

Selective degradation of organic dyes by a resin modified Fe-based metal-organic framework under visible light irradiation



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ABSTRACT

Metal organic frameworks (MOFs), a new class of porous crystalline materials have attracted attention because of potential applications in environmental remediation. In this work, an Fe-based MOF, FeBTC (BTC = 1,3,5-tricarboxylic acid), was successfully modified with Amberlite IRA-200 resin to yield a novel heterogeneous photocatalyst, A@FeBTC. The modification resulted in higher photocatalytic activity than FeBTC under the same conditions. After 60 min of visible light illumination ($\lambda \geq 420$ nm) 99% of rhodamine B was degraded. The modification lowers the zeta potential, enhancing charge-based selective adsorption and subsequent photocatalytic degradation of cationic dye pollutants. The composite also improved catalyst stability and recyclability by significantly reducing loss of iron leaching. Photoluminescence studies show that introduction of the resin reduces the recombination rate of photo-generated charge carriers thereby improving the photocatalytic activity of the composite. Finally, a plausible photocatalytic reaction mechanism is proposed.

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1. Introduction

Contamination of water bodies by organic pollutants is a major concern [1–3]. Photocatalytic techniques, based on metal-oxide semiconductor photocatalysts, such as TiO₂, efficiently degrade organic pollutants [4–11], but require ultraviolet light for activation. Among the photocatalysts developed to utilize visible light, metal organic frameworks (MOFs), composed of a metal or metal oxide cluster coordinated to an organic ligand, have attracted considerable attention. Compared with the traditional metal oxide photocatalysts, the flexible topological structure, high surface area and easily tunable band gap make MOFs a promising class of photocatalyst for degrading organic pollutants [12–17].

Due to iron's low toxicity and high biocompatibility, iron-based MOFs are particularly desirable for environmental applications [17,18]. Various iron (III)-based MOFs such as Basolite F300, MIL-

100(Fe) and MIL-88B (Fe) are able to efficiently degrade pollutants under visible light irradiation [1]. However, their practical application for environmental remediation is still limited by several drawbacks. Firstly, structural stability of MOFs must be improved because low stability under irradiation can alter photophysical properties, as reported by Silva et al. [19]. Secondly, Low photo-efficiency caused by rapid charge recombination must be addressed for MOFs to be practical. Selective degradation of a target pollutant would also be a highly desirable characteristic [20]. Hence, it is important to develop MOF photocatalysts displaying selective degradation, improved structural stability and a lower recombination rate of photogenerated charge carriers.

Selective adsorption is a powerful technique for imparting selectivity to photocatalytic degradation. For example, the surface of non-selective photocatalysts such as TiO₂ can be modified by fluorine or alkali to enhance selective adsorption [20]. BiOI displays selective adsorption of azo dyes due to terminal oxygen atoms and results in highly selective photocatalytic degradation [21].

Due to their pore size and surface charge, MOFs are ideal for selective adsorption of dyes. Zhao et al. reported on the selectivity of positive MOFs towards anionic dyes of comparable size, clearly demonstrating the primary role of columbic interaction in MOF dye

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adsorption [22,23]. Cd^{II}/Zn^{II}-based MOFs also display selective photodegradation of dyes [24]. In these reports, the selectivity of MOFs is attributed to intrinsic properties, such as pore size and surface charge.

Recently, MOFs have been immobilized on supports such as fiber glass [25], silica [26] and graphene [27] to enhance stability and photocatalytic activity. Cationic exchange resins, which are economical, ecofriendly, stable and versatile [28,29], have been used to immobilize soluble metal catalysts [30] and a resin supported iron (II) 2,2'-bipyridyl (Fe(bpy)₂²⁺) based MOF has been reported [31]. However, the effect of resin on photoelectrochemical behavior and its role in enhancing photocatalytic efficiency were not discussed.

In this study, an Fe-containing-MOF, FeBTC (BTC = 1,3,5-benzene tricarboxylate) was grafted [32–36] to a macroreticular polystyrene-based cation exchange resin (Amberlite IRA-200) containing the strongly acidic sulfonyl group to give a composite photocatalyst, denoted as A@FeBTC. The goals of this study include: (1) Produce a resin-MOF interface that increases separation of the photogenerated charge carriers and improves photocatalytic efficiency. (2) Use resin sulfonyl groups to induce charge based selective adsorption and photocatalytic degradation. (3) Reduce iron leaching and improve MOF structure. Finally, a plausible mechanism for the selective adsorption and photodegradation of dyes is proposed.

