Heterogeneous Catalytic Wet Persulfate Oxidation of Simulated Rhodamine-B Wastewater by Iron based Aliphatic Di-carboxylate MOFs

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Abstract: Metal Organic Frameworks were built from [Fe (µ-O) (COO)₆] clusters and aliphatic di-carboxylate ligands such as pimelic acid, suberic acid, azelaic acid and sebamic acid which are isomorphic to so called established MIL-88A(Fe) namely Fe-MIL-88a-Pima, Fe-MIL-88a-Suba, Fe-MIL-88a-Azla and Fe-MIL-88a-Seba have been synthesized separately and characterized using PXRD, FE-SEM, BET, FT-IR. The as-synthesized Fe-MOFs have been demonstrated as efficient heterogeneous catalysts for both fenton and photo-fenton wet persulfate oxidation of Rhodamine-B solution and factors affecting the oxidation process were examined. Optimal conditions were examined for degradation of Rhodamine-B and the isomorphic substitution of longer organic linker chains in the MIL-88a improved the degradation efficiency. Fe-MIL-88a-Seba exhibited 99.9% degradation efficiency in 250 min and displayed good recyclability over four cycles. Overall, this work successfully demonstrates not only the ability to perform isomorphic substitution of various different aliphatic dicarboxylate linkers within MOFs but also the effect of the linker length substitution on the resulting catalytic performance.

Keywords: Metal-Organic Frameworks, Rhodamine-B degradation, Advanced oxidation processes, Heterogenous catalysis

1 Introduction
Metal Organic Frameworks are porous crystalline materials which are formed by the co-ordination induced supra-molecular reaction of metal ions and organic ligands. [1-3] These smart materials attracted many researcher, due to its unprecedented specific surface areas, tunable porosities, high thermal stabilities, robust nanoscale cavities and unusual structural properties. The sensible choice of the organic ligand, metal-ion, reaction condition, metal-ligand ratio are the some crucial factors for the successful synthesis of functional MOFs for a specific application. [4-6]

Globally, environmental pollution is one of the essential issues existing which has gained attention all over the world. Talking about the water pollution, industrial wastes contributes 70% which is dumped directly into the water bodies amongst which textile dyes are considered as a major water pollutant because these dyes are carcinogenic, toxic and may affect the photosynthesis in water bodies. [7-9] Rhodamine B is highly water soluble cationic dye largely used as medicine (for animals) in staining of biological samples, in textile industry and in painting which is considered hazardous and cancer causing. In life threatening cases, it is responsible for respiratory diseases and kidney failure. [10] The removal of such dyes is vital which is carried out through several traditional and modern techniques. These techniques include coagulation, air stripping, and incineration process, filtration through membrane, adsorption on simulated carbon, electrochemical oxidation, wet oxidation, biological oxidation process and chemical oxidation techniques. [11-15] In this study, we synthesized some Fe-based MOFs based on aliphatic dicarboxylate linkers namely Fe-MIL-88a-Pima, Fe-MIL-88a-Suba, Fe-MIL-88a-Azla and Fe-MIL-88a-Seba to evaluate them as heterogeneous catalysts to activate persulfate for the degradation of Rhodamine B dye. The optimization of the factors affecting the dye degradation process such as pH, temperature, light, catalyst concentration etc. were carried out. A recyclability test was also performed to evaluate the long-term use of these synthesized Fe-MOFs to activate persulfate.

2 Experimental Section
2.1 Materials & Reagents
Ferric (III) Nitrate nonahydrate, pimelic acid, suberic acid, azelaic acid, sebamic acid, DMF, ethanol, Rhodamine B, Sodium Persulfate etc were acquired from sigma Aldrich. All chemical reagents were of analytical grade and directly utilized without any further refinement. During the experiment, deionized water was used to prepare all the aqueous solutions.

