Feasibility of NH_2-MIL-125 as an Adsorbent for the Removal of Organic Pollutant in Water

Aaron Shun Yao Liew[1], Szea Err Teo[1], Sing Yew Nguang[1], Nur Syafiqah Rizalman[1], Norini Tahir[1], Suzanna Rosli Wong[2], Pak Yan Moh[1,2 #]

1 Programme of Industrial Chemistry, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS,88400 Kota Kinabalu, Sabah, Malaysia.
2 Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia.
Corresponding author. E-Mail: pymoh@ums.edu.my

ABSTRACT Titanium-based benzenedicarboxylate metal-organic framework (MIL-125) is a nanoporous material that exhibits high surface area and unique pore architecture. The stability of MIL-125 in water, however, is the major drawback that limits the application of this material in aqueous condition. This study reports the water stability of amino-functionalized MIL-125 (as NH_2-MIL-125), as well as its adsorption capability towards cationic methylene blue (MB) in comparison to that of MIL-125. Both MIL-125 and NH_2-MIL-125 compound were prepared by reflux method followed by activation through conventional solvent-exchange technique. Framework of the as-synthesized of MIL-125 and NH_2-MIL-125 was confirmed by powder X-Ray diffraction whilst the amino-functional group was confirmed through FTIR spectroscopy. The C-N stretching vibration peak found at 1256 cm^{-1} was the characteristic feature for the NH_2-MIL-125 compound. Morphology of the as-synthesized MIL-125 and NH_2-MIL-125 realized by the scanning electron microscopy as circular-plate shape with the crystal size ranges between 0.5 to 1 µm. The obtained results showed that NH_2-MIL-125 had better water stability that exceeded 24 hours in comparison to MIL-125 which disintegrated in water in less than 1 hour. Furthermore, preliminary adsorption result revealed that NH_2-MIL-125 was able to adsorb 90% of MB in water (with 360.60 $mg.g^{-1}$ of the calculated adsorption capacity towards MB) whilst only 68% of MB was adsorbed by MIL-125 (with 272.58 $mg.g^{-1}$ of the calculated adsorption capacity towards MB) within 4 hours of reaction time. This study implies that NH_2- MIL-125 material can be a potential adsorbent for the removal of cationic organic pollutants in water.

KEYWORDS: Adsorption, Metal-organic framework, MIL-125, Water stability, Methylene blue
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INTRODUCTION

Metal-Organic Frameworks (MOFs) is a class of porous crystalline materials comprised of metal clusters that are linked through organic linkers (Cheong *et al.,* 2017; Tahir *et al.,* 2017; Cheong & Moh 2018). MOFs possess several unique properties such as high surface area, porosity and chemical functionality which can be applied in diverse areas including adsorption, separation of fluids and catalysis (Othman *et al.,* 2019; El-Shahat *et al.,* 2020). Among various types of MOFs, Materials of Institute Lavoisier-125 (MIL-125) is a titanium-based MOFs that constitutes of eight-membered rings of $TiO_5(OH)$ octahedra interconnected by benzene dicarboxylate ligand to form a quasi-cubic tetragonal structures which has garnered attention in studies as a potential adsorbent towards organic pollutant (Dan-Hardi *et al.,* 2009; McNamara *et al.,* 2015). However, the stability of this material in water has become a major drawback when considering for adsorption applications. Hence, MOFs that has been modified with enhanced water stability is useful in practical applications.

Water stability of MOFs is always an important criterion when considering adsorption and catalysis application. Regardless of the issue stated, there are two possible strategies that have been reported in previous studies which are encapsulation of hydrophobic guest molecules in the MOFs porous system and modification of their external surfaces through ligand substitution (Qian *et al.,* 2017). In this study, amino functionalized MIL-125 (as NH_2-MIL-125) was synthesized via ligand replacement as an approach to enhance the water stability of MIL-125 while maintaining most of its

chemical properties. The findings can provide better understanding in the stability and capability of NH_2-MIL-125 as an adsorbent towards organic pollutants in water.

