Extracting Metal-Organic Frameworks (MOFs) from Photovoltaic Modules for Wastewater Remediation

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Abstract

Photovoltaic (PV) energy adoption has increased drastically over the years and is expected to become a mainstream energy source for the future. However, waste management remains a problem as more PV panels reach their end-of-life. Many strategies have been employed to recycle PV panels, but upcycling efforts to form high-value products from these PV panels are underexplored. In this paper, we have developed 3 different synthetic routes to generate metal-organic framework (MOF), MIL-53(Al), by utilizing the polymeric backsheet and aluminum from solar panels. Characterisations have been performed to evaluate the morphologies, thermal stability, crystallinity, and specific surface areas of the MOFs synthesized. The adsorption performances of these MOFs on cationic Methylene Blue (MB) and anionic Methyl Orange (MO) were determined to be ranging from 186.2 to 263.2 mg/g for MB, and 256.4 to 304.0 mg/g for MO. These results therefore suggest the potential of upcycling solar panels waste to form metal-organic framework for application in wastewater remediation to remove cationic and anionic dyes.

1. Introduction

Fossil fuels have long been the major source of energy around the world. However, with increasing concern on global warming through greenhouse gases emitted from fossil fuels, along with a depleting supply of fossil fuels, more sustainable alternative sources of energy need to be explored (Capellán-Pérez et al. 2014; Mediavilla et al. 2013). Among the options in the shift to green and renewable energy, photovoltaic (PV) energy has emerged as a great alternative energy source. In fact, solar energy usage has increased tremendously over the years as it became more reliable and affordable. The annual PV installation has increased from 31.1 GW in 2011 to 119.6 GW in 2019, with the cumulative PV installation 2019 reaching 632.3 GW, 72.3% of which was installed in the last five years from 2019 (IEA 2020). However, after 25-30 years, PV panels have their efficiency dropped significantly, hence reaching their end-of-life (IRENA and IEA-PVPS 2016). Due to the drastic increase in PV usage, the amount of PV waste modules is projected cumulated to 78 million metric tonnes by 2050. Hence, the recycling of end-of-life solar panels is important in allowing PV energy to become fully sustainable as a closed-loop cycle. Typical approaches to recycling solar panels include mechanical, chemical (Shin et al. 2017) and thermal treatments (Wang et al. 2019). While many attempts have been made in recycling and retrieving the materials from solar panels, the research on upcycling the recovered materials for high-value products have yet to be extensively explored. Recovered silicon has been utilised as the material for lithium anode battery (Eshraghi et al. 2020), however the other predominant metal (aluminium) along with the plastic components have received only minimal attention to be upcycled to high value products. Due to the inherent low economic values of these components (e.g. US\$ 2,473 per metric ton in 2021 for Al (The World Bank 2022)), solely recycling them to raw materials would not be economically viable.

On the other hand, wastewater pollution has been a great health and environment concern due to rapid industrialization. Organic dyes are hazardous substances that are toxic and carcinogenic in nature (Ito et al. 2016; Khataee and Kasiri 2010). These synthetic dyes are being released more and more in

wastewater due to their prevalent in textile, leather, or cosmetics industries. Hence, efforts have been made in finding the effective methods for dye removal in wastewater through various methods, such as adsorption (Yagub et al. 2014), oxidation (Javaid and Qazi 2019), and biodegradation (Ali 2010). Among the different methods, adsorption has been regarded to be the promising approach as it is cost-effective and straight-forward. Hence, many types of adsorbents have been researched and used for dye removal treatment, such as activated carbon (Mezohegyi et al. 2012), zeolites (Tasić et al. 2019), carbon nanotubes (Rajabi et al. 2017) and metal-organic frameworks (MOFs).

