Visible-light photocatalysis over MIL-53(Fe) for VOC removal and viral inactivation in air

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ABSTRACT
MIL-53(Fe), synthesized by a one-step hydrothermal method, was investigated for the removal of toluene and inactivation of bacteriophage ΦX 174 in air under visible light illumination. MIL-53(Fe) exhibited superior photochemical activity to other metal organic frameworks synthesized by the same method with different metal precursors. Analytical methods of diffuse reflectance spectroscopy, BET specific surface area analysis, SEM-EDS, FT-IR analysis, XRD, Mott-Schottky analysis, and XPS were used to characterize MIL-53(Fe). The illuminated MIL-53(Fe) removed input toluene (C0 = 3.59 g/m3) by 66% in 6 h by adsorption and subsequent photocatalytic oxidation. High humidity and temperature, and the anoxic condition inhibited the toluene removal. MIL-53(Fe) showed sustainable toluene removal for five consecutive runs, even though the photocatalytic activity slightly decreased. Meanwhile, the illuminated MIL-53(Fe) also resulted in the inactivation of ΦX 174 suspended in air, achieving approximately 3 log inactivation in 60 min (N0 = ~106 PFU/mL air). Similar to toluene removal, the presence of oxygen and low humidity were beneficial for viral inactivation. The photo-generated holes are believed to be responsible for the organic degradation and viral inactivation by the illuminated MIL-53(Fe).

Keywords: Metal-organic frameworks, MIL-53(Fe), Photocatalysis, Virus inactivation, Visible-light photocatalyst, Volatile organic compounds

1. Introduction

VOCs are important indoor air pollutants and are frequently found at higher concentrations than outdoors [1-3]. A variety of VOCs can be emitted from different sources. VOCs commonly detected in indoor air include benzene, toluene, ethylbenzene, xylene, naphthalene, dichloromethane, chloroform, and acetone [2, 4-6]. These compounds are generated from different emission sources, such as aerosol sprays, paints, dry-cleaned clothing, and building construction materials [7-9].

Meanwhile, the COVID-19 pandemic has raised awareness of the airborne transmission of pathogenic microorganisms, and the resultant public health risk. Pathogenic microorganisms that are contained in dust particles and aerosol droplets circulate in air [12-14]. These microorganisms generally include influenza virus, enterovirus, norovirus, coronavirus, and respiratory syncytial virus [15]. Although particles greater than 10 μm quickly fall out of the air, smaller particles can be suspended, and possibly inhaled through the respiratory tract, causing harmful health effects [16].

To treat air pollutants including VOCs and airborne pathogens, three physical and chemical methods have been commonly addressed, i.e., adsorption (on porous materials such as activated carbon and zeolite), filtration, and photocatalytic oxidation [3, 17-19]. Among them, photocatalytic oxidation is a powerful tool that by chemical reactions at ambient room temperature and pressure is capable of degrading (or mineralizing) VOCs, as well as inactivating microorganisms [6, 20]. For the photocatalytic treatment of VOCs and microorganisms, titania (TiO2) has been most intensively studied [21-28]. However, TiO2, of which the bandgap is 3.0-3.2 eV, can only utilize UV light [6, 29], which limits versatile
applications of the photocatalyst. Extending the available wavelength of light (possibly to the visible light region) can offer the photocatalytic system that works under indoor lighting conditions (artificial lighting and natural daylighting). Several visible light-active photocatalysts based on WO₃, g-C₃N₄, V₂O₅, and In₄O₃ have been studied for the treatment of VOCs and microorganisms in air [30-36].

In this study, metal-organic frameworks (MOFs) were tested as visible light-photocatalysts for air treatment. In the past decade, MOFs have been extensively studied for various applications that include environmental cleanup [37, 38]. Owing to their extra-high porosity, ordered structures, and adjustable chemical functionalities, MOFs have been frequently suggested as adsorbents to remove organic contaminants and heavy metals [39-41]. Some MOFs also exhibited photocatalytic activity to degrade organic contaminants [42-45]. However, the photocatalytic applications of MOFs in air cleaning have rarely been reported. A few MOFs have been tested for toluene removal (MIL-88B, [46]) and E. coli inactivation (ZIF-8, [47]) in air under simulated solar illumination.

