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Fabrication and characterizations of hybrid membrane containing tannin-modified metal-organic framework for water treatment

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ABSTRACT

In the past decade, many researchers have focused on incorporating metal–organic frameworks (MOFs) as filler for hybrid membrane fabrication, predominantly due to their excellent polymer affinity, huge porosity, and tunable pore size. The hybrid membrane can significantly improve overall membrane properties. However, MOF/polymer membranes usually suffer low flux due to the hydrophobic nature of MOF's organic linker. Herein, this study modified MIL-100 an iron-based MOF with tannic acid to improve its hydrophilicity and subsequently hybrid membrane was fabricated using the phase inversion technique. Vast hydroxyl group from tannic acid plays an essential role in improving the hydrophilicity of MOF. Subsequently, improved the hydrophilicity of the prepared membrane. The Tannin-MOF/PES membrane experienced a high pure water flux of 357.9 L/m^{2}h, which is 1.9 times higher than the unmodified PES membrane.

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1. Introduction

Recently, metal–organic frameworks (MOFs) were introduced with promising potentials to be used as fillers for fabricating MOF/polymer hybrid membranes [1–4]. They are highly ordered and nanoporous networks that are derived from metallic centers bonded by terminal organic linkers. Compared to traditional fillers (e.g., metal oxide or bio-material), the prominent feature of the MOF lies in its excellent compatibility with soft polymer matrix attributed to its organic ligands. Besides, its tunable functionalities make the surface properties, pore size/shape and particle size of MOFs easily tailored to fit the prerequisites for membrane preparation and application [5]. Amongst the family of MOFs, MIL-100(Fe) (MIL stands for Material of Institute Lavoisier) is one of the subfamily of MOFs that has attracted scientific interest due to its rigid zeotypic crystal structure, high porosity, superior chemical and hydrolytic stabilities [6–8]. Moreover, the nature of the iron offers several advantages such as non-toxicity, environmentally friendly characteristics, and low cost in comparison to other metals [9], which make MIL-100(Fe) an attractive candidate for various applications [10–13].

Nevertheless, the application of MIL-100(Fe) in the development of hybrid membranes still lags despite its potentiality in the water treatment field. It was attributed to the hydrophobic nature of its organic linker (carboxylic acid) [8]. MIL-100(Fe) presence in the polymer matrix may not contribute much in improving membrane hydrophilicity and may adversely affect the phase inversion process, leading to lower membrane performance. Despite good inherent physical and chemical properties, MIL-100 (Fe) may be unfavorable to be directly incorporated into polymers. Thus, it is highly desirable to rationally modulate the compositional and morphological properties of MIL-100(Fe) to fully unlock its ability for water treatment with high-performance MOF/polymer hybrid membranes.

On the other hand, tannic acid (TA) is a natural polyphenol that consists of large multiples of galloyl structural units, typically used as a coating material for membranes to improve its water permeability [14–16]. Recently, due to its ability to coordinate with metal ions, TA has been proven to be an effective surface modification agent for MOFs [17,18]. Sun et al. [19] have recently modified ZIF-8 with TA then incorporated the modified ZIF-8 in the poly-

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meric membrane. The study highlighted that the modified ZIF-8 improves the morphology and properties of the fabricated hybrid membrane; by enhancing the MOF's hydrophilicity and overcoming the limitation of MOF in the polymer matrix.

Herein, hydrophilic MIL-100(Fe) was strategically synthesized in this study using TA through the surface functionalization technique. Then, the Tannin-MIL was incorporated into PES to prepare a hybrid membrane via phase inversion. The characterizations of modified MIL-100(Fe) and hybrid membrane were conducted to study the effect of post modification of MOF and its advantages towards polymer membrane.

2. Experimental

2.1. Materials

Iron (II) chloride tetrahydrate ($FeCl_2·4H_2O$, Merck), sodium hydroxide (NaOH, Merck), and trimesic acid (H_3BTC, Merck) were used to synthesize MIL-100(Fe) nanoparticles. Tannic acid (TA, Merck) and buffer solution pH 8 were used to modify MIL-100 (Fe) nanoparticle. Polyethersulfone (PES Radel® A300, Amoco Chemicals), polyvinylpyrrolidone (PVP K30, Merck), and 1-methyl-2-pyrrolidinone (NMP, Merck) were used to fabricate the membrane. Deionized (DI) water was used in all procedures.

