Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Green synthesis of the copper and iron phthalocyanine-based metal-organic framework as an efficient catalyst for methylene blue dye degradation and oxidation of cyclohexane

Rupali S. Bhise, Yogesh A. Patil, Ganapati S. Shankarling*

Department of Specialty Chemicals Technology, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai - 400019, India. Tel: 91-22-33612708, Fax: +91-22-33611020 E-mail address: gs.shankarling@ictmumbai.edu.in, gsshankarling@gmail.com

General

Experimental

Materials

Copper (II) nitrate tetrahydrate (Cu $(NO_3)_2$. $4H_2O$), Trimellatic anhydride ($C_9H_4O_5$), ammonium molybdic acid $(NH_4)_2MoO_4$, hydrogen peroxide (H_2O_2, 30%, w/v), ethanol (C_2H_5OH), Nitrobenzene ($C_6H_5NO_2$), Methylene Blue dye ($C_{16}H_{18}N_3SCl$), Cyclohexane (C_6H_{12}), tert-Butyl hydroperoxide (TBHP, 70 %), Acetonitrile were purchased S. D. Fine Chem Limited. All chemicals were employed as received without further purification. All degradation experiments were carried out using distilled water.

Synthesis of Tetra carboxyl Iron Phthalocyanine (TCFePc) [1]

The TCFePc was produced according to the method described[1.] The combination of trimellitic anhydride (33.0 g, 187 mmol), $FeCl_2.4H_2O$ (9.5 g, 50 mmol), NH_4Cl (4.5 g, 86 mmol), ammonium molybdic acid (0.5 g, 3 mmol) and finely crushed urea in 35 ml nitrobenzene was added into a 500 ml three-neck flask equipped with a magnetic stirrer and reflux condenser; This resulting mixture was stirred at 185°C for 3.5 hours. The resulting mixture was then washed with methanol until no nitrobenzene could be detected, and a black-blue solid iron tetraformamido phthalocyanine was obtained. After about 3 minutes of boiling in saturated sodium chloride solution and filtering, the filter cake was transferred to a 2.0 M NaOH solution saturated with NaCl in a 500 ml three-neck flask. The reaction was carried out at 90°C for 10 hours until the ammonia was released. The resultant solution, diluted with a suitable amount of deionized water, is adjusted to pH <3 with concentrated hydrochloric acid; Then centrifugation and filtration were carried out, followed by dissolving the well with 0.5 M NaOH filtration solution. After three repetitions, the resulting solid was neutralized first with water and then with methanol. Obtained as a blue-black solid (13.4 g, 34.8%) by drying in vacuum.

Synthesis of Copper-Iron Phthalocyanine Metal-organic framework (Cu-FePC MOF)

As shown in **Fig.S1**. The organometallic Cu-FePc framework was synthesized in water under ambient conditions using the organic linking salt method for a short period of synthesis time. In the preparation, a clear solution of 24 mg (0.1 mmol) of copper nitrate tetrahydrate salt, $Cu(NO_3)_2 \cdot 4H_2O$, in 10 mL of H_2O was added dropwise over another clear solution of 37 mg (0.05 mmol) of tetrasodiumcarboxylate iron phthalocyanine (Na_4 TCFePc) in 50 mL of H_2O formed by dissolving under stirring at room temperature. Such addition provokes the

immediate appearance of a precipitate. The mixture was then transferred to the sonication. The reaction mixture was kept under sonication at room temperature for 45 min. A representative aliquot was collected at different reaction times: 10 min, 20 min, 30 min, and 45 min. The blue-black precipitate of an aliquot was washed with distilled water repeatedly and dried at room temperature overnight. The synthesized Cu-FePc MOF was characterized by PXRD, FT-IR, SEM, TGA and BET analysis techniques.