MIL-53(X) has attracted attention due to its simple structure, and “breathing effect” upon the adsorption and desorption of water and other gases [48-52]. Compared to its chromium and aluminum analogues, MIL-53(Fe) in particular showed the greater breathing characteristic [52]. To date, MIL-53(X) has been examined only in aqueous system for the degradation of organic compounds [53-55]; to the best of our knowledge, no study has reported photocatalytic air treatment using MIL-53(X).

The objectives of this study were to assess the visible light-photocatalytic activity of MIL-53(X) (mainly MIL-53(Fe)) for VOC removal and viral inactivation in air, and to evaluate potential parameters affecting the performance of the photocatalytic treatment. For the photocatalytic experiments, toluene and bacteriophage ΦX 174 were chosen as a model VOC and a surrogate virus, respectively. The removal of toluene and the inactivation of ΦX 174 were examined under different conditions of relative humidity, atmospheric oxygen, and temperature. Based on the obtained results, the photocatalytic mechanisms were discussed.

2. Materials and Methods

2.1. Reagents

All chemicals were of reagent grade and were used without further purification. The chemicals used in this study included nickel(II) nitrate hexahydrate, copper(II) nitrate trihydrate, cobalt(II) nitrate hexahydrate, iron(III) chloride hexahydrate (FeCl₃·6H₂O), terephthalic acid (H₂BDC), toluene, acetaldehyde, ethanol, sodium sulfate, chitosan, sodium chloride, magnesium sulfate heptahydrate, potassium phosphate monobasic, potassium hydroxide, Nafion® perfluorinated resin solution, 2,3-bis(2-methyl-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) [all obtained from Sigma-Aldrich]. Other materials used were N,N-dimethylformamide (DMF, from Alfa Aesar), methanol (from Honeywell), and agar (from Becton-Dickinson). Deionized (DI) water (> 18.2 MΩ·cm) produced by a Milli-Q Water Purification System (Millipore) was used to prepare all solutions.

2.2. Culture and Analysis of ΦX 174

The culture and analysis of bacteriophage ΦX 174 (ATCC 13706-B1) was conducted following the ATCC manual [56]. The host E. coli (ATCC 13706) was cultivated in the medium containing 8 g/L nutrient broth and 5 g/L NaCl. ΦX 174 was inoculated in the suspension of host E. coli cells for 18-24 h at 37°C. The mixture of E. coli and ΦX 174 was centrifuged at 33,000 g for 15 min, to separate ΦX 174 in the supernatant. The population of ΦX 174 was quantified by the plaque assay method using media of the top and bottom double layer containing 0.5% and 1.5% of agar. The stock suspension of ΦX 174 contained approximately 10⁶ PFU/mL.

2.3. Synthesis

MIL-53(X) was prepared according to the previously reported method [53]. Briefly, the metal salt (i.e., nickel(II) nitrate hexahydrate, copper(II) nitrate trihydrate, cobalt(II) nitrate hexahydrate, and iron(III) chloride hexahydrate), H₂BDC, and DMF were mixed in molar ratios of 1:1:280. The mixture was transferred into a Teflon-lined autoclave and heated at 150°C for 15 h. After cooling the autoclave to room temperature, the resulting mixture was washed three times with methanol. The obtained powder was then dried at 60°C overnight.

2.4. Characterization

X-ray diffraction patterns of the synthesized materials were recorded by X-ray diffractometry (SmartLab, Rigaku) with Cu-Kα radiation. The obtained signal was compared through a computer simulation program (Mercury), and the CIF file for the simulation program was taken from Millange et al. [52]. Morphology and surface elemental distribution were analyzed by field emission scanning electron microscopy, coupled with energy dispersive X-ray spectrometry (FE-SEM/EDS, JSM-7800F Prime, Jeol). The specific surface area and pore structure were analyzed by BET-surface area analysis (ASAP 2020, Micromeritics). Diffuse reflectance spectra were obtained by UV/Vis/Near IR spectrophotometry ( Cary 5000, Agilent). X-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos) and Fourier transform infrared spectroscopy (FT-IR, Frontier, PerkinElmer) were used to examine the surface compositions and functional groups of the powered products. Mott-Schottky measurements were conducted by potentiostat (VSP, Bio-Logic Science Instruments). The MIL-53(Fe) photo-electrode was prepared according to the method reported by Zhao et al. [57], with a slight modification as follows: The MIL-53(Fe) powder (0.1 g) was dispersed in 1 mL chitosan solution (10 g/L), and ultrasonicated for 30 min. Then, the colloidal solution was coated on the indium-doped tin oxide (ITO) surface (5 cm × 4.5 cm) using the Doctor blade method, and dried at room temperature overnight. The measurements were performed in a standard three-electrode system (the MIL-53(Fe)-coated ITO as a working electrode, Pt foil as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode) with 0.5 M Na₂SO₄ solution as the electrolyte. A 150 W xenon arc lamp (LS 150, Abet Technologies) was used as a light source, together with an AM 1.5 G filter and a UV-cutoff filter (400 nm).
2.5. Setup and Procedure for Photocatalytic Experiments

