



Efficient degradation of high concentration azo-dye wastewater by heterogeneous Fenton process with iron-based metal-organic framework

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ABSTRACT

A novel iron-based metal-organic framework, possessing high surface area and good catalytic activity, was proposed as a heterogeneous Fenton catalyst for degrading high concentration methylene blue ($C_{MB} = 500$ ppm). The morphology and physicochemical properties of prepared catalysts were characterized by SEM, XRD, XPS, FT-IR, Raman spectra, etc. The obtained results showed that MOF-based catalysts MIL-100(Fe) and $Fe^{II}@MIL-100(Fe)$ possess high surface area of 1646 and 1228 $m^2 g^{-1}$, respectively. The MB removal through adsorption by MIL-100(Fe) and $Fe^{II}@MIL-100(Fe)$ is respectively 27 and 6% in 30 min, due to the electrostatic interaction between negative (or positive) adsorbent and positive pollutant. However, $Fe^{II}@MIL-100(Fe)$ exhibited highest Fenton catalytic ability compared to MIL-100(Fe) and Fe_2O_3 catalysts. The catalytic activity of each active site, evaluated by the turn over frequency (TOF) value, varied in the order of $Fe^{II}@MIL-100(Fe) > MIL-100(Fe) > Fe_2O_3$. The main role of determining the decomposition efficiency, i.e., hydroxyl radical ($\cdot OH$) generation, surface redox properties and surface reaction, was greatly enhanced by the synergistic effect between Fe^{II} and Fe^{III} in $Fe^{II}@MIL-100(Fe)$. Moreover, iron-based metal-organic framework retained the catalytic performance in a wide pH range of 3–8, and had a relative low iron leaching even in acidic condition.

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1. Introduction

Nowadays, increasing global attention of water pollution has become a serious issue facing humanity in the current situation, which promoting increasing demand for clean water environment. Heterogeneous Fenton and related reactions encompass the reactions of hydrogen peroxide with solid iron-based catalysts to form powerful hydroxyl radicals ($\cdot OH$) to remove organic pollutants. Importantly, the heterogeneous Fenton catalysts have already overcome the critical drawbacks of homogeneous Fenton reaction, i.e., rigorous operating pH range and the formation of iron sludge in the coagulation step, and been widely explored in wastewater treatment [1–3]. Additionally, in order to improve the activity of traditional Fenton catalysts [4,5], such as α -FeOOH, Fe_2O_3 , Fe_3O_4 , transitional metal substitutions (Fe, Cr, Mn, Co, Nb and Ni) can be added as secondary active sites for both improving activation H_2O_2 and enhancing stability [2,6]. Meanwhile, the structure and the morphology of catalysts can be also modified for

enhancing catalytic activity [7]. Another way is iron immobilization, which immobilized the active components iron-containing substances on carriers [8,9] like activated carbon (AC), mesoporous silica (SBA-15), mesoporous molecular sieves, and so on. Although lot of efforts similar with what we mentioned above have already made to improve the catalytic activity of heterogeneous Fenton catalysts, to some extent, they still have the problem of poor H_2O_2 utilization and catalytic activity [10,11]. Recently, iron complex got considerable attention for its application in Fenton-like systems, for example, Collins [12] designed a tetraamido macro cycle ligand Fe^{III} -TAML, which can activate hydrogen peroxide with high efficiency to rapidly decompose the persistent and nonbiodegradable sertraline from pH 7.25 to 10.25 [13]. But most iron complexes, i.e., Fe^{III} -TAML, are always water-soluble and unable to avoid the limitation of homogeneous Fenton reaction. Therefore, design and fabrication of effective heterogeneous catalysts for H_2O_2 activation in broader working pH range is the key issue to realize the desirable activity and long-term stability.

