Functionalization of Two-Dimensional Coordination Polymer in Small Organic Matters Removal from Organic Wastewater

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Abstract

Multicobalt(II) two-dimensional layer coordination polymer $\{[\text{Co}(\text{bitbu-OMe})_2(\text{NCS})_2] \cdot 2\text{MeOH}\}_n$ (**1**) was synthesized using a bis-imidazole ligand having a steric hindrance, *tert*-butyl, and one methoxy group expressed by bitbu-OMe (bitbu-OMe = 1,1'-[(5-*tert*-butyl-2-methoxybenzene-1,3-diyl)dimethanediyl]bis(*1H*-imidazole)). Since there are two methanol molecules trapped inside each void within **1**, the investigation of small organic matters removal from organic wastewater was conducted in order to reveal its ability in the purification process. The research findings indicate that **1** has the ability to capture methanol, acetone, acetonitrile, and tetrahydrofuran in organic wastewater with removal ratios of 29.17%, 63.22%, 42.77%, and 21.24%, respectively.

1 Introduction

The issue to have clean water has always been a topic of importance [1] and access to clean water is a major component to Sustainable Development Goal 6 [2]. Water pollution occurs because of a large number of waste discharges [3] from various sources [4–7]. One of the issues that arises in research activities from chemical laboratories is the production of organic wastewater [8–11]. Generally, organic wastewater from a chemical laboratory consists of a mixture of used water and waste organic solvents [12]. Various efforts have been being established to recycle organic wastewater to produce clean water, such as using zeolite as a purification agent to absorb organic matter dissolved in organic wastewater by utilizing its microporous [13–19].

In addition to using zeolite as an organic matter adsorbent in organic wastewater treatment, the use of materials having voids such as two-dimensional coordination polymers (CPs) [20] for organic wastewater treatment has become interesting to study due to the unlimited variation of metal ions and bridging ligands involved to form novel coordination polymers [21]. These have generated special interests because of the metal ions and the ligands used and thus, these substances should not have side effects on the human body and the environment. Therefore, the development of two-dimensional coordination polymers in the absorption process of small molecules [22, 23] as a purification agent has become useful in the process of organic wastewater purification. We reported on the synthesis and characterisation of a two-dimensional layer coordination polymer $\{[\text{Co}(\text{bitbu-OMe})_2(\text{NCS})_2] \cdot 2\text{MeOH}\}_n$ synthesized from $\text{Co}(\text{SCN})_2$ and bis-imidazole ligand having a steric hindrance *tert*-butyl, and a methoxy group called bitbu-OMe where this polymer, Fig. 1, has methanol molecules encapsulated within its voids [24].

In view of the above and in continuation with our research programme to study the purification of water [25–30], herein, we report the functionalization of $\{[\text{Co}(\text{bitbu-OMe})_2(\text{NCS})_2] \cdot 2\text{MeOH}\}_n$ (**1**), its action in the purification of organic wastewater in the removal of small organic molecules such as methanol, acetone, acetonitrile, and THF through the utilization of its voids.

2 Material And Methods

All solvents and reagents were available commercially and used without further purification. Powder X-ray diffraction (PXRD) measurement was conducted using the Rigaku Smart Lab. Nuclear magnetic resonance (NMR) measurement was carried out using JEOL ECA-600 Spectrometer. Thermogravimetry-differential thermal analysis (TG-DTA) was performed using Rigaku TG 8121.

The process of small organic molecules removal in organic wastewater by using **1** began with the identification of optimum temperature for desolvation process of **1**'s voids through the thermogravimetric analysis (TG analysis). Thus, the process of removing methanol molecules and the stability of the structure of **1** before and after desolvation process through heating was carried out by comparing the simulated PXRD patterns of **1** with and without methanol molecules and the observed PXRD patterns of **1** before and after desolvation process.