All experiments were conducted with illuminating visible light onto the MIL-53(X)-coated glass plate in a photo-reactor (a 45 mL stain-less steel chamber with a round quartz window (4 cm radius), refer to Fig. S1 of the Supplementary Data (SD)). The MIL-53(X)-coated glass plate (3.5 cm × 5 cm) was prepared using the Doctor blade method; MIL-53(X) was coated on the plate using 0.15 g/mL suspension in ethanol, then dried at room temperature for 1 h, and subsequently at 200°C for 1 h. The light illumination was performed using a 150 W xenon arc lamp (LS 150, Abet Technologies) equipped with an AM 1.5 G filter and a 400 nm UV-cutoff filter; the incident light intensity was adjusted to 100 mW/cm² without the UV-cutoff filter.

For the experiments, an aliquot of the liquid organic compound (mainly toluene, and acetaldehyde for some experiments) or the O₂ stock suspension was injected into the sealed photo-reactor with the MIL-53(X)-coated glass plate. The reactor was stablilized until the liquid in the reactor was completely evaporated (30 min for the organic compound, and 2 d for the O₂ stock suspension). The photocatalytic reaction was initiated by light illumination. Samples were taken at predetermined time intervals using a 100 μL gas-tight syringe (Hamilton). The concentration of the organic compound was measured by gas chromatography equipped with flame ionization detector (GC-FID, Agilent 7820A, Agilent Technologies). The separation was performed on a HP-5 capillary column using hydrogen (by the LC-H2 180 hydrogen generator, F-DGSi), air, and nitrogen as carrier gases. In the viral inactivation experiments, the sample in the syringe was diffused into 1 mL phosphate buffer solution (PBS, pH 7.2). The population of O₂ in the PBS solution was quantified by the plaque assay method.

The photocatalytic experiments were conducted under different conditions of temperature and relative humidity, which were adjusted using a heating plate and a humidifier (filled with DI), respectively. Sodium sulfate was used when reducing humidity in the reactor. For some experiments, pure nitrogen or oxygen was used as the gas medium in the reactor. All experiments were performed at least in duplicate; average values and standard deviations (error bars) are presented.

To verify the photo-generation of charge carriers, photoluminescence (PL) was measured in 1 g/L aqueous suspension of MIL-53(Fe) by spectrofluorimetry (F-7100, Hitachi). Upon excitation at 400 nm, luminescence emission was recorded over a range of 400-500 nm. Photocurrent was also measured on the MIL-53(Fe) electrode under visible light illumination. The MIL-53(Fe) photo-electrode was prepared as follows: The MIL-53(Fe) powder (0.05 g) was dispersed in 0.5 mL binder solution (Nafion:ethanol = 1:1), and ultrasonicated for 30 min. Then, the colloidal solution was coated on the indium-doped tin oxide (ITO) surface (2.3 cm × 4 cm) using the drop coating method, and dried at 150°C for 30 min. The experiments were performed in a standard three-electrode system (the MIL-53(Fe)-coated ITO as a working electrode, Pt mesh as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode) in 0.1 M Na₂SO₄ solution.

To detect the reactive oxidants possibly generated by the photocatalytic reactions of MIL-53(Fe), some experiments were performed in aqueous suspension containing MIL-53(Fe) and a spin trapping agent (DMPO for the electron paramagnetic resonance (EPR) analysis), or a probe compound (XTT) for superoxide radical anion (O₂⁻). Aqueous suspension of MIL-53(Fe) (0.5 g/L, DMPO (10 mM), or XTT (0.1 mM) in the photo-reactor was illuminated by visible light (100 mW/cm²). Samples were collected from the photochemical reactor, and transferred into a quartz flat cell for the EPR analysis. The signals were scanned by EPR spectrometry (JES-X310, Jeol) under the following conditions: microwave frequency at 9.42 GHz, microwave power at 1.00 mW, modulation frequency at 100 kHz, and modulation amplitude at 2.0G. For the XTT analysis, samples were filtered using a 0.45 μm PTFE syringe filter (Advantec), and the absorbance was measured by UV/visible spectrophotometry (Lambda 465, PerkinElmer) at 470 nm, resulting in a strong visible-light absorption band at 470 nm [58].