Metal-organic frameworks (MOFs) are an intriguing type of inorganic-organic hybrid porous crystalline materials, which possess a three-dimensional well defined structure and are constructed by metal-containing nodes connected by various organic bridges [14,15]. Owing to its characteristic of high surface area,

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large pore volume and tunable topology, MOF-based materials have been exploited diverse applications in separation, gas and vapor storage, catalysis, drug delivery, optical switching device and so on [16–20]. Besides to this, it is very interesting to find that iron-based MOF system possesses not only active sites (Fe^{III}) for heterogeneous Fenton reaction but also have the advantages of iron complex in homogeneous Fenton process due to its attractive properties of organometallic coordination. That is to say, MOFs-based samples can be potentially devoted as Fenton catalysts for removing organic contaminants. For example, MIL-53(Fe) was used to activate H_2O_2 for decomposing methylene blue dye with the help of visible light [21]. MOF1 (organotin-polymer $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6]$) was investigated as photo-Fenton catalyst with UV-light for discoloration of organic dyes [22]. However, pure MOF catalyst possesses only Fe^{III} sites with weak Fenton activity and contains low iron concentration, which restricts Fenton oxidation catalytic activity. That is why supplementary technique, i.e., UV-light, visible light, usually applied for enhancing the degradation efficiency with pure MOFs. So it is still essential to extend the fabrication of novel MOF catalysts by adding iron-based active sites with high Fenton catalytic ability and exploit its corresponding high catalytic performance.

Herein, we demonstrated the efficient Fenton catalytic activity of MIL-100(Fe), with chemical formula $\text{Fe}_3^{\text{(III)}}\text{O}(\text{H}_2\text{O})_2(\text{F})\{\text{C}_6\text{H}_3(\text{CO}_2)_3\}_2 \cdot n\text{H}_2\text{O}$ ($n \sim 14.5$) [23], for degradation high concentration azo-dye (500 ppm) wastewater. Apart from this, since the large surface area and porosity of MIL-100(Fe), it is very useful to fabricate novel MOF-based Fenton catalyst using MIL-100(Fe) as support to enlarge iron concentration and modify the surface charge in Fenton system. Therefore, novel $\text{Fe}^{\text{II}}@\text{MIL}-100(\text{Fe})$ heterogeneous Fenton catalyst was fabricated to enhance the catalytic performance by synergic effect between Fe^{II} and Fe^{III} active sites in this work. Methylene blue (MB) was selected as a model target contaminate for assessing the catalytic activity because it is respective of wide range of azo-dye modern and low biodegradability in water systems. Moreover, the activation mechanism of $\text{Fe}^{\text{II}}@\text{MIL}-100(\text{Fe})$ was investigated and proposed on the basis of experiment results of characterization of surface properties, detection of $\cdot\text{OH}$, and revelation of redox properties.

2. Experimental

2.1. Preparation of samples

MIL-100(Fe) was synthesized according to literature reported by Yoon et al. [24]. Typically, iron powder (532 mg), H_3BTC (1337 mg), hydrofluoric acid (40 wt%, 849 μL), nitric acid (65 wt%, 395 μL), and deionized water (47 mL) was mixed in a Teflon autoclave and held at 150 °C for 24 h. The as-synthesized MIL-100(Fe) was further purified in two steps using boiling water (stirring 1 g of MIL-100(Fe) in 350 mL of water at 80 °C for 5 h) to remove residual unreacted ions and hot ethanol (stirring 1 g of MIL-100(Fe) in 200 mL of ethanol at 60 °C for 3 h) until no detection of colored impurities in the mother liquor solution. The light-orange solid product was finally dried at 70 °C under vacuum overnight and then stored in a desiccator.

$\text{Fe}^{\text{II}}@\text{MIL}-100(\text{Fe})$ was synthesized by modified hydrothermal reaction according to the previous literature [25]. Briefly, the mixture of prepared MIL-100(Fe) (0.1 g), deionized water (13 mL), polyvinylpyrrolidone (PVP, 600 mg), FeCl_3 (26 mg) and KI (380 mg) were well stirred and then transferred to a 23 mL Teflon-lined stainless-steel autoclave, then heated at 180 °C for 1.5 h. The brown solid was recovered by centrifugation at 10 000 rpm for 5 min, and then washed with ethanol and deionized water for several times. Finally the obtained products were blow-dried with N_2 .