The organic wastewater representation was prepared by adding 2,2-dimethylpropan-1-ol (neopentyl alcohol, NPA) (0.018 g, 0.200 mmol) to 20 mL of D₂O. The NPA solution was separated into four vials (5 mL of solution for each vial). 0.400 mmol of each small organic molecule (MeOH, Me₂CO, MeCN, and THF) was added to each vial. 0.500 mL of each small organic matter solution was added into the NMR tube ¹H NMR for analysis (Fig. 2).

The capture of small organic molecules using desolvated **1** was conducted by mixing the powder of desolvated **1** powder (0.040 g, 0.05 mmol) with four small organic molecule solutions. The mixtures of desolvated **1** powder and small organic molecule solutions were stirred for one hour at room temperature. The mixtures were filtered using a filter attached to the syringe. 0.500 mL of each solution was added into the NMR tube for ¹H NMR analysis.

The equation used for small organic molecules removal ratio was derived from the relative quantitative NMR (qNMR) [31], equation (1),

$$\frac{n_x}{n_y} = \frac{I_x}{I_y} \frac{N_x}{N_y} \quad (1)$$

where n_x/n_y , I_x , I_y , N_x , and N_y are molar ratio of two compounds, the integrated signal area of compound x, the integrated signal area of compound y, the number nuclei of compound x, and the number nuclei of compound y, respectively. Equation (1) was used to calculate the molarity of organic molecules after removal treatment (n_a) from molarity of organic molecules before removal treatment (n_b), and by assuming the molarity of standard compound, the number nuclei of standard compound, the number nuclei of organic molecules before and after treatment to remain the same. The molar ratio of organic molecules before and after removal treatment was calculated using the equation (2).

$$\frac{n_b}{n_a} = \frac{I_b}{I_a} \quad (2)$$

The percentage of organic molecules removal was calculated using the equation (3)

$$\text{Percentage of organic molecules removal} = \frac{(I_b - I_a)}{I_b} \times 100\% \quad (3)$$

where I_b and I_a are the integrated signal area of organic molecules before and after removal treatment, respectively.

3 Result And Discussion

3.1 Thermogravimetric analysis result

The percentage by weight of methanol contained in **1** was calculated to be 7.23%. The result of thermogravimetric analysis exhibits a rapid decrease in mass of **1** up to 7.21% at 42.8°C and a slow decrease in mass of **1** below 250°C (Figure 3). It can be concluded that all methanol molecules were removed below 45°C, and the structure of **1** remains stable under 45°C.

3.2 PXRD result

The simulated PXRD pattern is provided as Figure 4, the presence of one peak in the range of 7° to 8° in Figure 4 reveals that there are no methanol molecule guests in the voids formed in **1**. The presence of one peak in the range of 7° to 8° in Figure 4 confirms that methanol molecules have successfully been removed after heating process below 45°C. It can be concluded that the voids are completely empty under 45°C.

3.3 Small organic matter removal in organic wastewater using **1**

The study of encapsulating small organic molecules in organic wastewater using **1** was conducted by calculating the ratio of the changes in the concentration of organic molecule and was interpreted from the changes in the integrated signal area of small organic molecules obtained from the ^1H NMR measurement. Neopentyl alcohol was used as a standard to calculate the removal ratio of organic molecule in the organic wastewater. Neopentyl alcohol was used due to its size which is relatively larger than the size of void within **1**. The van der Waals volume of neopentyl alcohol is 104.2 Å³ considering the van der Waals modeling with a 100% radius relativity [32b]. Therefore, the neopentyl alcohol was not captured by **1**.