3. Results and Discussion

3.1. Characterization of MIL-53(Fe)

The XRD patterns of the synthesized MIL-53(Fe) agreed well with the simulation (Fig. 1(a)), and were also consistent with those reported previously [52, 54]. In the SEM imagery, MIL-53(Fe) formed lozenge-shaped particles of approximate length 4 μm (Fig. 1(b)). The EDS elemental maps showed that carbon (C), oxygen (O), and iron (Fe) were uniformly dispersed on the particle surface with the composition of 63.11, 30.98, and 5.91 wt.%, respectively. In the FT-IR spectrum, characteristic peaks appeared at 3,300, 1,706, 1,580, 1,450, 748, 538 cm⁻¹ (Fig. 1(c)) which are assigned to O-H and C=O bonds in the carboxylic acid group, C=C and C-H bonds in the benzene ring, and the Fe-O bond, respectively [55, 59]. The N₂ adsorption-desorption isotherm showed that MIL-53(Fe) displays the unrestricted monolayer-multilayer adsorption characteristic (type II) (Fig. 1(d)). The BET specific surface area, total pore volume, and average pore diameter were calculated to be 1,696.1 m²/g, 2.000 cm³/g, and 6.397 nm, respectively.

The diffuse reflectance spectrum showed that MIL-53(Fe) has broad absorbance in the visible light range (Fig. 1(e)). The Kubelka-Munk function (Eq. (1)) was used to determine the band gap energy of MIL-53(Fe) [60]:

\[
F(R) = \frac{(1 - R)^2}{2R}
\]

where, R is the relative reflectance ratio of the sample to the standard BaSO₄. The plot of \(F(R)E^{1/2}\) versus E (light energy) calculated the bandgap energy as 2.76 eV (refer to the inset of Fig. 1e), which was consistent with the reported values [53]. The Mott-Schottky measurements were performed to determine the band position of MIL-53(Fe) (Fig. 1(f)). The flat-band potential of MIL-53(Fe) measured at 68,100 Hz was determined to be -0.61 V vs. SCE (equivalent to -0.37 VNa). The flat-band potential was 0.1 V higher than the conduction band (CB) potential for MIL-53(Fe) [55], which calculates the CB potential of MIL-53(Fe) as -0.47 VNa. The valence band of MIL-53(Fe) was determined to be +2.29 VNa.
The XPS survey spectrum revealed that MIL-53(Fe) was composed of C, O, and Fe elements (Fig. 2(a)). The XPS C 1s spectrum exhibited three peaks at the binding energies of 284.5, 285.8, and 288.5 eV, which indicate C=C and C-C bonds in the benzene ring, and C-O bonds in the carboxylic acid group, respectively (Fig. 2(b)) [55, 61]. The O 1s spectrum was deconvoluted into two peaks at 531.5 and 533.2 eV, indicating C-O bonds in the carboxylic acid group and Fe-O bonds, respectively (Fig. 2(c)) [55, 61]. In the Fe 2p spectrum, two peaks assigned to Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) appeared at 711.3 and 725.4 eV, respectively (Fig. 2(d)). In the middle of the two peaks (at 715.8 eV), an additional peak associated with shake-up lines for metal transitions was detected [61, 62].

### 3.2. Photocatalytic Removal of Organics by MIL-53(Fe)

The photocatalytic activity of MIL-53(Fe) was evaluated for the removal of gaseous toluene under visible light illumination (Fig. 3(a)). Toluene was removed by 26% for 6 h via adsorption under dark conditions. Under illumination, the toluene removal was significantly accelerated due to the photocatalytic degradation (66% removal for 6 h). The removal process of toluene followed pseudo
first-order kinetics under both dark and illumination conditions (refer to the inset of Fig. 3(a)), where the observed rate constants were calculated as 0.0009 and 0.0039 min\(^{-1}\), respectively. In addition, the removal of gaseous acetaldehyde by MIL-53(Fe) was examined under dark and illumination conditions (Fig. S2 in the SD). Compared to toluene, acetaldehyde was removed to a greater extent by both adsorption and photocatalytic degradation, due to the lower molecular weight [63].