METHODOLOGY

Synthesis of NH_2-MIL-125

In this study, MIL-125 was prepared by reflux method (Nasalevich *et al.*, 2013) with slight modification. 1.75 g of terephthalic acid (H_2-BDC) and 28 mL of *N*,*N*-dimethylformamide (DMF) were mixed and placed in a two-neck round bottom flask. The mixture was heated at 100 ℃ for 1 hour with continuous stirring. Subsequently, 7 mL of methanol (MeOH) was added and a reflux condenser was applied. The mixture was then refluxed under stirring for 1 hour followed by followed by addition of 2.1 mL of titanium isopropoxide (TTIP) to the mixture. The reflux was continued with consistent stirring for the next 72 hours. After that, the mixture was left to cool to room temperature and the precipitate (product) was obtained by filtration. The product was then respectively immersed in DMF and MeOH for 2 hours. Finally, the white product was dried in an oven at 155 °C for 12 hours. Similarly, NH_2-MIL-125 was synthesized following the method as mentioned above but the H_2-BDC linker was replaced by 2-aminoterephthalic acid (NH_2-BDC) linker and eventually a yellowish product was obtained.

Identification and Characterization of NH_2-MIL-125

The as-synthesized MIL-125 and NH_2-MIL-125 was identified using powder X-ray diffraction (PXRD) (Model: PHILIPS X'PERT PRO PW 3040) with 5° to 80° of 2θ scanning range. The morphology of sample was examined by scanning electron microscope (SEM) (JEOL JSM-5610LV) with a tungsten filament. The surface functional groups of MIL-125 and NH_2-MIL-125 were analyzed using Fourier Transform Infrared (FTIR) spectroscopy on Perkin Elmer FTIR Spectrum 100. The IR absorption spectrum was collected from 4000 to 450 cm^{-1}.

Water Stability Study

Both MIL-125 and NH_2-MIL-125 were tested for water stability using an in-house method. Approximately 0.2 g of the material was placed in 100 mL of distilled water and magnetically stirred for duration of 4 hours and 24 hours, respectively. The solid material was filtered and analyzed using PXRD. The solid material was confirmed by comparing its PXRD patterns with the simulated MIL-125 and NH_2-MIL-125 PXRD pattern, respectively.

Adsorption Study

The adsorption capability of MIL-125 and NH_2-MIL-125 were studied towards the removal of 20-ppm MB in water. 200 mL of MB solution with 20 ppm initial concentration was poured into a circular-shape beaker. Next, 0.01 g of the adsorbent was into the MB solution along with continuous stirring for 4 hours. Subsequently, 3 ml of MB solution was withdrawn at 0, 10, 15, 30, 60, 90, 120, 150, 180, 210, and 240 minutes of time intervals. Each sample was filtered with 0.2 μm membrane filter prior to analysis. The adsorption intensity of MB at its maximum absorbance wavelength, λ_{max} of 665 nm was measured by UV-Vis Spectrophotometer (Agilent Technologies, Model Cary 60) and the concentration of MB adsorbed ($C_0 - C_t$) over certain period was calculated as Equation (1). The amount of MB adsorbed by the adsorbent over a certain period, *t* was calculated as Equation (2).

$$C_0 - C_t (mg.L^{-1}) = C_0 \times [(A_0 - A_t) \div A_0] \quad (1)$$

$$q_t (mg.g^{-1}) = (C_0 - C_t) \times V \div m \quad (2)$$

where A_0 and A_t are the absorbance of MB solution, C_0 and C_t are the concentration of MB solution at t = 0 and at certain time interval t, respectively. V is the volume of the solution in liter and m is the mass of adsorbent used in gram.

RESULT AND DISCUSSION

Characterization of NH_2-MIL-125

Figure 1(a) shows that the PXRD patterns of as-synthesized MIL-125 and NH_2-MIL-125 were comparable to the simulated PXRD patterns (Oveisi *et al.*, 2018). Distinct diffraction peaks were found at 2θ values of 6.790°, 9.741° and 11.665°, which can be indexed to the (101), (200) and (211) planes, respectively (Zhao *et al.*, 2019). Besides, the FTIR spectra in Figure 1(b) have confirmed the existence O-Ti-O vibrations (400 and 800 cm^{-1}), carbonyl symmetric stretching vibrations (1450-1350 cm^{-1}) and carbonyl asymmetric stretching vibrations (1600 to 1500 cm^{-1}) in both MIL-125 and NH_2-MIL-125 (Dan-Hardi *et al.*, 2009). The absence of primary amine corresponding band for the as-synthesized NH_2-MIL-125 can be attributed to the strong interconnection of NH_2 group of organic linkers with OH group on the metal-oxo-cluster (Stavitski *et al.*, 2011). However, the occurrence of NH_2 functional group in the as-synthesized NH_2-MIL-125 group can be evidenced by the existence of C-N stretching vibration at 1256 cm^{-1} (Santaclara *et al.*, 2016). Figure 2(a) and 2(b) shows the SEM images of MIL-125 and NH_2-MIL-125. Both materials have similar morphology that is circular-plate shape with particle size falls between 0.5 to 1 μm.