2.2. Preparation of tannin-modified MIL-100(Fe) nanoparticles

Following a sustainable method [7], two solutions were prepared first. Solution 1 contains H_3BTC dissolved in 1 M NaOH, while Solution 2 contains $FeCl_2·4H_2O$ dissolved in water. After both solutions became homogenous, Solution 1 was introduced into Solution 2 under continuous stirring for 24 h at room temperature. The product was centrifuged and washed with DI water and ethanol before left the sample at room temperature. Brown powder of MIL-100(Fe) was collected and added to TA solution (dissolved in buffer solution pH 8) under continuous stirring for 20 min. The modified MIL-100(Fe) was collected by centrifugation washed with DI water and methanol. The sample was left overnight in a vacuum oven at 60℃, and the dark grey powder was collected. The product was denoted as "Tannin-MIL."

2.3. Fabrication of nanocomposite membrane

First, 1 g of PVP K30 was dissolved in 39 g of NMP solvent, followed by 3 g of Tannin-MIL dispersed in the solution under stirring at 550 rpm at 60℃. Then, 10 g of dried PES pellets were added into the mixture until the homogeneous suspension was obtained. The prepared dope solution was left standing at 50℃ for 5 h in the sonicator to be degassed. The uniform suspension was cast on a glass plate then immersed in a DI water bath for phase inversion. The water bath replacement was made every day for 3 days, then allowed to dry at room temperature before use.

2.4. Characterizations

The membrane cross-section was scanned under Scanning Electron Microscopy (SEM, Hitachi TM3000). The functional group of samples was determined using Fourier Transform Infrared-Attenuated Total Reflectance Spectrometer (FTIR-ATR, IRTRACE100 Shimadzu). The water contact angle was measured using the sessile-drop method by an automated DataPhysics with a goniometer (G10, KRUSS, Germany). Mechanical properties of each membrane were tested using Zwick/Roell Z020 according to the ASTM 882 standard followed by interpretation using TestXpert® III to yield average value.

2.5. Pure water flux of the membrane

A lab-scale cross-flow filtration was set-up for a flat-sheet membrane, operating at 2 bars. The water flux (F, L/m^{2}h) can be calculated using the equation below:

$$F = V/A \times \Delta t$$

where V, A, and t represent the volume of permeate (L), the effective membrane area (m^2), and the filtration time (h), respectively.

3. Results and discussion

3.1. The effect of post modification of MIL-100(Fe) nanoparticles with tannic acid

Fig. 1 presents the FTIR spectra of MIL-100(Fe) and Tannin-MIL nanoparticles. After modified MIL-100(Fe), the nanoparticle shows an increase in the intensity peaks of –OH, aromatic C=O, and aromatic C=C of MIL-100(Fe) around 3429 cm^{-1}, 1699 cm^{-1}, and 1619 cm^{-1}, accordingly. These spectra match original TA chemical compounds, where the typical signals associated with –OH, C=O and C=C of TA were around 3318.5 cm^{-1}, 1698.2 cm^{-1}, and 1607.9 cm^{-1}, respectively [20]. The results indicate that the galloyl groups from the TA presence on MIL-100(Fe) nanoparticles surface. Nevertheless, a peak at 682 cm^{-1} represents the C–H vibration of the benzene ring is disappeared for Tannin-MIL nanoparticles suggesting surface functionalization of MIL-100(Fe) by TA occurs at the benzene ring. Moreover, other new peaks at 1043 cm^{-1} and 1229 cm^{-1}, most likely due to C-O-C stretching of the alkyl-aryl-ether with asymmetric bonds, appear in the FTIR spectra Tannin-MIL. The disappearance of C–H vibration of the benzene ring was replaced with the formation of C-O-C bonds proved that MIL-100 (Fe) was chemically reacted with tannic acid, as illustrated in Fig. 2.

