Doping Metal Organic Frameworks with Ionic Liquids for Adsorption of Tetracyclines from Water Samples

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Keywords: Metal Organic Frameworks, Ionic Liquids, Tetracyclines, Adsorption.

Abstract: Ionic liquids (ILs) were supported on metal organic frameworks (MOFs) for adsorption of tetracyclines (TCNs) from water samples. Benzothiazolium haxafluorophosphate IL when combined with Zeolitic imidazolate framework-8 MOF ([HBth][PF_6] @ZIF-8) demonstrated successful adsorption performance.

1 INTRODUCTION

The tetracyclines (TCs), including tetracycline, chlorotetracycline and oxytetracycline, are a chemically related group of bacteriostatic antibiotics. They exhibit a broad spectrum of antimicrobial activity, being effective against gram positive and gram-negative aerobic and anaerobic bacteria. Despite their introduction more than 50 years ago, tetracyclines are still widely popular for human medicines (Katrin et al., 2016). Although exposure to tetracyclines is well tolerated, they do produce several adverse effects including gastrointestinal irritation, phototoxicity and teeth staining. They can also be introduced in surface waters due to their veterinary use for livestock, which have been ubiquitously available in the aquatic environment via manure dispersion and animal excretion. Their presence in natural waters inevitably yields the spread of antibiotic resistance in microorganisms. Therefore, there is a need to bring effective method for the decontamination of these drugs from water bodies.

The aim of this study is to enhance the efficiency of potential adsorbents such as Metal Organic Frameworks (MOFs), which have attracted considerable attention for adsorption technology owing to their high porosity, in removing TCs from aquatic system. Metal–organic frameworks are a class of crystalline porous hybrid materials constructed after infinite connectivity of metal ions or nodes and organic molecules called linkers via self-assembly mechanism. MOFs have superior adsorption properties compared to other porous materials due to their large surface areas as well tunable pore sizes varied from microporous to mesoporous scale. Hence, the reported MOFs (Rocío-Bautista et al., 2015) with various structural topologies and unique functionalities is increasing rapidly. Recently, MOFs have been studied for adsorption of TCs from environmental waters. Wang and coworkers (Wang et al., 2018) employed Fe-based MOFs in removal of TCs by adsorption and photocatalytic degradation simultaneously. Moreover, some active species like metal nanoparticles were also incorporated into the pores of MOFs for better adsorption of TCs. Yang group (Yang et al., 2019) reported an increase in adsorption capacity of Cu and Co nanoparticles co-doped MIL-101 (Cr) (Material Institute Lavoisier) for TCs compared with the pristine MOF.

MOFs could be further customized by combining with ionic liquids (denoted as IL@MOFs) which could be able to overcome the drawbacks of parent MOFs related to their poor dispersion in water. Ionic liquids (ILs) are salts consist of positive and negative charges bound together by electrostatic interactions with melting points below 100^{o}C. The chemical and structural versatility of ILs make them suitable guest molecule candidates for the facile post-modification of MOFs as a host materials (Kitagawa et al., 2015). As a consequence of the coalition with MOFs, the ILs lose their liquid nature but they still maintain their thermal stability and chemical properties. Despite its great potential, limited studies have been conducted on IL@ MOF composite for adsorption applications. Jhung and coworkers (Jhung et al., 2014) incorporated 1-butyl-3-methylimidazolium chloride into the pores of

Alula, Y., Tang, J. and Yao, S.
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DOI: 10.5220/0008185700690072
In *The Second International Conference on Materials Chemistry and Environmental Protection (MEEP 2018)*, pages 69-72
ISBN: 978-989-758-360-5

MIL-101 by means of simple impregnation for the adsorptive removal of benzothiophene from liquid fuel. Later on, the same research group synthesized the IL inside inside MIL-101 porous cavities via a ship-in-bottle (SIB) technique for similar objectives (Jhung et al., 2016). In this work, we explored several ILs and MOFs when combined produces synergetic effect for successful adsorptive elimination of TCs from water samples. To the best of our knowledge, no other published work attempted to investigate IL@MOF for the same application.

2 EXPERIMENTAL

2.1 Chemicals

Terephthalic acid (TPA, 98%), Chromium chloride ($CrCl_3.6H_2O$, 96%), Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99%), 2-Methylimidazole (H-MIM, 99%), Benzene- 1,3,5-tricarboxylicacid (H_3btc, 95%), $Cu(NO_3)_2.2.5H_2O$, Chlorotetracycline, Oxytetracycline and Tetracycline were supplied by Kelong Chemicals (Chengdu, China). Ultrapure water was obtained by a water purification system A10 MilliPore (Bedford, MA). The ten ionic liquids were chosen for this study, which included 1-butyl-3-methylimidazolium chloride ($[C_6MIM][Cl^-]$), 1-hexyl-3-methylimidazolium chloride ($[C_4MIM][Cl^-]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4MIM][BF_4]$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($[C_6MIM][BF_4]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$), benzothiazolium tetrafluoroborate ($[HBth][BF_4]$), benzothiazolium hexafluorophosphate ($[HBth][PF_6]$), 8-hydroxyquinolinephosphate ($[HOQu][H_2PO_4]$), 8-hydroxyquinolinesulfate ($[HOQu][HSO_4]$) and were synthesized in our lab according to reported methods.