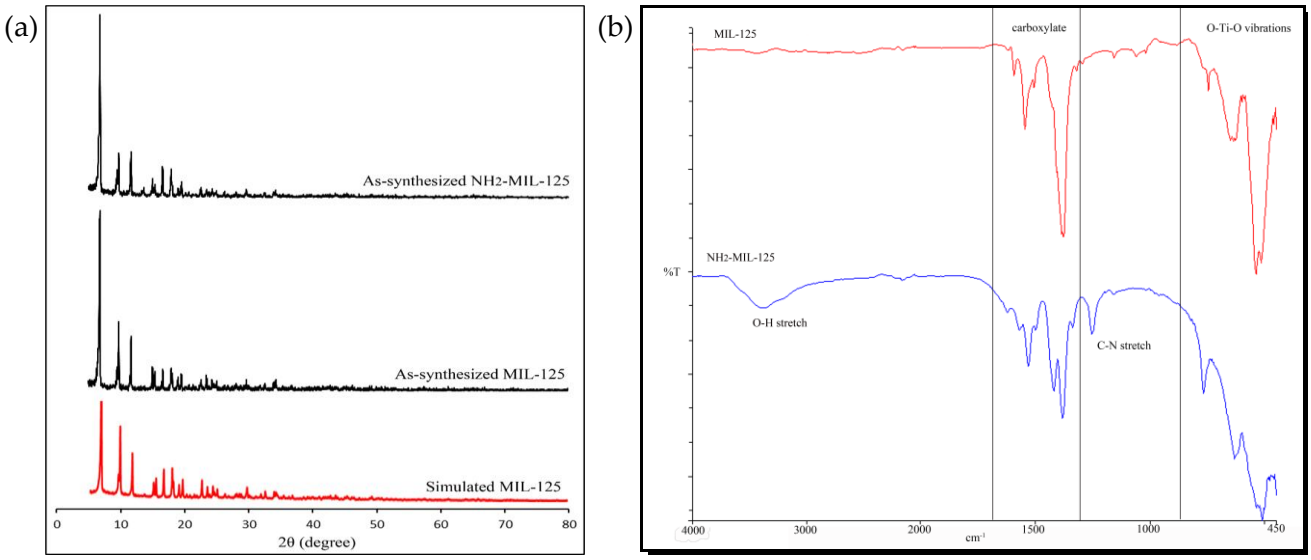

Figure 1. (a) PXRD pattern of MIL-125 and NH_2-MIL-125 (b) FTIR spectra of MIL-125 and NH_2-MIL-125.

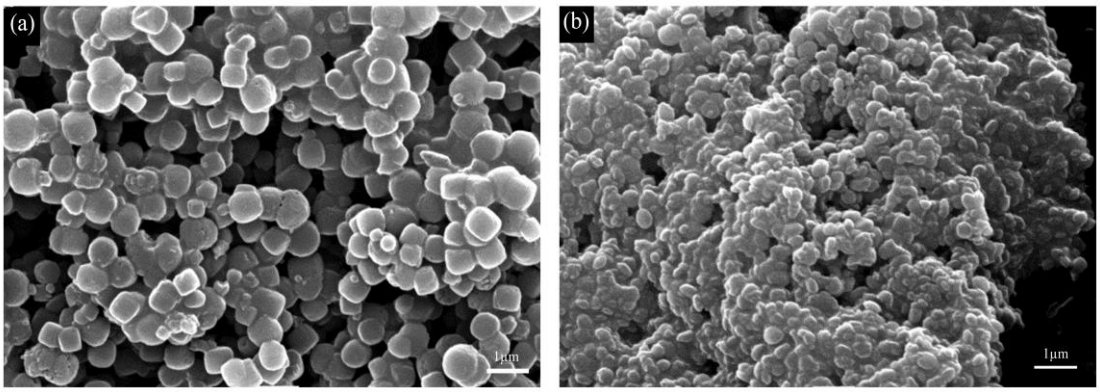

Figure 2. SEM image of (a) MIL-125 and (b) NH_2-MIL-125.

