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Integrated adsorption and visible-light photodegradation of aqueous clofibric acid and carbamazepine by a Fe-based metal-organic framework

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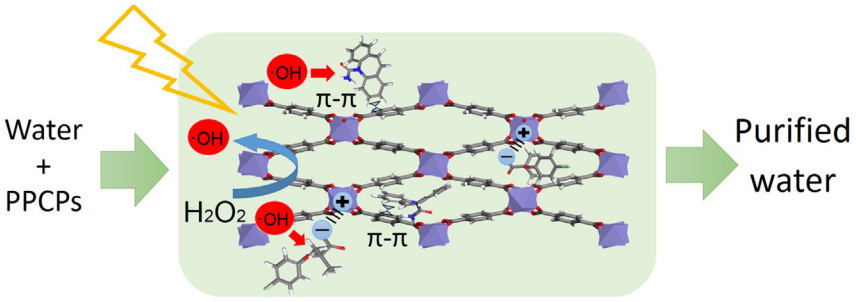
HIGHLIGHTS

- MIL-53(Fe) is successfully synthesized as a novel photocatalytic adsorbent.
- MIL-53(Fe) shows high adsorption capacities for CA and CBZ.
- Photodegradation efficiencies for CA and CBZ reach 90% in MIL-53(Fe)/H_2O_2/vis system.
- MIL-53(Fe) can be recycled and applied in real wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient materials for removing pharmaceuticals from water has been a matter of great concern. As a new class of porous materials, metal-organic frameworks (MOFs) have attracted considerable attention in the field of environmental remediation. In this article, a photocatalytic adsorbent MIL-53(Fe) was successfully prepared by solvothermal method and used for the removal of two typical pharmaceuticals clofibric acid (CA) and carbamazepine (CBZ) from water. MIL-53(Fe) exhibited good adsorption performance and the maximum adsorption capacities of CA and CBZ are about 0.80 mmol/g and 0.57 mmol/g, respectively. The adsorption mechanisms of CA and CBZ are mainly due to electrostatic interaction and π-π interaction, respectively. Further, MIL-53(Fe) exhibited high photocatalytic activity and stability under visible light. The photocatalytic efficiency could be improved significantly with the addition of a small amount of H_2O_2, and the corresponding photodegradation efficiencies for CA and CBZ both reached up to 90%, which are higher than those of Fe(II)/H_2O_2 and TiO_2 under visible light. The photocatalytic performance was strongly dependent on the solution pH. The Fenton-like reaction, charge carriers directly generated in the photo-excited MIL-53(Fe) and the synergistic effect of H_2O_2 were the main mechanisms. The formation of humic acids-like and fulvic acids-like organic matter in the degradation process was detected by 3D EMMs. MIL-53(Fe) also revealed excellent performance for the removal of CA and CBZ from real municipal wastewater and river water. Therefore, MIL-53(Fe) may be used as a promising photocatalytic adsorbent for wastewater purification.

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1. Introduction

Due to the increasing population and elevated living standards, the consumption of pharmaceuticals and personal care products (PPCPs) has continued to grow over the last few decades [1,2]. PPCPs residues from industry or urban regions can enter into the aquatic ecosystem by wastewater treatments, thus various PPCPs has already been detected in surface water and ground water, which becomes a serious environmental issue because of their toxicity, solubility and pseudo persistence [3,4]. Clofibric acid (CA) and carbamazepine (CBZ) (the structures are shown in Table S1) are considered as typical and representative PPCPs with high environmental risk, which are frequently found in aquatic ecosystem [5,6]. Clofibric acid and carbamazepine are very common drugs used to treat high blood lipids and epilepsy, respectively. However, their negative effect on metabolism, reproduction, embryonic development and behavior of aquatic organisms and potential risk for human health have been reported [7–10]. Therefore, developing effective and economical techniques to remove these emerging pollutants from wastewater to prevent affecting the aquatic environment is of vital concern to researchers.

Various technologies have been developed to eliminate PPCPs, such as microbial degradation, adsorption, photocatalysis, electrolysis, and membranes separation [11]. Among them, integrated adsorption and degradation are regarded as one of the most promising methods for the removal of organic pollutants [12]. The main challenge of developing integrated adsorption and degradation method is the selection of suitable material. However, to date traditional integrated photocatalytic adsorbents still suffers from some technical barriers, such as low adsorption capacity for hydrophobic pollutants, the inefficient exploitation of visible light (>420 nm), and difficult post-recovery of the catalyst, limiting their real applications [13]. Recently, Metal-organic frameworks (MOFs), consisting of poly-functional organic ligands and metal-oxo clusters, have received more and more attention as a new class of porous materials. Due to their unique properties, MOFs have shown potential applications in gas capture and storage, heterogeneous catalysis, adsorption and separation, sensing, and drug delivery [14–17]. Of note, in most cases, MOF-based adsorbents display shortcomings due to their micropores (less than 2 nm), which prevents the access of molecules to their internal channels [18]. Meanwhile, they are usually instable during photochemical operations in aqueous solution. In addition, when applied for the aqueous environment, the environmental friendliness and biocompatibility of MOFs should also be considered. Therefore, developing suitable MOFs as a novel photocatalytic adsorbent for efficient removal of aqueous pollutants is still a great challenge.

