



Submicron sized water-stable metal organic framework (bio-MOF-11) for catalytic degradation of pharmaceuticals and personal care products



Muhammad Rizwan Azhar^a, Periasamy Vijay^a, Moses O. Tadé^a, Hongqi Sun^b, Shaobin Wang^{a,*}

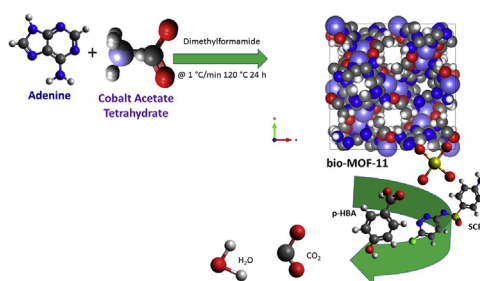
^a Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

^b School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Perth, WA 6027, Australia

HIGHLIGHTS

- Bio-MOF-11-Co was synthesized by a simplified benign method.
- Bio-MOF-11-Co presented high activity for peroxymonosulfate (PMS) activation.
- Bio-MOF-11-Co/PMS effectively degraded pharmaceuticals and personal care products.
- Lewis bases in bio-MOF-11-Co promotes electron transfer for PMS activation.

GRAPHICAL ABSTRACT



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ABSTRACT

Water-stable and active metal organic frameworks (MOFs) are important materials for mitigation of water contaminants via adsorption and catalytic reactions. In this study, a highly water-stable Co-based MOF, namely bio-MOF-11-Co, was synthesized by a simplified benign method. Moreover, it was used as a catalyst in successful activation of peroxymonosulfate for catalytic degradation of sulfachloropyridazine (SCP) and para-hydroxybenzoic acid (p-HBA) as representatives of pharmaceuticals and personal care products, respectively. The bio-MOF-11-Co showed rapid degradation of both p-HBA and SCP and could be reused multiple times without losing the activity by simply water washing. The effects of catalyst and PMS loadings as well as temperature were further studied, showing that high catalyst and PMS loadings as well as temperature produced faster kinetic degradation of p-HBA and SCP. The generation of highly reactive $p\text{-HBA} / \text{SCP} + \text{HO}^{\bullet} \rightarrow \text{several...steps} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-}$ and HO^{\bullet} radicals during the degradation was investigated by quenching tests and electron paramagnetic resonance. A plausible degradation mechanism was proposed based on the functionalities in the bio-MOF-11-Co. The availability of electron rich nucleobase adenine reinforced the reaction kinetics by electron donation along with cobalt atoms in the bio-MOF-11-Co structure.

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1. Introduction

Parabens are the esters of para-hydroxybenzoic acid (p-HBA), which are widely used in food preservation, cosmetics,

* Corresponding author.

E-mail address: Shaobin.wang@curtin.edu.au (S. Wang).

pharmaceuticals and personal care products (PPCPs). Also, on an industrial level, they are used in cigarettes, varnishes, glues and animal feeds (Soni et al., 2005; Dodge et al., 2015). However, parabens are biodegradable into their derivatives, mainly p-HBA, which is more persistent to further biodegradation than parabens and can be often found in wastewater treatment plants (Evans et al., 2016; Wang and Kannan, 2016). Various studies on parabens and p-HBA have shown that their estrogenic nature produces various adverse effects on living organisms including impotency in male and breast cancer in females (Pugazhendhi et al., 2005; Tavares et al., 2009).

Moreover, the rapid growth in population increases a widespread use of antibiotics. The persistent nature of antibiotics, particularly sulfonamide antibiotics, is a major concern due to their strong toxic effects on aquatic life (Brain et al., 2008; Bu et al., 2013; Cruz et al., 2014). One of the sulfonamide antibiotics is sulfa-chloropyridazine (SCP), which is widely used in animal husbandry. The detection of PPCPs in sewage wastewater is alarming and has attracted researchers to develop the processes for efficient elimination of the hazardous chemicals from wastewater including p-HBA and SCP (Wu and Fang, 2003; Kang et al., 2016; Wang and Kannan, 2016).

In recent years, various materials have been used in removal of parabens, their derivatives and SCP, e.g. activated carbons, carbon nanotubes, heteroatom doped carbons, zeolites, and metal oxides. The usual methods for such toxic chemical removals include adsorption, catalytic and photocatalytic degradation (Bai et al., 2015; Duan et al., 2015; Huang et al., 2015; Kebir et al., 2015; Nichela et al., 2015; Pouya et al., 2015; Arshadi et al., 2016). Adsorption performs well in phase separation without completely destroying the contaminants. However, low adsorption capacities, difficulty in recycle and reuse of adsorbents are the drawbacks (Ahmed et al., 2015). On the other hand, advanced oxidation processes (AOPs) can transform the contaminants into small non-toxic fragments and subsequently to CO₂ and H₂O. However, selection of a suitable material to activate available oxidants is one of main challenges in AOPs (Wang et al., 2015c; Chen et al., 2016).