2.2 Synthesis of MOFs

2.2.1 Synthesis of ZIF-8

ZIF-8 (Zeolitic Imidazolate Framework) was synthesized according to the procedure of Kitagawa group (Kitagawa et al., 2015). A methanol solution (75 mL) of $Zn(NO_3)2•6H_2O$ (1.10 g, 3.70 mmol) was added to a methanol solution (75 mL) of H(MeIM) (1.22 g, 14.8 mmol) and triethylamine (3.00 g, 29.7 mmol) at ambient temperature. The mixture was stirred vigorously for a period of 1 h at room temperature. The resultant white-colored precipitate was collected using centrifugation, and washed five times by methanol followed by drying at 150°C.

2.2.2 Synthesis of MIL-101

MIL-101(Cr) was synthesized according to Jhung (Jhung et al., 2016) group. In a typical synthesis, MIL-101 was prepared from $CrCl_3•6H_2O$, TPA and deionized water with reactants composition 1.0 $CrCl_3•6H_2O$: 1.0 TPA : 300 H_2O. The precursor of 30 g was loaded in a Teflon-lined autoclave and put in a preheated electric oven at 210 °C for 8 hours. After the reaction, the autoclave was cooled to room temperature and solid green-colored products were recovered by filtration. The MOF obtained was purified in three steps. In the first step, 1.0 g MIL-101 was added to 300 mL water and stirred magnetically for 5 hours at 70 °C. Then the MOF was filtered and dried overnight. In the second step, the dried MOF was added to 250 mL ethanol; stirred magnetically at 60 °C for 3 hours and then filtered. In the third step, the MOF from the second step was added to 150 mL 30 mM NH_4F solution and stirred for 10 hours at 60 °C. Finally, it was filtered, washed five times and then dried at 150 °C.

2.2.3 Synthesis of HKUST-1

HKUST-1 was synthesized according to the literature (Rocío-Bautista et al., 2015). Typically, H_3btc (0.630 gram, 3 mmol) was dissolved in 15 mL of ethanol. Secondly, $Cu(NO_3)_2•2.5H_2O$ (1.255 gram, 5.4 mmol) was dissolved in 15 mL of deionized water and then added dropwise to the ethanolic solution of H_3btc while stirring for 10 min. The resultant solution mixture was transferred into a 45 mL Teflon lined stainless steel autoclave and kept at 110°C for 24h. Then, the autoclave was cooled down to room temperature and the crystalline powder was isolated by filtration, washed with ethanol several times and air dried at 50°C. Finally, the purified MIL-101 was dehydrated at 150°C overnight.

2.3 Synthesis of IL@MOF Composites

Wet impregnation method (Henni et al., 2018) was used for synthesizing the IL/MOF composites. The specified amount of IL was weighed out in a scintillation vial. Then 3 mL of methanol was added to the specified amount of IL, and the vial was gently mixed until the IL was dissolved. The total

amount of ionic liquid used for the impregnation varied depending on the maximum value of IL desired in the resulting composite. The solution was added dropwise to the preweighted ZIF-8 material, and the composite was dried at 70 °C overnight to remove any remaining solvent and stored in a desiccator.

2.4 Characterization

The size and image of microcrystals was observed with JSM-7001F scanning electron microscopy (SEM) (JEOL Co., Ltd., Tokyo, Japan) and X-ray diffraction (XRD) patterns were recorded on a D8 X-ray diffractometer equipped with accessional analytical system (Bruke, Karlsruhe, Deutschland). Thermogravimetric analysis (TGA) was performed on a TG 209 Fl Iris instrument (NETZSCH-Gerätebau GmbH, Selb, Deutschland) with a heating rate of 10 ºC min-1 from 30 to 800 ºC under nitrogen.

2.5 Adsorption Experiment

All the IL@MOFs were heated at 150 ºC for 12 hours in a vacuum oven before being used as an adsorbent. The adsorption study was carried out as follows: 5 mg IL@MOF mixed with 20 mL sample solution of 10 ppm in 50 mL Erlenmeyer flask. The mixture was shaken in a water-bath oscillator (100 rpm) for 35 min 25ºC. After full adsorption, the flask was centrifuged at 6000 rpm for 5 min, and then the UV-visible absorbance of the supernatant was measured at 355 nm.

Table 1: Data for adsorption efficiency of Oxytetracycline over ZIF-8 and [HBth][PF_6]@ZIF-8.

Adsorbent	E (%)
ZIF-8	49
10% IL@ZIF-8	62
20% IL@ZIF-8	71
25% IL@ZIF-8	77
30% IL@ZIF-8	75

Table 2: Data for adsorption efficiency of TCNs over [HBth][PF_6]@ZIF-8 in 0.30 to 1 molar ratio.

