comparison of yield and characterization of synthesis results

No.	Composition	Solvent and volume	Conditions	Dry MOF obtained per batch (g)	Yield (%)	MOF-303 characterization	Water uptake capacity (wt%)	Reference
1.	$AlCl_3 \cdot 6H_2O$; NaOH; $H_2PZDC \cdot H_2O$	H_2O (100 mL)	Flask reflux, 2h	1.87	94	BET surface area: 1,384 m^2g^{-1}	39 (at 20% RH)	(Zheng, et al., 2022)
		H_2O (60 L)	Vessel reflux, 6h	3,590	91	BET surface area: 1,380 m^2g^{-1}		
2.	$AlCl_3 \cdot 6H_2O$; NaOH; $H_2PZDC \cdot H_2O$	H_2O (50 L)	Reflux, 6h	3,590	91	BET surface area: 1,379 m^2g^{-1}; Pore volume: 0.471 cm^3g^{-1}; Pore size: 9.54 Å	39 (at 40% RH)	(Zheng, Alawadhi, & Yaghi, 2023)
3.	$AlCl_3 \cdot 6H_2O$; NaOH; $H_2PZDC \cdot H_2O$	H_2O (50 mL)	Flask reflux, 3h	1.87	94	BET surface area: 1,392 m^2g^{-1}; Pore volume: 0.498 cm^3g^{-1}; Pore size: 9.4 Å	11.8	(Zheng, Hanikel, Lyu, & Yaghi, 2022)
		H_2O (50 L)	Vessel reflux, 6h	3,590	91	BET surface area: 1,374 m^2g^{-1}; Pore volume: 0.498 cm^3g^{-1}; Pore size: 9.4 Å		
4.	$AlCl_3 \cdot 6H_2O$; pydc	H_2O (180 mL)	Hydrothermal reflux, 12h	17.76	93	BET surface area: 1,030 m^2g^{-1}; Pore volume: 0.348 cm^3g^{-1}; Pore size: 5.7 Å	40	(Cho, et al., 2022)
5.	$AlCl_3 \cdot 6H_2O$; NaOH; $H_2PZDC \cdot H_2O$	H_2O (10 mL)	Reflux, 2h	0.301	66	BET surface area: 1,916 ± 2 m^2g^{-1}; Pore volume: 0.67 cm^3g^{-1}; Pore size: 11 Å	68 (at 26% RH)	(Nikita Hanikel, et al., 2023)

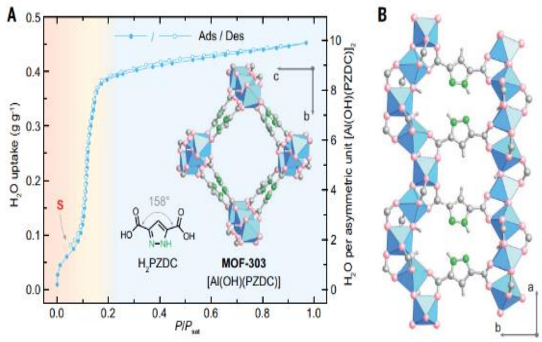


Figure 1. MOF-303 water sorption isotherm and crystal structure (Hanikel, et al., 2021)

The procedures for reflux-based synthesis involve the addition of AlCl3·6H2O solution to H2PZDC·H2O and NaOH at a particularly slow addition rate, and then heating the reaction mixture under reflux for a particular amount of time. The reflux-based methods allow for an exceptionally high reaction yield of approximately >90%. Although, a 3:1 molar ratio of NaOH:H2PZDC is critical for an outstanding yield improvement, and the yield will be significantly reduced when this ratio is diverged from (Zheng, et al., 2022). While utilizing the reflux method in a flask is more suitable for small-scale synthesis, vessel reflux aids the achievement of an impressive high-scale production of up to 3.5 kg of MOF-303 per batch. In addition, using water only instead of any other toxic organic solvents in the synthesis makes this method harmless to the environment or human health.

The results of the synthesis exhibit excellent water uptake capabilities at low relative humidity, making it highly efficient for water harvesting from the air. In spite of this, it appears that adjustments can be made to the materials in the synthesis process that may lead to improvements in the qualities of MOF-303 characters. Hanikel et al (2023) have managed to replace PZDC by the use of a molecule called (E)-5-(2-carboxylatovinyl)-1H-pyrazole-3-carboxylate (PZVDC2-) to extend ligand length. Despite leading to a decreased reaction yield (66%), this method results in an enlarged pore volume (0.67 cm3g-1) without compromising the hydrophilic-hydrophobic pocket environment of the pores, hence, enhancing its water harvesting abilities by about 50% (68 wt% at 26% RH).

CONCLUSION

Reflux-based methods allow for an exceptionally high reaction yield, with MOF-303 results showing impressive qualities for efficient atmospheric water harvesting. Using water as the only solvent marks them as breakthroughs in the green synthesis of MOF-303, and their high-scale potency make them desirable for commercial production.

Further research should be conducted regarding the potential optimization of MOF-303 qualities for water-uptake through modifications in synthesis procedures, especially in the usage of natural materials and/or linkers. Extensive research is needed to address how its water uptake can be improved without compromising the reaction yield of the synthesis.

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