Photo-Fenton abatement of aqueous organics using metal-organic frameworks: An advancement from benchmark zeolite

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HIGHLIGHTS

- MIL-47(V) and MIL-53(Al) are active for photo-decolourization of methylene blue.
- Fe/MIL-47 shows better photo-Fenton activity than Cu/MIL-47 at acidic pHs.
- Fe/MIL-47 gives higher TOC mineralization than zeolite-based Fenton catalyst.
- Metal-loaded MIL-47 is a robust photo-Fenton catalyst for practical applications.

GRAPHICAL ABSTRACT
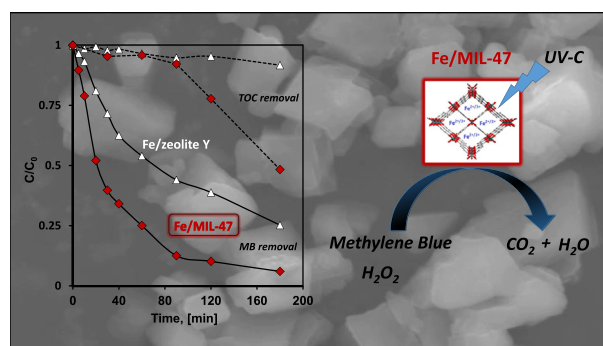
ABSTRACT

A new and environmentally benign photocatalyst is introduced in this study, which was synthesized *via* incipient wetness impregnation onto MIL-47(V) using an ethanolic Fe(III) chloride solution. The resultant materials were characterized by XRD, FE-SEM, and HR-TEM analyses. The photocatalytic capability of Fe/MIL-47 towards removal of methylene blue (MB) was evaluated in comparison to MIL-53(Al), Cu/MIL-47, and Fe/zeolite-Y. The unmodified MIL-47 achieved 55% MB removal after 20-min exposure to UV/H_2O_2, through photodegradation as the dominant mechanism. Incorporation of Fe species into MIL-47 significantly increased the MB removal rate by 2.4-fold and accomplished nearly complete removal (98.2%) in 60 min, outcompeting the performance of Cu/MIL-47 and Fe/zeolite-Y. Based on the results of XRD, the impregnation of Fe retained the crystalline characteristics of MIL-47. The significance of temperature, catalyst dose, pH, and molar ratio of H_2O_2:MB was also evaluated in governing the photocatalytic activity of Fe/MIL-47. The reusability of Fe/MIL-47 was evidenced through its repetitive uses in MB photodegradation. The current work highlighted the potential of Fe impregnation for modification of MOFs in order to fabricate highly efficient and water-stable heterogeneous photocatalyst for degradation of organic pollutants. With the use of an economical and environmentally safe reagent (*i.e.*, Fe), robust photocatalyst can exhibit high sustainability to warrant clean environmental remediation.

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1. Introduction

Metal-organic frameworks (MOFs) are an emerging type of crystalline microporous materials, of which the crystal lattice structure comprises metal ion vertices in coordination with organic bridging ligands

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(Tian et al., 2017; Wang et al., 2017). Tremendous research interests have been given to MOFs over the last few years in view of their advanced and tunable properties, including ultrahigh pore volume (up to 90% free volume) (Zhou et al., 2012) and large surface area (up to 6000 m^2 g^{-1}) (Ayati et al., 2016). A lot of variable combinations between metal ions and organic bridging ligands are feasible in MOFs synthesis. The easily tailorable physical/chemical properties of MOFs have expedited the development of diverse types of MOFs that can be used in various applications such as drug delivery (Teplerisky et al., 2017), adsorption (Alonso et al., 2017), gas separation (Wu et al., 2015), hydrogen storage (Roes and Patel, 2011), heterogeneous catalysis (Lin et al., 2015), and photocatalysis (Kaur et al., 2016).

Among these applications, utilizing MOFs for photocatalysis is of practical significance because photocatalysis is a convenient and environmental-benign way that utilizes solar energy in chemical reactions, including degradation of contaminants (Foteinis et al., 2018; Ramezanalizadeh and Manteghi, 2018). In comparison to conventional semiconductors as photocatalyst (*e.g.*, TiO₂ and ZnO), MOFs with adjustable characteristics offer more opportunities in the field of environmental remediation, where diverse environmental compartments with varying pollutant profiles are often encountered. As MOFs receive energy higher than band gap energy value from UV irradiation, the negative electrons (e^-) moves to the metallic cluster and then positive holes (h^+) are generated in the organic linker, in which the reduction and oxidation half reactions occur between the electrons and holes (Qiu et al., 2018). The photocatalytic ability of MOFs-based materials has been primarily determined by their electronic/electrochemical properties, which are associated with the nature of the organic ligands (linkers) and metal-oxide clusters (Kozlova et al., 2016). A few researchers have investigated the feasibility of using MIL-47 (Kozlova et al., 2016), HKUST-1 (Sofi et al., 2018), ZIF-8 (Jing et al., 2014), MOF-5 (Silva et al., 2010), and UiO-66 (Zhao et al., 2016) in the photocatalytic removal of organic pollutants in aqueous solution.