Metal-Organic Frameworks (MOFs) are highly porous materials containing both inorganic and organic components. The metal ions/clusters are coordinated with organic ligands to form 3-D structures, resulting in formation of small pores and high void spaces, enabling the applications in diverse arenas such as gas storage (Alhamami et al. 2014), drug delivery (Wu and Yang 2017), heavy metal removal (Goyal et al. 2021) and dye adsorption in aqueous solution (Navarro Amador et al. 2017). Many MOFs have been employed as adsorbents in wastewater remediation to remove organic dyes including MOF-235 (MB: 187 mg/g, MO: 477 mg/g) (Haque et al. 2011), cationic CPM-97-Fe (MB: 304 mg/g) (Tian et al. 2019), UV-012 (MO: 1410 mg/g) (Ramírez et al. 2021). Among the MOFs, an aluminium-based MOF - MIL-53(Al) - has gained interest due to its unique breathing effect and stability under acid or neutral condition. MOFs are typically synthesized through hydrothermal and solvothermal manner. Recent works have demonstrated the feasibility of synthesising MOFs from recycled sources (El-Sayed and Yuan 2020). Carboni *et. al.* has successfully synthesised MIL-53(Al) using waste PET bottles and leachate from lithium-ion batteries (Lagae-Capelle et al. 2020). However, no attempts have been made to synthesise MIL-53(Al) from solar panel waste. Having the backsheet that mainly made up of PET, and the solar cells containing aluminium, the waste materials from solar panel could potentially be used to form MIL-53(Al).

In this work, we demonstrated the synthesis and dye removal ability of MIL-53(Al) as an upcycling strategy for waste solar panels utilising polymeric backsheet and the aluminium present. Characterisation were performed on the synthesised MOFs to evaluate the quality of the materials. The ability of the materials in water purification was evaluated through their removal performance of the organic dyes - cationic Methylene Blue (MB) and anionic Methyl Orange (MO).

2. Experimental Procedure

Preparation of Al-rich leachate. The leaching experiment was performed on silicon solar cell with 1.0 M HCl solution (80°C, 1 hour, 250 rpm). The mixture was filtered and the metal concentrations in the leachate were analyzed before proceeding with the MOF syntheses.

Syntheses of Aluminum Metal-organic Frameworks (Al-MOF)

MOF-1: Dissolved backsheet solution (10.6 mL) was added into a mixture of DMF and aluminum leachate solution (diluted to 4.8 g/L) (20 mL each). The resultant mixture (pH = 5.36) was heated to 90°C for 12 hours and centrifuged upon cooling. The supernatant was removed, and the remaining solids were washed with fresh DMF for 12 hours at 150°C and water for 4 hours at 90°C. After removal of the

solution, the solid collected was dried in a 75°C oven for at least 2 days. **MOF-2**: The dissolved backsheet solution was replaced with re-dissolution of precipitated terephthalic acid in NaOH (resultant) mixture pH = 3.74). **MOF-3**: Precipitated terephthalic acid was suspended in ultrapure water and reacted with the mixture of DMF and leached solution (resultant mixture pH = 3.28).

Full experimental details can be found in the supplementary information.

Dye adsorption experiments

10 mg/L of aqueous Methylene Blue (MB) and Methyl Orange (MO) solutions were prepared by dissolving the dyes in ultrapure water. The synthesized MOFs were dried overnight in vacuum oven at 100°C and left in the desiccator until used. For the adsorption kinetics study, exactly 10 mg of adsorbent was mixed with 10 mg/L dye solution (50 mL) in the orbital shaker at 160 rpm in dark environment. After the desired adsorption time, the resultant solutions were filtered through syringe filter (PES0, 0.45 µm) to obtain clear filtrates for UV-vis measurements. The kinetics data are fitted to pseudo first-order and pseudo second-order. Maximum adsorption capacity was determined through undergoing dye adsorption in 50 mL solutions at varying concentration solutions (5, 10, 25, 50, 100, 150 mg/L) for 24 hours. The data obtained was then fitted in Langmuir and Freundlich adsorption isotherms models to investigate the adsorption mechanism and determine the maximum adsorption capacity. More details are available in the Supplementary Information.