2.2 Catalyst Preparation
The Solvothermal method, a typical method for synthesizing Metal-Organic Frameworks was assimilated to synthesize Fe-MOFs that were further applied for the degradation of RhB. Fe-MOFs namely, Fe-MIL-88a-Pima, Fe-MIL-88a-Suba, Fe-MIL-88a-Azla and Fe-MIL-88a-Seba were synthesized according to the literature. [16, 17] In a typical solvothermal experiment, Ferric Nitrate Nonahydrate (1.0 eq) was dissolved in DMF (15ml), and simultaneously the respective organic linkers such as Pimelic acid, Suberic acid, Azelaic acid and Sebamic Acid were dissolved in another set of DMF solvent. Then, the two respective solutions were mixed and stirred for 10 minutes to obtain homogeneous suspension. After that the suspension was transferred into a 100 ml. Teflon-lined stainless steel autoclave that was sealed and heated at 110°C for 48-56 hours consecutively. Subsequently, the autoclave was cooled to room temperature in natural conditions. The obtained suspension was centrifuged and brown-red solids of the respective Fe-MOFs were separated from the suspension. These solid samples were washed with water and then with ethanol to activate the samples. Finally, solid samples were dried under vacuum at 60°C overnight. After cooling to room temperature, the solid catalysts were ground to the desired powders and used for further experiments.
2.3 Rhodamine B Oxidation Test using persulfate activated by Fe-MOFs

Catalytic degradation of Rhodamine B (RhB) was performed via batch type experiments at a constant temperature at 40°C (using a water bath) in 500 mL RBF that was stirred using a magnetic stir plate approximately at 400 rpm with samples removed at regular time intervals. In a typical experiment, 200 mg of the catalyst was used along with 250 mL of 25 mg/L dye solution of RhB and 50 mg of persulfate. For each sample, 2 mL of solution was removed using a 2 mL syringe and filtered through 0.22μm syringe filter and then a UV-Vis spectrum was obtained to determine the concentration of RhB in solution. All the experiments were performed in a dark environment as well as in sun-light for the fenton and photo-fenton reactions. During the reactions, the persulfate was added and the light source was turned on at the zero time point, with the MOF being added to the solution starting at the -30 min time point.

3 Results and Discussion
3.1 Catalysts Characterisation

All the four Fe-MOFs were characterized using Powder X-ray diffraction (PXRD), Thermal gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectrophotometer, N2 sorption measurements and FE-SEM. UV−vis spectroscopy measurements for the dye adsorption and degradation were also performed. The XRD patterns of all the Fe-MOFs i.e. MIL-88a-Fe-Pima, MIL-88a-Fe-Suba, MIL-88a-Fe-Azla, & MIL-88a-Fe-Seba respectively, were different but the strong peak position almost approached at 2θ = 8°, 10.5°, 13° respectively. The Fe-MOFs examined by IR-spectra shown in which revealed that a featured a broad adsorption feature between 3500-2700 cm⁻¹ caused by (OH) stretched from the water molecules in the complex and other bands such as the asymmetric stretch around 1600 cm⁻¹ and a symmetric stretch just below 1500 cm⁻¹ in all the four Fe-MOFs.

Figure 1 (A) SEM Images of Fe-MOFs: a) & b) Fe-MIL-88a-Seba, c) & d) Fe-MIL-88a-Azla, e) & f) Fe-MIL-88a-Suba and g) & h) Fe-MIL-88a-Pima and (B) IR Spectra of Fe-MOFs

The morphology of Fe-MOFs were examined by SEM as shown in the. It can be seen that the samples present a standard form as colloidal spheres like morphology from a single sample scanning electron microscopy. We observed that the crystal size grew little over the time with increase in the surface area, while morphology of Fe-MOFs had no significant change. It was obvious that not only the size of the samples became larger with the increase in length of aliphatic dicarboxylate linkers, but also the overlapping and porous surfaces of the samples increased. The results shown in exhibits N2 sorption/desorption isotherms of Fe-MIL-88a-Seba which was considered to be a combination of the type II and III sorption isotherms Figure 2a Error! Reference source not found. And the pores within Fe-MOFs were mesoporous with a dominant range from 5 to 90 nm and 16 ~ 23 nm were the most. The thermal stability of the Fe-MOFs were analyzed through TGA shown in Figure 2b which indicated that the synthesized Fe-MOFs loses significant amount of weight in two regions on heating. The first of these is between 65°C and 110°C where 20-25% of initial weight is lost which can be consistent with the loss of all water i.e. both lattice and co-ordinated from the structure. In addition to this, weight loss consistent with the decomposition of the framework to produce Fe₂O₃ occurs between 270°C and 350°C leading to final weight of 34%.
The removal and degradation of Rhodamine B (RhB) were investigated. After 120 mins, no noticeable amount of RhB was decolorized except by Fe-MIL-88a-Azla and Fe-MIL-88a-Seba which displayed 23% and 27% of dye adsorption respectively. This indicates that RhB could not be removed by Fe-MOFs simply through adsorption mechanism. Moreover, efficiency of persulfate to decolorize RB simulated solution was also evaluated which showed that although persulfate can decolorize very negligible concentration of RB, the decolorization efficiency was quite limited to 8% which was lesser than the efficiency displayed by Fe-MIL-88a-Azla and Fe-MIL-88a-Seba. However, when Fe-MOFs were combined with persulfate, the RhB solution degraded significantly under fenton conditions after 120 mins and the degradation efficiency reached ~ 88%, 90%, 90% and 91% for Fe-MIL-88a-Pima, Fe-MIL-88a-Suba, Fe-MIL-88a-Azla and Fe-MIL-88a-Seba respectively. Moreover, the combination of persulfate and Fe-MOFs as well as light can effectively degrade the simulated RhB solution. Since, Fe-MOFs were unable to adsorb significant amount of RhB and persulfate alone did not degrade RhB, therefore this result suggests that persulfate was activated either in the presence of Fe-MOFs or Fe-MOFs and light both generated sulfate radicals to degrade RhB.