^1H NMR results, Fig. 5, suggest that desolvated **1** powder has the ability to capture methanol, acetone, acetonitrile, and tetrahydrofuran with the removal ratios of 29.17%, 63.22%, 42.77%, and 21.24%, respectively. Interestingly, **1** has an ability to capture acetone better than other organic molecules even though acetone has a larger size than methanol and acetonitrile. The volume of the molecules was estimated using Density Functional Theory and computations were performed using the ORCA program [32a]. All the molecular structures were optimized using B3LYP functional hybrid and 6-311G(d,p) basis set. The visualization of optimized structure was performed using Vega ZZ software [32b], to obtain the

information of volume. The van der Waals volume of acetone is $64.3 \text{ \AA}^3$ while the van der Waals volume of methanol and acetonitrile is $36.9 \text{ \AA}^3$ and $45.2 \text{ \AA}^3$, respectively [32b]. The low removal ratio of tetrahydrofuran was related to its relatively large volume of $77.4 \text{ \AA}^3$ and considering the van der Waals modeling with a 100% radius relativity [32b].

4 Conclusions

Further to the synthesis of **1**, there are two methanol molecules encapsulated by each void within **1** and thus it became interesting to study the organic molecules removal in organic wastewater using **1**. Based on the experimental results, **1** has an ability to capture methanol, acetone, acetonitrile, and tetrahydrofuran with the removal ratios of 29.17%, 63.22%, 42.77%, and 21.24%, respectively. The findings of this research work can help towards the purification of organic waste water.

Declarations

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Conflicts of interest/Competing interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Availability of data and material

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Code availability

Not applicable.

Authors' contributions

M. K. conceived and supervised this research. B. O. A. F. carried out the experiment and analyses, drafted and refined the manuscript. P. R. calculated size of neopentyl alcohol, methanol, acetone, acetonitrile, and tetrahydrofuran using ORCA [32a] and VEGA ZZ [32b] software. M. I. E, L. R, and P. R. refined the manuscript.

Ethics approval

Not applicable.

Consent to participate

Confirm.

Consent for publication

Confirm.

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Notes

‡ Crystal data for 1: formula = $C_{42}H_{56}CoN_{10}O_4S_2$, $M = 888.01$, lattice = 'monoclinic', $a = 9.9613(3) \text{ \AA}$, $b = 23.9517(5) \text{ \AA}$, $c = 10.2582(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 113.963(4)^\circ$, $\gamma = 90^\circ$, $V = 2236.55(12) \text{ \AA}^3$, space group = P21/c (No. 14), $Z = 2$, $\rho(\text{calcd}) = 1.319 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.529 \text{ mm}^{-1}$, radiation = $0.71073 (\text{\AA})$, temp = 173.15 K, reflns collected = 6126, unique reflns = 5340, param refined = 273, $R1 [I > 2\sigma(I)] = 0.0556$, $wR2 [\text{all data}] = 0.1672$, GOF = 1.064. CCDC-2121123 contains the supplementary crystallographic data for this work and can be obtained through www.ccdc.cam.ac.uk/data_request/cif.

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Figures

Figure 1

(a) Infinite structures of $\{[\text{Co}(\text{bitbu-OMe})_2(\text{NCS})_2] \cdot 2\text{MeOH}\}_n$ viewed along a axis, (b) side view of $\{[\text{Co}(\text{bitbu-OMe})_2(\text{NCS})_2] \cdot 2\text{MeOH}\}_n$. (Hydrogen atoms are omitted for clarity. Color code: magenta, cobalt;

cyan, nitrogen; black, carbon; yellow, sulfur).

Figure 2

The illustration of small organic matters removal in organic wastewater using desolvated 1 powder.

Figure 3

TG and DTA graph of 1 powder (TG result, green line; DTA result, blue line).

Figure 4

(a) The simulated PXRD pattern of 1 with MeOH guest molecule based on single crystal XRD data, (b) The simulated PXRD pattern of 1 without MeOH guest molecule based on single crystal XRD data, (c) the Observed PXRD pattern of 1 powder before heated, (d) the Observed PXRD pattern of 1 powder after heated at 45°C. The patterns are shown in the range from 5° to 15°.

Figure 5

^1H NMR spectrum of (a) methanol, (b) acetone, (c) acetonitrile, and (d) tetrahydrofuran guest molecules before and after removal treatment using desolvated **1** powder.