3. Results And Discussion

The powder X-ray diffraction (XRD) of **MOF-1**, **MOF-2** and **MOF-3** depicted similar characteristic peaks (2θ (°): 9.0, 15.2, 18.1) as simulated and reported patterns of MIL-53(Al) (Lagae-Capelle et al. 2020) (Figure 2a). The broadness of the peaks could suggest low level of crystallinity and crystal size for the 3 MOFs. The peaks of **MOF-2** and **MOF-3** were relatively more refined and could be attributed to a lower impurity level of its precursor.

The Fourier-transform infrared (FT-IR) spectra recorded adsorption signals at 1670 cm^{-1} attributing to C=O stretching vibration and, 1609 and 1509 cm^{-1} are likely corresponding to the asymmetric stretching vibrations of CO_2^- (Figure 2b). The signal recorded at 1418 cm^{-1} possibly arise from the symmetry stretching mode of CO_2^- moiety. The broad signal at 3455 cm^{-1} was likely attributed to the presence of water molecules trapped within the crystalline lattice. These signals are consistent to that reported in other synthetic accounts of MIL-53(Al) (Al Sharabati and Sabouni 2020; Li et al. 2015).

Thermogravimetric analysis (TGA) was conducted from 25-800°C and illustrated in Figure 2c. The thermal stabilities depicted the small weight loss of 2.7, 3.5 and 1.4% below 100°C which might be attributed to the loss of water from the surfaces for **MOF-1**, **MOF-2** and **MOF-3** respectively. The first big drop in weight was likely due to the removal of trapped DMF molecules from the frameworks. The three synthesized adsorbents were thermally stable up to approximately 470°C. The major weight loss between

470-640°C indicated the breakdown of the frameworks, accounting for 34.2, 40.9 and 49.4% weight loss. The residual mass at 800°C which weighs 30.6, 26.9 and 30.6%, for **MOF-1**, **MOF-2** and **MOF-3** respectively, is attributed to the Al₂O₃ obtained at the end of the thermal analysis (Khodayari and Sohrabnezhad 2021).

The porosity and specific surface areas of all samples were determined by nitrogen adsorption-desorption isotherms (Figure 2d). BET analysis indicated similar adsorption/desorption patterns of N₂ between **MOF-1**, and **MOF-2** that resemble Type IV isotherm, while **MOF-3** had a largely different adsorption-desorption pattern exhibiting Type I, where the hysteresis loop has become negligible (Figure 2d). Regardless, all three samples exhibited very high BET surface area (**MOF-1**: 1004 < **MOF-2**: 1110 < **MOF-3**: 1231 m²/g). Such surface areas are comparable to reported BET surface area values of MIL-53(Al) synthesized (MIL-53(H₂O): 1002 and MIL-53(DMF): 1084 m²/g) (Warfsmann et al. 2018). Despite the similar surface areas measured, the amounts of micropore area in the samples recorded were vastly different (**MOF-1**: 596 m²/g, **MOF-2**: 815 m²/g and **MOF-3**: 1015 m²/g). These micropore areas therefore suggested an increasing share in total area from 59.4%, 73.4–82.4% for **MOF-1**, **MOF-2** and **MOF-3**, respectively.

Scanning electron microscopy (SEM) analysis illustrated morphological differences among the 3 synthesized samples (Figure 3). At 50,000x magnification, all three MOFs showed nanosized particles agglomerating into bigger clusters, with only **MOF-3** having a regular spherical cluster shape (Figure 3a-c). At 10,000x magnification, the agglomerations in **MOF-3** were more regular and spherical in size (1 µm) as compared to the other two samples (**MOF-1** and **MOF-2**: ~1-10 µm) (Figure 3d-f).