Stability of NH_2-MIL-125 in Water

Figure 3(a) shows the PXRD pattern of the MIL-125 after dispersion in water. It was found that the PXRD pattern has a good match with that of H_2-BDC. This indicates that the framework of MIL-125 had collapsed within 1 hour of dispersion in water. Dispersion of NH_2-MIL-125 in water, on the other hand, has shown comparable diffraction patterns with its fresh sample even though it was left dispersed in water for 24 hours (Figure 3(b)). Higher water stability exhibited by the NH_2-MIL-125 can be reasoned by the NH_2 functional group in the framework that may alter the water sorption property while ensuring framework to remain intact (Jeremias *et al.*, 2013; McNamara *et al.*, 2013). Therefore, it can be concluded that additional of NH_2 group in MIL-125 could enhance the stability of MIL-125 in water.

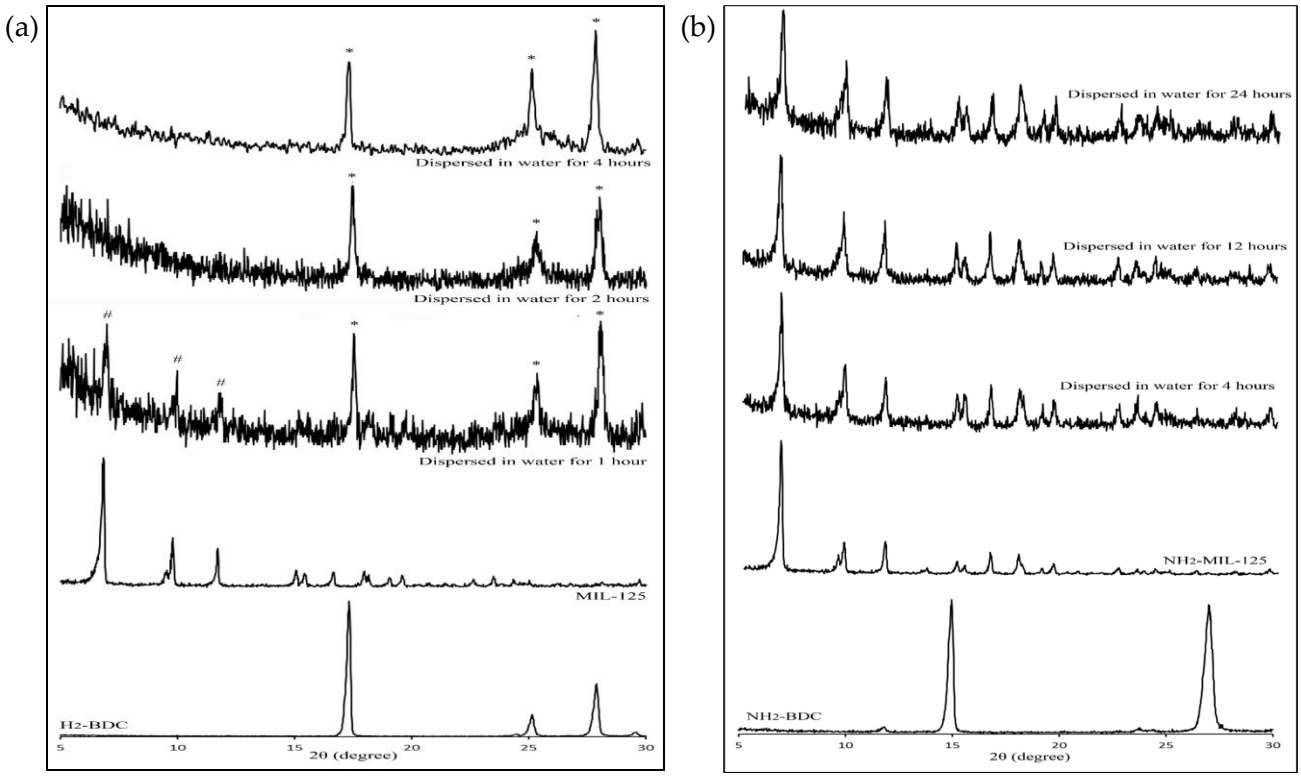

Figure 3. XRD pattern of MIL-125(a) and NH_2-MIL-125 (b) sample after water dispersion within 4 and 24 hours, respectively. Note that MIL-125 is not stable in water and fully decomposed in water within 1 hour. (* represent H_2-BDC linkers peaks; # represent MIL-125 peaks).