3.2. Interaction between Tannin-MIL nanoparticles and polymer matrix

The FTIR spectra of the prepared membranes in Fig. 3 shows the physicochemical interaction between Tannin-MIL nanoparticles and polymer matrix. It could be seen that a broadened peak around 3413 cm^{-1} to 3535 cm^{-1} for the modified membrane, which originated from the vast hydroxyl group from tannin-MIL nanoparticles. Hydroxyl group plays an essential feature in improving membrane hydrophilicity, as high capabilities to adsorb more

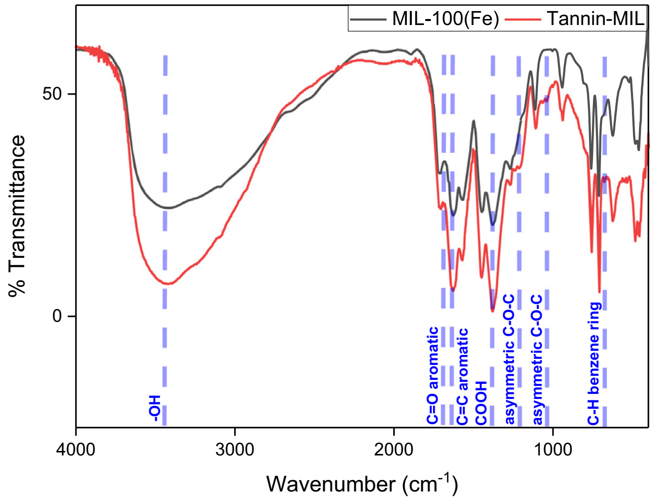

Fig. 1. FTIR spectra of prepared MOFs.

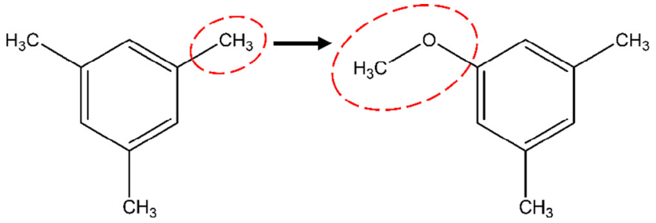

Fig. 2. Illustration of the alkyl-aryl-ether bond formation at benzene ring after post modification with tannic acid.

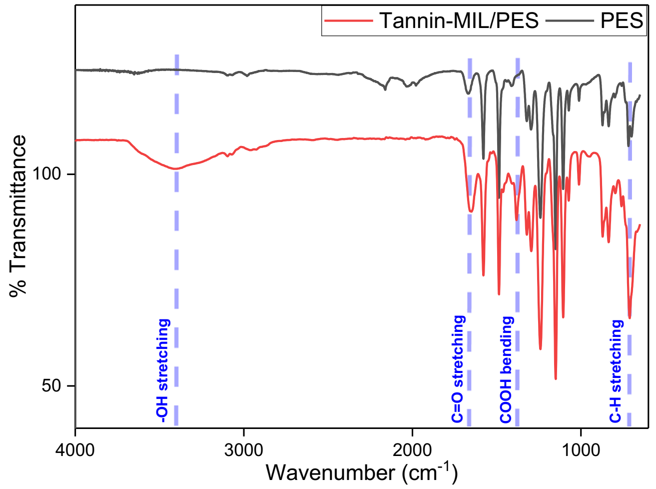

Fig. 3. FTIR spectra of PES and Tannin-MIL/PES membranes.

water molecules [21,22]. Besides, intensity peaks were observed around 1652 cm^{-1} and 1382 cm^{-1}, ascribed to carbonyl/carboxyl groups and aromatic groups in Tannin-MIL. Thus, demonstrate the successful modification of the PES membrane with Tannin-MIL. The possible interaction mechanism between Tannin-MIL nanoparticles and PES polymer is intermolecular hydrogen bonding, as illustrated in Fig. 4. The H-donating group (hydroxyl) from Tannin-MIL may react with the strong electronegative group, such as oxygen in the ether bond in PES's main chain, to form a hydrogen bond [23].

3.3. Influence of Tannin-MIL blending on membrane morphology, water contact angle and pure water flux

Membrane cross-section was observed under SEM to study the morphology of membranes, as shown in Fig. 5. It can be seen that both membranes possessed typical asymmetrical structure with a dense top layer and microvoid sublayer. As expected, the modified PES membrane exhibits longer finger-like structure and more porous sublayer than the unmodified PES. Hydroxyl group from Tannin-MIL nanoparticle promotes water penetration rate through the polymer during the phase inversion process, resulting in thinner membrane size. Previous studies reported that a thinner membrane flat sheet tends to have higher water permeability [24,25].