In particular, MIL-47 possesses three-dimensional orthorhombic structure due to the infinite chains of $V^{4+}O_6$ octahedra linked together by terephthalic linkers (Biswas et al., 2013). While MIL-47 has been proved to be effective in adsorption and oxidation reactions (Biswas et al., 2013; Xu et al., 2016), its potential in serving as a photocatalyst has not been explored to the best of our knowledge. In the conventional applications, MIL-47 generally exhibits good performance with its large pore size and high volumetric working capacity that facilitate access of target chemicals (Llewellyn et al., 2013; McNamara et al., 2013). Such favourable accessibility of MIL-47 emerges as an attractive feature for photocatalysis. In addition, the band gap of MIL-47 (2.76 eV) is comparable to that of an effective photocatalyst, namely MIL-100(V) (2.75) (Kozlova et al., 2016), showing a high potential in serving photodegradation.

Nevertheless, chemical modification may be needed to activate/enhance the photocatalytic ability of MIL-47. Previous studies suggested that doping of Fe was effective in enhancing the photocatalytic activity by either reducing the band gap or changing the facets property of TiO₂ catalyst (Carbrera Reina et al., 2017; Nasirian and Mehrvar, 2016; Sui et al., 2018). For example, Fe incorporation onto TiO₂ increased the photocatalytic degradation of methyl orange from 16.3 to 28.7% under sunlight (Nasirian and Mehrvar, 2016). Sui et al. (2018) reported that nano TiO₂–1.07Fe catalyst exhibited higher efficiency of oxidation of Rhodamine B (83.1%) within 160 min under visible light compared to that by nano TiO₂ (17.7%). We hypothesized that the incorporation of transition metal ions may be applicable for introducing and/or improving the photocatalytic capability of MOFs. More importantly, the use of Fe species in light-driven water treatment system has been reported to show higher environmental sustainability than other advanced oxidation processes, because Fe is relatively safe in the ecosystems and the photo-Fenton process does not generate harmful by-products (Foteinis et al., 2018). Therefore, it is imperative to capitalize the environmental merits of Fe in designing robust and green photocatalyst for remediation applications.

In this work, transition metal-doped MIL materials (Fe/MIL-47 and Cu/MIL-47) were prepared *via* incipient wetness impregnation, and their photocatalytic ability was evaluated with photo-Fenton abatement of methylene blue (MB) used as a model target contaminant. The purposes of this work were (1) to prepare and characterize the surface morphology and mineralogical phase of MIL materials, (2) to identify the photocatalytic ability of pristine MILs [MIL-47 and MIL-53(Al)], (3) to explore the effects of transition metal ions (Fe and Cu) impregnation on the photocatalytic degradation of MB by MIL-47, and (4) to investigate the effects of various parameters including temperature, catalyst dose, and molar ratio of H₂O₂:MB on the removal of MB and total organic carbon (TOC) by modified MIL-47. While most of the MOFs have low water stability (Burtch et al., 2014), Fe/MIL-47 was proved to be effective for MB removal (98.2%) in aqueous medium in this study, highlighting its feasible application in industrial wastewater treatment.

2. Experimental section

2.1. Chemicals & materials

Aluminum nitrate nonahydrate [Al(NO₃)₃·9H₂O, 98%], copper(II) chloride (CuCl₂, 98%), iron(III) chloride (FeCl₂, 98%), iron(III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O, >98%], methylene blue (MB, C₁₆H₁₈ClN₃S, 99%), terephthalic acid [H₂BDC, 98%], and vanadium(III) chloride (VCl₃, 98%) were purchased from Sigma Aldrich, USA. Na-zeolite Y and hydrogen peroxide (H₂O₂, 30% w/v) were obtained from Zeolyst International Company and Fisher Scientific, respectively. All the chemicals were used without any further treatment.

2.2. Preparation of MIL-47 samples

MIL-47 sample was synthesized following the reported procedure of Barthelet et al. (2002). In brief, VCl₃, H₂BDC, and DW were mixed at a molar ratio of 1:0.25:100, and the mixtures were placed into a Teflon-lined stainless Parr Acid Digestion Vessel. The solid powders were collected after hydrothermal reaction at 200 °C for 96 h, then were washed with acetone several times. The resulting material was calcined at 300 °C for 21 h to remove non-reacted H₂BDC from its surface/pores. Two modified MIL-47 samples (Cu/MIL-47 and Fe/MIL-47) were prepared *via* incipient wetness impregnation method as used in the literature (Khan and Jhung, 2012). The ethanolic solutions containing CuCl₂ and FeCl₃ were employed to impregnate metal ions onto MIL-47, and each molar ratio of Cu and Fe to V was 0.05:1. Besides MIL-47 samples, MIL-53(Al) sample was separately synthesized from literature methods described by Loiseau et al. (2004). The mixture was prepared by mixing Al(NO₃)₃·9H₂O, H₂BDC, and DW at molar ratio of 1:0.5:80, and then hydrothermally reacted using Teflon-lined stainless Parr Acid Digestion Vessel under the same condition as MIL-47 sample. The resulting material was also purified by calcination at 300 °C for 21 h. In addition, Fe/zeolite-Y sample was obtained by inducing ion exchange of Na-Y by Fe³⁺ with dropping of 0.1 M Fe(NO₃)₃ solution (MacDonald et al., 2014; Roque-Malherbe et al., 1993). The sample was collected through filtration after the reaction, and dried at 70 °C in a drying oven.

2.3. Characterization of MIL-47 samples

The X-ray powder diffraction (XRD) analysis of MIL-47, Fe/MIL-47, and reacted Fe/MIL-47 samples was conducted by a PW1700 computer-controlled diffractometer (Philips, USA) with a graphite monochromator and Co Kα radiation. The surface morphologies of samples were analyzed by using a JSM 7000F field emission scanning electron microscopy (FE-SEM, JEOL Hitachi, Japan). The energy dispersive X-ray spectroscopy (EDX) measurements were performed using a