Adsorption Capability of NH_2-MIL-125

Figure 4 (a) and 4 (b) illustrates that NH_2-MIL-125 material has higher adsorption capability towards 20-ppm MB in water in comparison to that of MIL-125. NH_2-MIL-125 was able to adsorb 90% of 20-ppm MB in water, while MIL-125 only able to adsorb 68% of 20-ppm MB in water. Besides, the adsorption capacity of NH_2-MIL-125 and MIL-125 after 4 hours were empirically calculated as 360.60 $mg.g^{-1}$ and 272.58 $mg.g^{-1}$, respectively. This indicates that the existence of amino group in MIL-125 framework has greatly improved the adsorption properties of the material towards MB. Amino functional group in the NH_2-MIL-125 framework contributes higher surface electronegativity due to the existence of lone electron pair in nitrogen which attracts cationic MB. Besides that, nitrogen atom in the NH_2-MIL-125 also facilitates the formation of hydrogen bonding with MB in water (Fan *et al.*, 2018). The results in this study have confirmed the favourable effect of amino functional group in NH_2-MIL-125 in adsorption of MB in water.

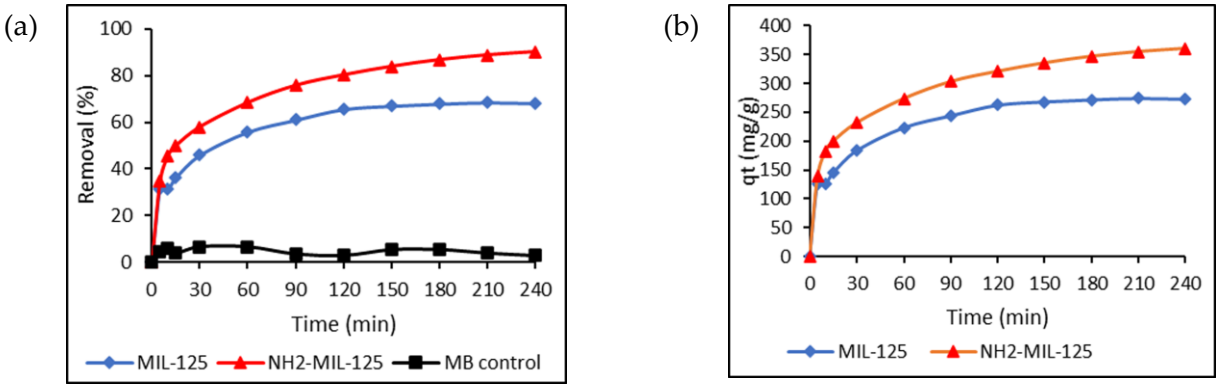

Figure 4. Removal by means of adsorption (a), and Adsorption capacity (b) of 20-ppm MB by MIL-125 and NH_2-MIL-125 in dark condition.

CONCLUSION

This study revealed that amino-functionalized MIL-125 (as NH_2-MIL-125) is stable in water for at least 24 hours. NH_2-MIL-125 material, with 360.6 $mg.g^{-1}$ of adsorption capacity, is relatively an excellent material for the adsorption of cationic methylene blue (MB) in water (see Table 1). The good adsorption properties of NH_2-MIL-125 can be attributed to the addition of NH_2 group that has increase the electronegativity of the material. This is also a characteristic feature of NH_2-MIL-125 for the selective adsorption of cationic MB in water. Thus, NH_2-MIL-125 can be a potential adsorbent for water and wastewater treatment with a good selectivity towards cationic pollutants.

Table 1. Adsorption capacities of various adsorbent towards MB at room temperature.

Adsorbent	Amount, $g.L^{-1}$	MB concentration, $mg.L^{-1}$	Contact time, *hr*	Adsorption capacity, $mg.g^{-1}$	Reference
Activated carbon	1	4-37	3	263.5	Li *et al.*, (2013)
MOF-235	1	20-200	12	187.0	Haque *et al.*, (2011)
ETS-10	0.1	10-60	2.5	125.1	Nguang *et al.*, (2017)
NH_2-MIL-125	0.05	20	4	360.6	This study
MIL-125	0.05	20	4	272.6	This study

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