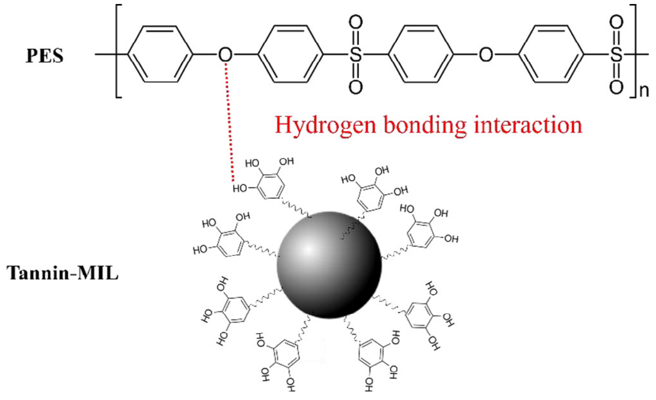

Fig. 4. Illustration of interaction between Tannin-MIL nanoparticles and PES.

The membranes' hydrophilicity was determined by measuring the water contact angle with membrane surface and membrane pure water flux, as presented in Fig. 6. The contact angle of water on the unmodified PES membrane's surface is 85.5°, reflecting the relatively hydrophobic nature of this type of membrane. The water contact angle gradually decreased to 40.3° for the modified PES membrane after adding Tannin-MIL nanoparticles in the polymer matrix, attributed to the hydroxyl group from TA in modified MIL-100(Fe) distributed throughout the polymer matrix. Besides, the Tannin-MIL/PES membrane experienced higher water permeation up to 357.9 L/m^{2}h, which is 1.9 times more than the unmodified PES membrane (185.4 L/m^{2}h). The addition of modified MIL-100(Fe) into the membrane matrix caused surface hydrophilicity enhancement and possibly due to larger finger-like microvoids in the modified membrane. Previous studies reported similar findings in which the pure water flux amelioration in the membranes can associate with ease of water transport through the membranes via large cavities [19,22,25,26] (Fig. 5).

3.4. Mechanical properties of Tannin-MIL/PES membrane

Mechanical properties of the prepared membranes were assessed based on their elongation at break, Young's modulus and tensile strength, as summarized in Table 1. It is found that the incorporation of Tannin-MIL nanoparticle improves mechanical properties of the prepared hybrid membrane with 1.23 times higher than the unmodified PES membrane. This can be attributed to the homogeneous distribution of Tannin-MIL nanoparticle throughout the polymer matrix, and strong hydrogen bonding formed between vast hydroxyl group of tannic acid and the ether bond of PES.

3.5. The potential application for Tannin-MIL/PES membrane

This study focuses on improvement in membrane permeability by modifying MOF with tannic acid. Considering the SEM, FTIR, water contact angle, pure water flux and mechanical properties improvement, it is possible to expect the fabricated modified PES membrane to be suitable for water treatment. However, further analysis should be performed on a different type of water/wastewater to ensure its practicability. As some hybrid membranes incorporating tannin-modified nanomaterials (e.g., MOF or metal-phenolic network), several studies have proved the use of these membranes exhibit high flux during water filtration with excellent antifouling properties. This type of membrane could act as a hybrid adsorbent for pollutants from water bodies [19,27]. Besides, the modified PES membrane's additional adsorptive feature was expected from the presence of iron-metal in the MIL-100 nanoparticles itself. The Tannin-MIL/PES membrane's high permeation flux has potential in water and wastewater treatment. Nonetheless, further work should be carried out in the future on these particular applications.

4. Conclusion

MIL-100(Fe) nanoparticle was successfully modified with tannic acid via surface functionalization technique, and a mixed matrix