$\alpha\text{-Fe}_2\text{O}_3$ was prepared by a typical hydrothermal process [26]. Typically, FeCl_3 (163 mg) was dissolved into 50 mL deionized water

to form a transparent solution. NaAc (248 mg) was added to the above solution for modifying and improving the size and morphology of catalyst. Then the mixture was transferred and sealed into a 75 mL Teflon-lined autoclave, and heated at 180 °C for 24 h. The precipitate was collected by centrifugation at 10 000 rpm for 5 min, and then washed with deionized water and ethanol for several times, finally dried at 70 °C under vacuum overnight.

2.2. Characterization methods

Power X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-Ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.540562 \text{ \AA}$, 40 kV, 40 mA) as the X-ray source at a scanning rate of 3°/min in the range from 2.5° to 60°. The scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. N_2 adsorption-desorption analysis was measured on a Micromeritics TriStar 3000 instrument, Brunauer–Emmet–Teller (BET) special surface area was estimated from the relative pressure range from 0.05 to 0.20, pore volumes were determined using the adsorbed volume at a relative pressure of 0.99033. Fourier transform infrared spectra (FT-IR) were examined in the region from 400 to 2000 cm^{-1} at room temperature using a Nicolet 6700 spectroscopy on KBr pellets. Raman spectroscopy was performed by a Renishaw Raman micro spectrometer using an Ar^+ ion laser (514.5 nm line) as the excitation source. The X-ray photoelectron spectroscopy was carried out on a Kratos ASIS-HS X-ray photoelectron spectroscope fitted with a standard and monochromatic source ($\text{Al K}\alpha$) operated at 150 W (15 kV, 10 mA). The iron content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PE OPTIMA 2100DV). Zeta potentials of the catalysts in deionized water were measured on a zeta potential analyzer (Zetasizer 2000, Malvern, UK). H_2 -TPR measurements were performed using AutoChem II 2920 instrument (Micromeritics). Prior to the TPR run, the fresh sample was pre-treated in situ for 2 h at 150 °C in air flow. After cooling and a step of purge of the lines in Ar flow, an H_2 : Ar mixture (H_2 : Ar volume ratio of 10% and total flow of 50 mL min^{-1}) was sent through the sample while increasing the temperature up to 800 °C with a rate of 10 °C min^{-1} .

2.3. Experimental procedure

All the catalysts would be dried at 150 °C for 12 h before each use. All degradation experiments of MB were carried out in a beaker (100 mL) at room temperature. The initial concentration of MB was 500 mg L^{-1} , and the total volume of reaction solution was 50 mL. The reaction suspension was prepared by adding the required amount of catalyst (1 g L^{-1}) into 50 mL solution that had been adjusted to the desired pH value by 0.1 M H_2SO_4 or 0.1 M NaOH. A known concentration (40 mM) of H_2O_2 was added to the solution to initiate the reaction after adsorption for 45 min. Samples were taken at set intervals using a 5 mL syringe, centrifuged at 100 000 rpm for 5 min, then filtered the supernatant immediately through a 0.22 μm filter film, and quenched with excess isopropyl. In order to test the adsorption of MB behave during the Fenton reaction, the desorption studies were conducted in the thermostated shaker using 0.5% HCl (v/v) ethanol solution as eluent for one night.

2.4. Sample analysis

The concentration of MB during the reaction was analyzed by a UV-vis spectrophotometer (Agilent, 8453) with the maximum absorbance wavelength for MB at 665 nm. ESR spectra were obtained on a Bruker EMX X^{plus}-10/12 with Microwave Bridge (microwave frequency, 9.853 GHz; microwave power, 20 mW; modulation amplitude, 1 Gauss; modulation frequency,

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