3.2 Degradation of RB using persulfate activated by Fe-MOFs:
To evaluate each sample’s activity for the removal and degradation of Rhodamine B (RhB) from the simulated aqueous solution, the sample were evaluated based on three criteria: (i) dye adsorption (ii) dye degradation using fenton reaction conditions and (iii) dye degradation using photo-fenton reaction conditions. Firstly, Fe-MOFs were added to the RB solution in the absence of the persulfate and the result shown in . Even though, Fe-MOFs were mixed with the RB solution for 150 mins, no noticeable amount of RB was decolorized except by Fe-MIL-88a-Azla and Fe-MIL-88a-Seba which displayed 23% and 27% of dye adsorption respectively. This indicates that RB could not be removed by Fe-MOFs simply through adsorption mechanism. Moreover, efficiency of persulfate to decolorize RB simulated solution was also evaluated which showed that although persulfate can decolorize very negligible concentration of RB, the decolorization efficiency was quite limited to 8% which was lesser than the efficiency displayed by Fe-MIL-88a-Azla and Fe-MIL-88a-Seba. However, when Fe-MOFs were combined with persulfate, the RhB solution degraded significantly under fenton conditions after 120 mins and the degradation efficiency reached ~ 88%, 90%, 90% and 91% for Fe-MIL-88a-Pima, Fe-MIL-88a-Suba, Fe-MIL-88a-Azla and Fe-MIL-88a-Seba respectively. Moreover, during the photo-fenton conditions, the degradation efficiency was improved remarkably and reached nearly 98% for Fe-MOFs which portrays that the combination of persulfate and Fe-MOFs as well as light can effectively degrade the simulated RhB solution. Since, Fe-MOFs were unable to adsorb significant amount of RhB and persulfate alone did not degrade RhB, therefore this result suggests that persulfate was activated either in the presence of Fe-MOFs or Fe-MOFs and light both generated sulfate radicals to degrade RhB.