Similar MOF materials (MIL-53(X)) were synthesized using different metal precursors, i.e., copper, nickel, cobalt, and iron (X = Cu, Ni, Co), and their performance for the removal of toluene was compared to that of MIL-53(Fe). The pseudo first-order rate constants for the toluene removal under dark and illumination conditions are presented for each material (Fig. 3(b), refer to Fig. S3 of the SD for the time-dependent removal of toluene). Among the four materials, MIL-53(Fe) exhibited the greatest photocatalytic activity. While MIL-53(Cu) demonstrated greater adsorption capacity of toluene compared to MIL-53(Fe) (the removal under dark conditions), it did not show much photocatalytic activity.

3.3. Effects of Temperature, Atmospheric Condition, and Humidity

The effects of temperature, atmospheric condition, and relative humidity (RH) on the removal of gaseous toluene by the illuminated MIL-53(Fe) were examined; the pseudo first-order rate constants for the toluene removal (bars) and the percent removals after 6 h treatment (red cycles) are presented for varied conditions (Fig. 4).

Increasing temperature inhibited toluene removal by the illuminated MIL-53(Fe) (Fig. 4(a)). With raising temperature from 20 to 50°C, the observed removal rate constant and the percent removal decreased by 65.2 and 52.6%, respectively. This result can be explained by the temperature-dependent adsorption capacity of MIL-53(Fe). At higher temperature, the toluene adsorption was lower (Fig. S4(a) of the SD), possibly due to the structural changes of MIL-53(Fe); the dehydration with elevating temperature led to the contraction of pores [52].

The anoxic condition significantly inhibited the removal of toluene by the illuminated MIL-53(Fe) (compare to the toluene removal under air and O\(_2\) conditions) (Fig. 4(b)). The toluene removal rate under N\(_2\) condition (0.011 min\(^{-1}\)) was approximately three-fold lower than those under air and O\(_2\) conditions. The percent removal of toluene after 6 h under N\(_2\) condition was 34.5%, which was approximately half of those under air and O\(_2\) conditions, of 64-67%. The removal of toluene in dark was also lower under N\(_2\) condition (Fig. S4(b) of the SD), suggesting that the lesser adsorption of toluene suppressed the subsequent photocatalytic degradation. The lesser adsorption capacity of toluene under N\(_2\) condition may be attributed to the selective binding of N\(_2\) onto iron [64, 65], which limits the competitive adsorption of toluene.

Increasing relative humidity inhibited the removal of toluene (Fig. 4(c)). When relative humidity increased from 10% to 80%, the observed removal rate constant and the percent removal decreased by 33.3% and 20.2%, respectively. Notably, a different trend was observed for the toluene removal under dark conditions, where the adsorption of toluene increased with increasing relative humidity from 10% to 50%, then rather decreased at 80% relative humidity (Fig. S4(c) of the SD). The increased adsorption of toluene in the humidity range of 10-50% may be a transient phenomenon due to the enlargement of pores by the hydration of MIL-53(Fe) [66]. The exposure to water led to the structural destruction of MIL-53(Fe) (Fig. S5 of the SD), which is believed to be responsible for the decreasing photocatalytic activity (Fig. 4(c)) and the lower
adsorption efficiency at 80% relative humidity (Fig. S4(c) in the SD). The characteristic XRD patterns of MIL-53(Fe) were distorted by the treatments in 80% relative humidity air, and in water (Fig. S5(a) of the SD). The peaks for released terephthalic acid were in the HPLC spectrum of the water in which MIL-53(Fe) has been suspended (Fig. S5(b) of the SD). The SEM images successfully visualized the water-induced destruction of MIL-53(Fe) (Figs. S5(c)-(e) of the SD).

3.4. Reusability of MIL-53(Fe)
To test the reusability of MIL-53(Fe), the toluene removal by MIL-53(Fe) was examined for five repeated runs under dark and illuminated conditions (Fig. 5). The removal and photochemical reactions were conducted for 6 h for each run (Fig. 5). Under dark conditions, the toluene adsorption capacity of MIL-53(Fe) was kept constant for the repeated runs (Fig. 5(a)). Even though a slight activity decrease was observed, the photocatalytic activity of MIL-53(Fe) for toluene removal during the repeated use was sustained (Fig. 5(b)).