3.3. Dye Adsorption

Adsorption Kinetics. Adsorption kinetics showed both MB and MO adsorption rate being rapid at the start and gradually slowed down (Figure 4a,b). **MOF-3** presented the best adsorption kinetics capability for adsorption of MB, while **MOF-2** had the best absorption under MO. All samples demonstrated better capabilities to adsorb MO in aqueous solution, with close to 100% of MO removed after 4 hours. The surface area and micropore area could be the reasons for dye adsorption performance differences of the samples. The precipitation of terephthalic acid from dissolved backsheet solutions for **MOF-2** and **MOF-3** resulted in higher purity of materials. For both MB and MO adsorptions, pseudo second-order model produced R-square values of >0.99 for all samples, with lower R-square values for pseudo first-order (Figure 4e). This indicates that for all the samples, the adsorption of both MB and MO follows the pseudo second-order model.

Adsorption Isotherms. 24-hr adsorption at different dye concentrations showed different performances of the samples under MB and MO (Figure 4c,d). **MOF-3** showed superior performance in MB while **MOF-2** had the best performance in MO. Fitting the data into the Langmuir models has the R² coefficients to be >0.99 for all the samples in both MB and MO dyes. The Freundlich models, on the other hand, showed the R² coefficients that are less than ideal compared to Langmuir. The maximum capacity (q_{max}) data

obtained from Langmuir were very close to the experimental adsorption data. This suggests that for all the MOF samples in both MB and MO, the adsorption can be explained to be through monolayer adsorption.

4. Conclusion

With the ever-growing photovoltaic industry, it is important to design a proper waste management to handle the waste panels. We herein demonstrated the upcycling of panels components (aluminium and backsheet) to high-value metal-organic framework (MOF) for dye removal application in wastewater remediation. The synthesised MOFs demonstrated great thermal stabilities, high BET surface areas and good adsorption performances with MB (186.2 to 263.2 mg/g) and MO (256.4 to 304.0 mg/g). Their adsorption kinetics follow pseudo second-order model, while the adsorption isotherms fit the Langmuir model. This study provides an efficient way to recover aluminum and polymeric backsheet from solar panel for synthesis of high-value MOFs, contributing to waste management efforts and simultaneously tackling the problem in wastewater treatment.

Declarations

Funding

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Conflicts of interest

There is no conflict of interest.

Ethics approval

Not Applicable.

Consent to participate

Not Applicable.

Consent for publication

All authors have given consent for publication.

Availability of data and material

All additional supporting information can be found in the supplementary data provided.

Code availability

Not Applicable.

Authors' contributions

Pham performed syntheses and analyses reported, Sim worked on drafting the manuscript and Carboni, Meyer and Mathews validated and edited the manuscript.

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Figures

Figure 1

Three synthetic routes reported in this study. The reaction of leached solution with dissolved backsheet solution led to formation of **MOF-1**, while that with re-dissolved precipitated terephthalic acid resulted in **MOF-2** and lastly reacting with precipitated terephthalic acid in water gave **MOF-3**.

Figure 2

(a) XRD, (b) FT-IR, (c) TGA, and (d) N₂ adsorption-desorption isotherms of **MOF-1**, **MOF-2** and **MOF-3**. The XRD and FTIR analyses are identical and similar to that reported. TGA analysis suggested similar amounts of solvent molecules present in the 3 MOFs while the weight loss accounted for breakdown frameworks differed. The surface areas increase from 1004, 1110 to 1231 m^2/g across **MOF-1**, **MOF-2** to **MOF-3**.

Figure 3

SEM Images of (a,d) **MOF-1**, (b,e) **MOF-2** and (c,f) **MOF-3** with 50,000x and 10,000x magnification, respectively. Agglomeration of nano-sized particles shown at 50,000x magnification. **MOF-3** was observed to be more spherical and regular in size.

Figure 4

(a,b) Adsorption Kinetics and (c,d) Adsorption Isotherms for MB and MO, respectively; (e) Parameters from Pseudo First and Second Order as well as Langmuir and Freundlich Isotherm. **MOF-3** showed greatest adsorption performance in MB, while **MOF-2** had the best performance in MO. The adsorption kinetics for all MOFs fit the pseudo second order while adsorption isotherms data fit the Langmuir model.

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