3.3 Effects of Persulfate Dosage & Fe-MOFs loading on Degradation of RhB
Since the persulfate dosage and Fe-MOFs loading are the two important parameters in this persulfate activation reaction, we further investigated the effects of these factors on the RhB decolorization and attempted to obtain an optimal condition for the RhB decolorization. For optimization of the degradation of RhB, persulfate dosages were optimized from 50 to 400 mg/L and Fe-MOFs loading range was optimized from 100 to 1500 mg/L. When the Fe-MOFs loading was fixed relatively low i.e. 100-300 mg/L, an increase in the persulfate dosage did not result in significant enhancement in the RhB degradation. However, when the concentration of Fe-MOFs was fixed to 400 mg/L and greater, the increase in persulfate was found to improve the RhB degradation. This suggested that a low Fe-MOFs loading, the amount of Fe-MOFs were not sufficient to activate the existing persulfate, even though more persulfate was added to the reaction. On the other hand, at higher Fe-MOFs loading, a higher amount of persulfate was activated leading to the improved RhB degradation, whereas, when the persulfate dosage was fixed and the Fe-MOFs loading was varied, RhB degradation changed correspondingly regardless of the persulfate dosage. This result indicates that the Fe-MOFs loading was more dominant factor in this persulfate activation reaction. Therefore, to degrade 25 mg/L of simulated RB simulation, the optimal persulfate dosage and Fe-MOFs loading were 200 mg/L and 700 mg/L, respectively.
3.4 Effects of temperature and pH on the degradation of RB:
The two important parameters i.e. temperature and pH were investigated to examine the effects on the degradation of RhB as well as persulfate activation by Fe-MOFs. For the optimization of the temperature conditions, the degradation of RhB and persulfate activation was inspected at the temperatures 20°C - 50°C. From the optimization experiment, we examined that as and when temperature was increased gradually, the degradation efficiency of the Fe-MOFs increased remarkably, for instance, as shown in the, Fe-MIL-88a-Seba exhibited an evident change in the degradation efficiency from 35% to 55% when temperature was increased from 20°C to 30°C, whereas, when the temperature was raised from 40°C to 50°C, the degradation efficiency of Fe-MIL-88a-Seba was enhanced from 84% to 95%. A similar trend of enhancement was observed by rest of the Fe-MOFs utilized for the degradation of RhB.

We further examined the pH of the solution as it is also considered as one of the critical factors in persulfate activation reaction as shown in the fig. We observed that as the pH of the solution was increased from 3 to 11, the RhB degradation efficiency of Fe-MOFs decreased accordingly, implying that alkaline conditions were unfavorable for RhB degradation using Fe-MOFs to activate persulfate radicals whereas degradation efficiency remained quite stable in the acidic pH. For instance, the degradation efficiency of Fe-MIL-88a-Seba was enhanced from 93% to 95% at pH=3 and a similar trend was palpable for the other synthesized Fe-MOFs as well.

3.5 Photo-Fenton Reaction and Role of Inhibitors on the degradation of RB in water
Light, yet another form of facilitation to activate persulfate radicals on the degradation of RhB by Fe-MOFs. We investigated the role of light as photo-fenton reaction on the degradation of RB in water. The result revealed that the RhB degradation in presence of light i.e. when the sunlight was introduced the degradation efficiency was greatly enhanced. To ensure that the decomposition of RB was not due to sunlight irradiation, a blind experiment was performed without using Fe-MOFs for the degradation of RhB. It was observed that the sunlight alone was unable to decompose RhB within the testing time. Thus, it could be concluded that the improvement in the degradation efficiency of RhB by Fe-MOFs can be attributed to the sunlight irradiation which facilitated the generation of persulfate radicals in a way to enhance the degradation capacity of the Fe-MOFs as catalysts. Generally, the degradation process always proceeds by a persulfate radical mechanism when Fe based catalysts are applied for the catalytic wet oxidation persulfate oxidation of organic effluents. However, it was unclear whether the catalytic degradation mechanism here was the same as other Iron based catalysts for the catalytic oxidation of RhB in water. Therefore, we examined the role of inhibitors to determine a plausible mechanism for the degradation of RhB in water by Fe-MOFs. Tert-Butanol, a kind of common scavenger, was employed for investigating the mechanism. When, tert-butanol was added into the reaction system, there was almost no change in the color over all the experimental process. It seemed that the RhB was not degraded at all in presence of tert-butanol. The degradation of RhB was less than 10% that resonates the negligible degradation of RhB which was a result of the adsorption capacity posed by Fe-MOFs. Thus, Fe-MOFs followed the persulfate radical mechanism in accordance with other catalysts.
3.7 Conclusion
In conclusion, four isomorphic aliphatic dicarboxylate variants of MIL-88a(Fe) were synthesized and characterized. The results exhibited that the catalytic degradation efficiency for both fenton and photo-fenton reactions can be improved by the incorporation of longer linker length. Fe-MIL-88a-Seba exhibited a good recyclability over four cycles amongst all the synthesized Fe-MOFs, demonstrating that the high surface area and robust Fe-MIL-88a has the potential to be used for fenton and photo-fenton reactions in water purification applications. Moreover, factors influencing the activation of persulfate and RB degradation were examined. Hence, these features accomplishes the synthesized Fe-MOFs in this work as an effective and recyclable heterogeneous catalysts for the activation of persulfate.

References