3.5. Photocatalytic Viral Inactivation by MIL-53(Fe)
The photocatalytic inactivation of air-suspended φX 174 by MIL-53(Fe) was examined under visible light illumination (Fig. 6(a)). Under dark conditions, the inactivation of φX 174 was negligible. The visible light illumination without MIL-53(Fe) resulted in 1.6 log inactivation of φX 174 in 1 h possibly due to the thermal effect; the temperature increased to 30°C by 1 h illumination, and the control experiment confirmed that the temperature elevation to 30°C led to more than 1 log inactivation (data not shown). The illuminated MIL-53(Fe) inactivated φX 174 by 2.9 log in 1 h, indicating that the photocatalytic reactions contribute to the viral inactivation. The inactivation of φX 174 by the illum-
nated MIL-53(Fe) was examined under 80% relative humidity and N₂ conditions; the average inactivation rate (log inactivation/min) and the log inactivation degree in 1 h are presented (Fig. 6(b)). Under 80% relative humidity and N₂ conditions, the inactivation of ΦX 174 was suppressed, compared to the ambient condition. This observation is consistent with the effects of relative humidity and nitrogen on the toluene removal (Figs. 4(a) and 4(b)), suggesting that similar photocatalytic mechanisms may be responsible for both the toluene removal and viral inactivation.

### 3.6. Photocatalytic Mechanisms

MIL-53(Fe) is composed of iron-oxo clusters that are linked together by organic ligands (terephthalic acid). The photocatalytic activity of MIL-53(Fe) is known to mainly result from the excitation of iron-oxo clusters [53, 67]. The pathways for the generation of reactive oxidants by the illuminated MIL-53(Fe) can be postulated as follows. Upon visible light illumination, fast charge separation occurs, generating CB electrons and VB holes [53]. The photo-generation of charge carriers was evidenced by PL and transient photocurrent measurements (Figs. S7(a) and S7(b) of the SD); a broad PL peak appeared at around 442 nm, which corresponds to the bandgap energy of MIL-53(Fe) (2.76 eV), and the discontinuous light illumination successfully produced responsive alternating photocurrent. The hole oxidation is believed to be mainly responsible for the degradation of toluene, and the inactivation of ΦX 174. The oxidation power of VB holes of photoexcited MIL-53(Fe) (+2.29 VNHE, Fig. 1(f)) is high enough to destroy toluene; the oxidation potential of toluene is known to be +1.733 VNHE [68]. The generation of hydroxyl radical (·OH) by the hole oxidation of water is thermodynamically unfavorable ($E^\circ[\cdotOH/H_2O] = +2.80$ VNHE, [69]); the EPR analysis failed to detect the DMPO-OH spin adduct (Fig. S6(a) of the SD).

Meanwhile, the CB electrons of MIL-53(Fe) can be trapped by oxygen to yield O₂⁻ ($E^\circ[O_2/O_2^-] = -0.33$ VNHE, [70]); note that the CB level of MIL-53(Fe) was -0.47 VNHE (Fig. 1(f)). Such electron-trapping prevents the electron-hole recombination, enhancing the hole oxidation of toluene. However, in the spectrophotometric measurement using XTT (Fig. S6(b) of the SD), the signal of O₂⁻ was not detected, which rules out the possibility of O₂⁻ generation in this system.

### 4. Conclusions

MIL-53(Fe) synthesized by a simple hydrothermal method exhibited good crystallinity, and high surface area and porosity as well as photocatalytic properties, as confirmed by various characterization methods. Under visible light-illumination, MIL-53(Fe) led to toluene removal (by both adsorption and photocatalytic oxidation) and ΦX 174 inactivation in air. The adsorptive and photocatalytic efficacies of MIL-53(Fe) for the control of contaminants were found to be influenced by humidity, temperature, and the presence of N₂. These effects are assumed to result from the structural distortion of MIL-53(Fe), depending on the conditions. The oxidation by photo-generated holes appears to be the primary pathway for toluene degradation and the inactivation of ΦX 174 by illuminated MIL-53(Fe). No evidence was found for the generation of ·OH or O₂⁻. The observations in this study demonstrate that MIL-53(Fe) can be used to improve indoor air quality by controlling VOCs and pathogenic microorganisms. Potential applications of MIL-53(Fe) include photocatalytic air purification systems, and different antimicrobial coatings that are applicable under indoor lighting conditions.

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