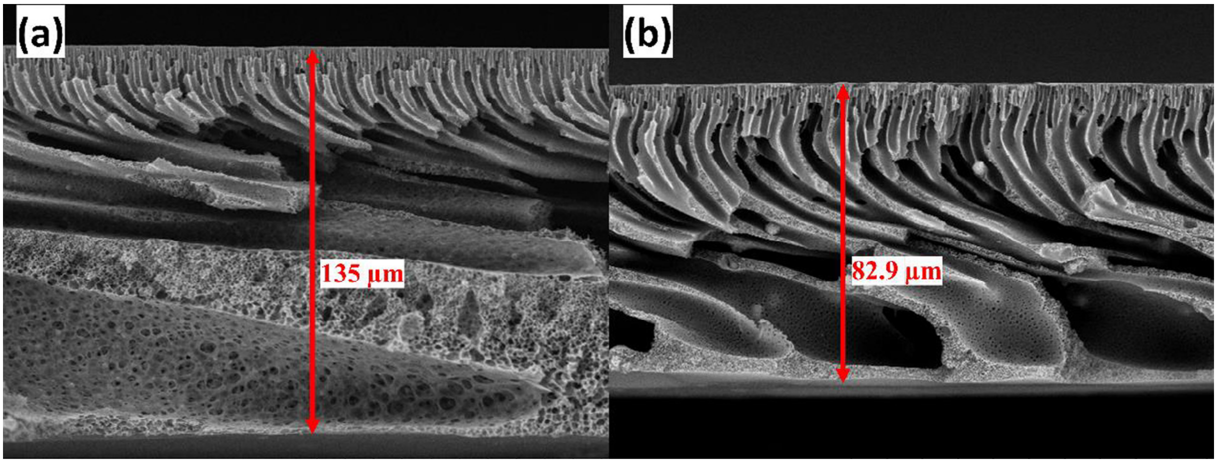

Fig. 5. Cross-sectional of SEM images of (a) PES and (b) Tannin-MIL/PES membranes.

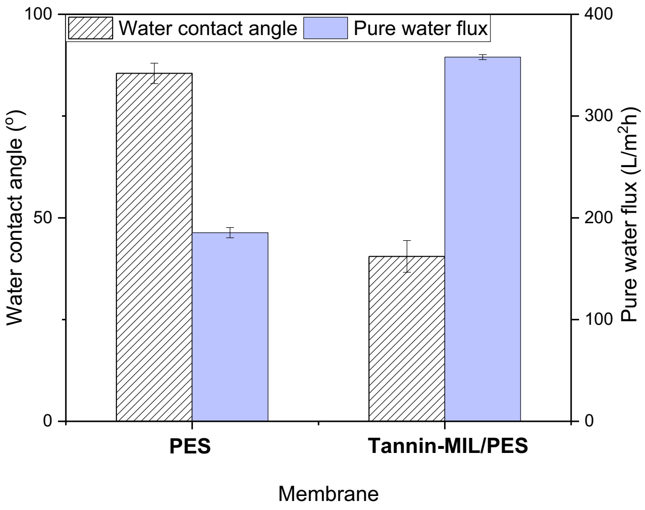

Fig. 6. Water contact angle and pure water flux of fabricated membranes.

Table 1
Mechanical properties of hybrid membranes.

Membrane	*Tensile strength (MPa)*	*Young's modulus (MPa)*	*Elongation at break (%)*
PES	1.32	31.95	14.73
Tannin-MIL/PES	2.95	36.50	24.68

membrane incorporating tannin-modified MIL-100(Fe) nanoparticle was fabricated by the phase inversion method. As confirmed by a series of characterizations, vast hydroxyl groups from TA provides MIL-100(Fe) with a high hydrophilic surface. It plays a vital role during the phase inversion process and improves membrane hydrophilicity, leading to enhancement of membrane permeability. Therefore, it is considered that the tannin-MIL/PES membrane provides an excellent alternative to other nanocomposite membranes used for water/wastewater treatment due to its valuable potential and high mechanical strength.