In the past decade, a lot of research has been conducted in synthesizing hybrid organic-inorganic materials namely, metal organic frameworks (MOFs). High surface area, tuneable porosity, and availability of various functional groups make these materials highly interested (Martin and Haranczyk, 2013; Marques et al., 2015; Liu et al., 2016; Marshall et al., 2016). However, most of the MOFs have been used in gas-phase processes, e.g. CO₂ and H₂ adsorption and storage (Li et al., 2013a; Chen et al., 2015; Almasi et al., 2016). Although, other uses in catalysis, drug delivery, lithium ion batteries, and cooling are increasing, still few attempts have been made in catalytic degradation of water contaminants using MOFs (Kim et al., 2013; Li et al., 2014; Erucar and Keskin, 2016; Jonckheere et al., 2016; Kozlova et al., 2016; Ning et al., 2016). A major problem associated with the use of MOFs in water treatment is their instability to sustain in aqueous media (Qadir et al., 2015).

Some water-stable MOFs have been studied in adsorptive removal of toxic organic wastes in the last few years. However, the investigations are limited to Al, Cr and Zr based MOFs with carboxylic acid linkers (Kim et al., 2013; Haque et al., 2014; Wang et al., 2015a). Similar to adsorption studies on MOFs in wastewater treatment processes (WWTPs), only limited MOFs have been investigated in catalytic degradation to date and most of such studies focus on degradation of dyes. In some cases, H₂O₂ has been used for degradation by generating •OH (Du et al., 2011; Sun et al., 2013; Zhu et al., 2014). However, activation of other oxidizing agents in AOPs such as peroxydisulfate (PDS) and peroxy-monosulfate (PMS) is a more interest to effectively use MOFs in

AOPs. PMS is a promising oxidizing agent, proved to be effective in various catalytic degradation processes (Ghanbari and Moradi, 2017). Although various studies are reported in activation of PMS using metal based or metal free catalysts (Shukla et al., 2010; Saputra et al., 2013b, c; Lin and Chang, 2015; Duan et al., 2016), MOFs offer simultaneous availability of organic-inorganic moieties for diverse applications.

Recently, adenine based MOFs, typically known as bio-MOFs, have been studied in drug delivery and CO₂ adsorption. However, the synthesis of bio-MOFs is complicated and requires cryogenic steps along with solvent exchange activation by chloroform or methanol (An et al., 2012; Li et al., 2013a). In the present study, a facile method for the preparation of bio-MOFs has been proposed. Moreover, a cobalt based bio-MOF, namely bio-MOF-11-Co, possesses a high water stability and was used in catalytic degradation of p-HBA and SCP via effective activation of PMS.

2. Experimental

2.1. Materials and methods

Co(CH₃COO)₂, adenine, *N,N*-dimethylformamide (DMF), Cu(CH₃COO)₂, H₂O₂, PDS and PMS (Oxone[®]) were purchased from Sigma-Aldrich, Australia and used without further purification. Ultrapure water (15 Ω) was produced by an Agilent water purification system in our laboratory.

The bio-MOFs were synthesized by a facile method without any cryogenic step (An et al., 2010). Specifically, 0.90 mmol cobalt acetate was dissolved in 18 mL DMF. Meanwhile, 2.70 mmol adenine was added to 54 mL DMF and stirred vigorously for 1 h to achieve complete dissolution. Subsequently, the two solutions were added to a 120 mL autoclave and 0.25 mL of ultrapure water was also added in. The autoclave was heated in a temperature-controlled oven at a heating rate of 1 °C/min to 120 °C and maintained at 120 °C for 24 h. A purple crystal product was filtered, washed three times with 54 mL DMF in each washing cycle and dried at 130 °C overnight to obtain bio-MOF-11-Co.

Similarly, bio-MOF-11-Cu was synthesized as stated above using copper acetate instead of cobalt acetate. Moreover, another MOF, copper benzene tricarboxylate (CuBTC), was prepared using previously reported method and details of the synthesis and characterization are given in previous studies (Chui et al., 1999; Azhar et al., 2016).

2.2. Characterization of MOFs

The synthesized bio-MOFs were characterized using Fourier transform infrared spectroscopy (Perkin Elmer's Spectrum 100-FT-IR), X-ray diffraction (Bruker D8, Co K α irradiation), scanning electron microscopy (Neon Zeiss), thermal gravimetric-differential scanning calorimetry (TG-DSC, TGA/DSC1 STAR^e system from Mettler-Toledo), N₂ adsorption-desorption isotherms (Micromeritics Tristar 3000II) and elemental analysis (2400 Series II CHNS/O analyzer by Perkin-Elmer for carbon, nitrogen and hydrogen). Particle size distribution was carried out on a Malvern Zetasizer nano ZS instrument by dispersing small amount of MOF (25 mg/L) particles in ultrapure water. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMS-plus to detect free radicals generated during activation of PMS. Total organic carbon (TOC) was measured on a Shimadzu TOC-vcph analyzer.

2.3. Catalytic degradation of p-HBA and SCP

All the degradation experiments were conducted using a batch

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