TCNs	E(%)
chlorotetracycline	82.2
oxytetracycline	89.8
tetracycline	91.5

$$E\ \% = ((C_0 - C_1) \times 100\%)/C_0 \quad (1)$$

3 RESULTS AND DISCUSSION

3.1 Properties of Adsorbents

The SEM images presented in Figure 1 and 2 show that the surface morphology of ZIF-8 changed after incorporation of ILs which indicates the existence of guests inside the pores of MOFs. The XRD experiment illustrated that the crystal phases of pristine and modified MOFs have remarkable similarity, which is confirming successful synthesis and stability of the MOFs even after decorated with ionic liquids. TGA analysis revealed the synthesized adsorbents are stable up to nearly 400ºC.

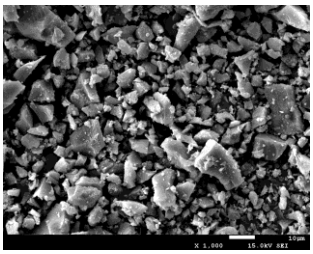

Figure 1: SEM image of ZIF-8 before incorporation of IL.

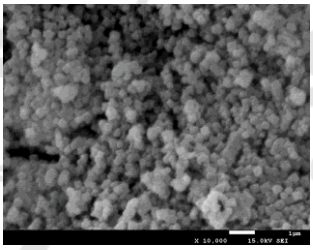

Figure 2: SEM image of [HBth][PF_6]@ZIF-8 composite.

3.2 Adsorption Efficiency of MOFs

An initial investigation was carried out to identify the appropriate MOF as an adsorbent based on calculation of adsorption efficiency (E %) for each MOF according to equation 1, where, C_0 and C_1 (mgL^{-1}) are Concentrations of TCs before and after adsorption respectively. Considering that the adsorption is performed in aqueous solution, the potential adsorbents needs to be water stable. Three Metal Organic frame works specifically, MIL-101, HKUST-1 and ZIF-8 were chosen and examined for adsorptive removal of one type of TCs (named oxytetracycline, OTC) from aqueous solution. Parameters that affect the adsorption condition such as, initial concentration of adsorbent and adsorption time were optimized for each of the three MOFs before the study of their adsorptive performances.

The results reveal that E (%) is 58.2%, 55.6%, 49.3 % for MIL-101, HKUST-1 and ZIF-8, respectively. This trend could be attributed to the complex formation reaction between TCNs and coordinatively unsaturated (CUS) sites in MIL-101 and HKUST-1. The absence of open metal site may have an impact in the case of ZIF-8 for its relatively lowered adsorption performance.

3.3 Effect of Ionic Liquids

One of the alternatives considered to upgrade the adsorption properties of those MOFs was to decorate with ILs following a post-synthetic modification. It was expected to lead to a higher performance for adsorption than the pristine MOFs. Ten ionic liquids were tested as potential guests, introduced into the pores of virgin MOFs targeted for TCs adsorption. Tetracyclines are complex hydrophilic drugs having high solubility in water and can exist both in acidic and basic form. The highest adsorption efficiency of 77.4% were obtained for the three TCs during the combination of [HBth][PF6] with ZIF-8. The best result was specifically obtained when [HBth][PF6] to ZIF-8 ratio was increased to 25 % as depicted on Table 1. The high adsorption efficiency of the IL@MOFs could be due to the capability of ILs to create complex interaction of columbic forces and π-π interaction with TCs. Generally the ILs improves the adsorption efficiency of all the studied MOFs to a greater extent.

3.4 Doping by Capillary Action

Once [HBth][PF6] @ZIF-8 was selected as the best adsorbent, improving the stability of the hybrid composite, in order to keep the ILs inside the pores of MOF was considered. The effect of capillary action was studied as an alternative synthesis strategy, since ZIF-8 has no open metal sites. The [HBth][PF_6] was mixed with activated ZIF-8 powder using mortar and pestle in a molar ratio of 0.20:1, 0.25:1, 0.30:1 and 0.35:1. The mixture was heated and stored overnight to enhance the diffusion of the IL through pores of ZIF-8. As shown in Table 2, the adsorbed quantities of TCNs increased to a significant extent until the IL to MOF ratio became 0.30 to 1. The capillary action improves the confinement of IL inside ZIF-8 pores and hence, the stability of the resulting composite, which brought great potential in the way of increasing the adsorption efficiency of TCNs.

4 CONCLUSIONS

In summary, imidazolium, hydroxyquinolium and benzothiazolium ionic liquids were impregnated on water stable metal organic frameworks and investigated for adsorption of TCNs. ZIF-8 when combined with one type of benthothiazolium IL showed highest adsorption efficiency, especially after doping by capillary action. The result proves that the adsorption properties of MOFs could be well improved by using appropriate ILs.

ACKNOWLEDGEMENTS

The authors thank the National Natural Science Foundation of China (No. 81373284, 81673316).

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