CRediT authorship contribution statement

Nur Azizah Johari: Conceptualization, Methodology, Data curation, Investigation, Formal analysis, Writing - original draft, Visualization. **Norhaniza Yusof:** Conceptualization, Visualization, Writing - review & editing, Supervision, Funding acquisition. **Ahmad Fauzi Ismail:** Formal analysis, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] F. Dorosti, A. Alizadehdakhel, Chem. Eng. Res. Des. 136 (2018) 119–128.
[2] J. Duan, Y. Pan, F. Pacheco, E. Litwiller, Z. Lai, I. Pinnau, J. Memb. Sci. 476 (2015) 303–310.
[3] G. Gnanasekaran, S. Balaguru, G. Arthanareeswaran, D.B. Das, Sep. Sci. Technol. 54 (2019) 434–446.
[4] M. Samari, S. Zinadini, A.A. Zinatizadeh, M. Jafarzadeh, F. Gholami, Sep. Purif. Technol. 251 (2020) 117010.
[5] N.R. Champness, Dalt. Trans. 40 (2011) 10311.
[6] F. Zhang, J. Shi, Y. Jin, Y. Fu, Y. Zhong, W. Zhu, Chem. Eng. J. 259 (2015) 183–190.
[7] K. Guesh, C.A.D. Caiuby, Á. Mayoral, M. Díaz-García, I. Díaz, M. Sanchez-Sanchez, Cryst. Growth Des. 17 (2017) 1806–1813.
[8] L. Xie, M. Xu, X. Liu, M. Zhao, J. Li, Adv. Sci. 7 (2020) 1901758.
[9] P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, Chem. Commun. 100 (2007) 2820–2822.
[10] A. Dhakshinamoorthy, M. Alvaro, H. Chevreau, P. Horcajada, T. Devic, C. Serre, H. Garcia, Catal. Sci. Technol. 2 (2012) 324–330.
[11] A. Rita, R.P.P.L. Ribeiro, J.P.B. Mota, V.D. Alves, I.A.A.C. Esteves, Sep. Purif. Technol. 202 (2018) 174–184.
[12] J. Yao, Y. Liu, J. Wang, Q. Jiang, D. She, H. Guo, N. Sun, Z. Pang, C. Deng, W. Yang, S. Shen, Biomaterials 195 (2019) 51–62.
[13] N.A. Johari, N. Yusof, A.F. Ismail, F. Aziz, W.N.W. Salleh, J. Jaafar, N.H.H. Hairon, N. Misdan, J. Adv. Res. Fluid Mech. Therm. Sci. 75 (2020) 68–80.
[14] Y.Z. Song, Y. Zhang, J.J. Yuan, C.E. Lin, X. Yin, C.C. Sun, B. Zhu, L.P. Zhu, J. Electroanal. Chem. 808 (2018) 252–258.
[15] J. Wei, Y. Liang, Y. Hu, B. Kong, G.P. Simon, J. Zhang, S.P. Jiang, H. Wang, 6102 (2016) 1355–1359.
[16] L. Fan, Y. Ma, Y. Su, R. Zhang, Y. Liu, Q. Zhang, Z. Jiang, RSC Adv. 5 (2015) 107777–107784.

[17] M. Hu, Y. Ju, K. Liang, T. Suma, J. Cui, F. Caruso, Adv. Funct. Mater. 26 (2016) 5827–5834.
[18] N.A. Johari, N. Yusof, W.J. Lau, A.F. Ismail, 8th Int. Grad. Conf. Eng. Sci. Humanit., School, of Graduate Studies Universiti Teknologi Malaysia, 2020, pp. 105–109.
[19] H. Sun, B. Tang, P. Wu, J. Memb. Sci. 551 (2018) 283–293.
[20] C. Ong, Y. Shi, J. Chang, F. Alduraiei, N. Wehbe, Z. Ahmed, P. Wang, Sep. Purif. Technol. 227 (2019) 115657.
[21] S.N.W. Ikhsan, N. Abdullah, N. Yusof, F. Aziz, N. Misdan, N.H.H. Hairom, J. Appl. Membr. Sci. Technol. 20 (2017) 11–17.
[22] N. Abdullah, R.J. Gohari, N. Yusof, A.F. Ismail, J. Juhana, W.J. Lau, T. Matsuura, Chem. Eng. J. 289 (2016) 28–37.
[23] P. Schuster, G. Zundel, C. Sandorfy, The Hydrogen Bond : Recent Developments in Theory and Experiments, American Elsevier Pub. Co., 1976.
[24] A.F. Ismail, A.R. Hassan, Sep. Purif. Technol. 55 (2007) 98–109.
[25] N. Abdullah, N. Yusof, M.H. Abu Shah, S.N. Wan Ikhsan, Z.C. Ng, S. Maji, W.J. Lau, J. Jaafar, A.F. Ismail, K. Ariga, Environ. Sci. Pollut. Res. 26 (2019) 20386–20399.
[26] N. Abdullah, N. Yusof, R.J. Gohari, A.F. Ismail, J. Jaafar, W.J. Lau, N. Misdan, N.H.H. Hairom, Water Environ. Res. 90 (2017) 64–73.
[27] X. Fang, J. Li, X. Li, S. Pan, X. Sun, J. Shen, W. Han, L. Wang, B. Van Der Bruggen, J. Colloid Interface Sci. 505 (2017) 642–652.