2. Experimental section

2.1. Materials and reagents

Amberlite IRA-200 was obtained from Nankai University, China. 1,3,5-benzene tricarboxylic acid, iron powder (400 mesh), hydrofluoric acid (40%) and nitric acid (65%), Benzoquinone (C₆H₄O₂), sodium azide (NaN₃), ammonium oxalate (NH₄C₂O₄) and isopropyl alcohol (C₃H₈O) were purchased from Sigma-Aldrich. All other reagents were of analytical grade and deionized or doubly distilled water was used throughout the study. Aqueous solutions of HCl and NaOH were used to adjust pH. X-ray Powder Diffraction (XRD) patterns were obtained with a Bruker D8 advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered Cu K α irradiation ($\lambda = 0.15406$ nm). The data were recorded in the 2 θ range of 5–50°. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were

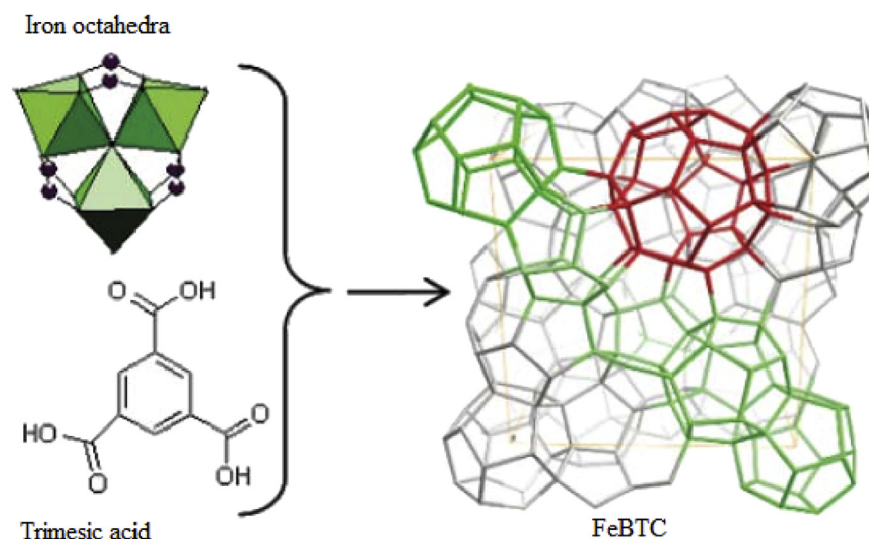
obtained using a UV–Vis spectrophotometer (Varian Cary 500) with BaSO₄ as the reflectance standard. Fourier transform-infrared (FT-IR) spectra were obtained on a Nicolet iS 50 Fourier transform infrared spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were made on a VG Multilab 2000 XPS system equipped with an Al X-ray source. Total organic carbon (TOC) was measured on an automated TOC/TN Analyzer (Analytikjena, Multi N/C 3000). Particle morphology was characterized using a scanning electron microscope (SEM, JEM-3010) and the zeta potential of A@FeBTC in aqueous solution was determined using a ZEN3690 (Malvern Instruments). Photoluminescence (PL) was recorded over the range 200–800 nm, using a F-4500 fluorescence spectrometer.

2.2. Preparation of composite photocatalyst

FeBTC was synthesized using the hydrothermal method as previously reported [37]; 1,3,5-benzene tricarboxylic acid (H₃BTC, 0.0134 mol) was added to a solution containing iron (0.02 mol), hydrofluoric acid (0.04 mol), nitric acid (0.012 mol) and water (5.54 mol). The reaction mixture was stirred at room temperature for 1 h and then transferred to a Teflon-lined pressure vessel at 433 K for 12 h. The suspension was filtered and FeBTC was washed with deionized water and dried at 373 K for 12 h. Before being grafted on FeBTC, the resin was rinsed with 1 M HCl and then 1 M NaOH repeatedly and washed with water until the effluent did not absorb in the UV region. To increase the surface area and improve adsorption, the resin was ground to a powder. The composite catalyst was prepared by stirring the powdered resin in an aqueous suspension of FeBTC for 24 h. The product was removed by filtration and air dried. FeBTC was composited with resin in 5 proportions (resin/FeBTC (wt %); 2%, 5%, 10%, 20%, 30%). The effect of the catalyst dosage was investigated by varying the amount of catalyst; 0.27 g/L, 0.33 g/L, 0.40 g/L, and 0.53 g/L.

2.3. Photoreactor and light source

The photocatalytic activity, under visible light, of each catalyst was examined by degrading organic dyes, primarily rhodamine B (RhB), in a 75 mL test tube at room temperature, open to air, at pH 7. The reaction was irradiated using a 450 W Xe lamp with a 420 nm cutoff filter. The distance between the light source and reaction vessel was fixed at 10 cm and 0.4 g/L photocatalyst was placed in



Scheme 1. Schematic representation of FeBTC structure [36].

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