The MIL series of MOFs, pioneered by Férey and his co-workers, has exhibited attractive properties with outstanding stability and large pores [19]. Among them, MIL-53 can be synthesized cheaply from terephthalic acid (produced in huge amount for polyesters) and common metal salts. Moreover, MIL-53 is very interesting because of its breathing effect, and has been studied in adsorption [20,21]. In our previous study on photosensitivity of MOFs, we also found under visible light irradiation, MIL-53 system can produce reactive oxygen species including $^1O_2$, $O_2^{\cdot-}$ and ·OH, which provides the possibility for photocatalytic applications [22]. However, some of MIL-53 contain toxic chromium, which may cause potential pollution problems. Therefore, we focused on the synthesis of less-toxic MIL-53(Fe), which has been used as a new photocatalyst with the ability to degrade organic matter. Zhang et al. obtained magnetic MIL-53(Fe) for the degradation of Rhodamine B under visible light irradiation [23]. Interestingly, in that report, with the assistance of H_2O_2 remarkable enhancement of the photocatalytic efficiency of MIL-53(Fe) was observed, which may be due to the Fenton-like reaction between Fe and H_2O_2. Other reports found MIL-53(Fe) was able to activate H_2O_2 for potential applications in bio-sensing and environmental photocatalysis [24,25]. Despite these outstanding characteristics, research on the applications of MIL-53(Fe) for the removal of emerging pollutants in aqueous system is very limited. To the best of our knowledge, there has been no report on the applications of MIL-53(Fe) as an integrated photocatalytic adsorbent for the removal of pollutants in water.

Inspired by this and taking the above considerations, we synthesized Fe-based MOFs MIL-53(Fe) as an integrated photocatalytic adsorbent. We quantitatively investigated the adsorption and visible-light-driven photodegradation of two representative PPCPs CA and CBZ by MIL-53(Fe). The adsorption kinetics, isotherms and the effect of pH were subsequently studied. A possible adsorption mechanism was also suggested. Further, the photocatalytic performance, mechanism, recyclability and preliminary application on the real wastewater treatment of this MOFs were investigated.

2. Materials and methods

2.1. Materials

All solvents and reagents were obtained from commercial sources and used as supplied without further purification. Terephthalic acid and dimethylformamide (DMF) were purchased from Sigma-Aldrich (USA) and Peking Reagent (China), respectively. $FeCl_3{\cdot}6H_2O$ of analytical grade were offered by Sinopharm (China). Clofibric acid and carbamazepine were obtained from Strem Chemicals (USA). *p*-chlorobenzoic acid (*p*CBA) was purchased from J&K Scientific (China). Activated carbon was purchased from Jingke Activated Carbon Co. (China). All solutions were prepared with ultrapure water (resistivity >18 MU) prepared with a Mill-Q system (Milli-pore, Billerica, USA).

2.2. Preparation of MOFs

Solvothermal method was referenced from previous literature [26,27]. MIL-53(Fe) was solvothermally synthesized (autogenous pressure) from a mixture of $FeCl_3{\cdot}6H_2O$, terephthalic acid and DMF in the certain molar ratio. Reactants were introduced in a Teflon-lined steel autoclave, and the temperature was set at 393 K for 3 days. Products were washed by methanol for 3 times to remove organic residues. Then they were dried at 150 °C and ground into powder.

2.3. Characterization of MOFs

The Powder X-ray Diffraction (PXRD) patterns of MOFs were collected on a D/MAX-RB (Rigaku, Japan) X-ray diffractometer equipped with a Cu-K_α radiation source. The functionality of MOFs was confirmed by using samples pelletized with KBr and analyzing the FT-IR spectra recorded on a Thermo Nicolet Nexus 870 FT-IR spectrometer system (Thermo Fisher, USA). Scanning Electron Microscope (SEM) (Zeiss, Germany) operating at 10 kV with magnification of 5000–30,000 was used to obtain SEM photographs of the samples. The nitrogen adsorptions were conducted at −196 °C on Autosorb-1MP (Quantachrome, USA).

2.4. Adsorption experiments

5 mg of dried MIL-53(Fe) powder was added into the flasks containing 50 mL of 40 mg/L CA or CBZ solution and placed in an orbital shaker at 150 rpm and 25 °C for certain time. The adsorption isotherm experiments were done with the initial concentrations at the range of 5 –100 mg/L. In the experiments about the effect