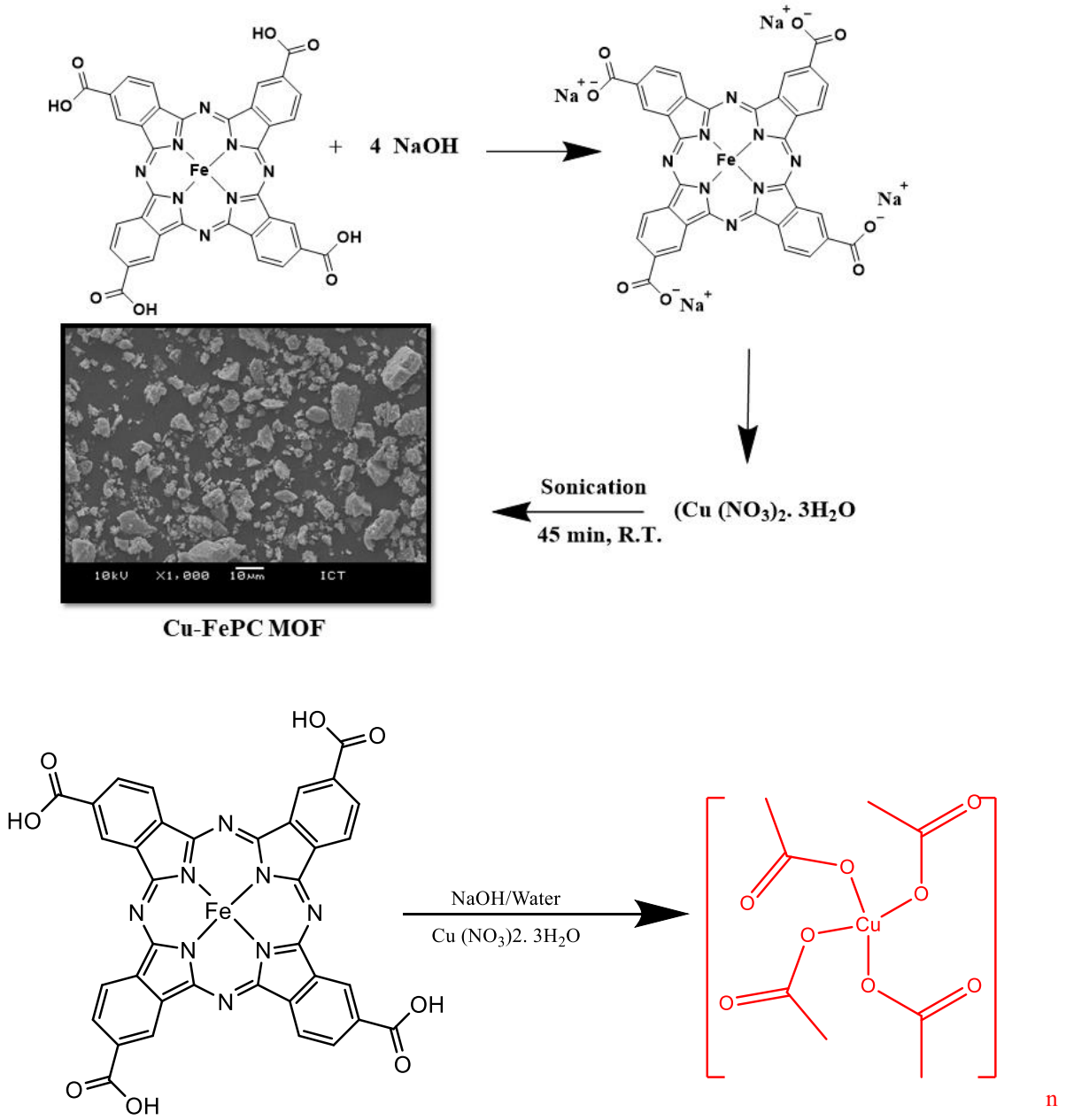

Fig. S1. Synthesis of copper iron phthalocyanine-based Metal-organic framework[2]

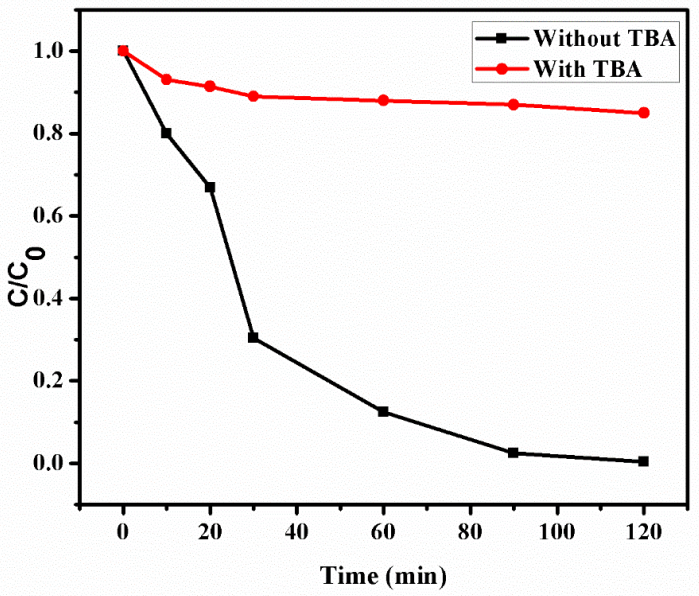

Figure S2. MB dye degradation experiments with and without TBA.

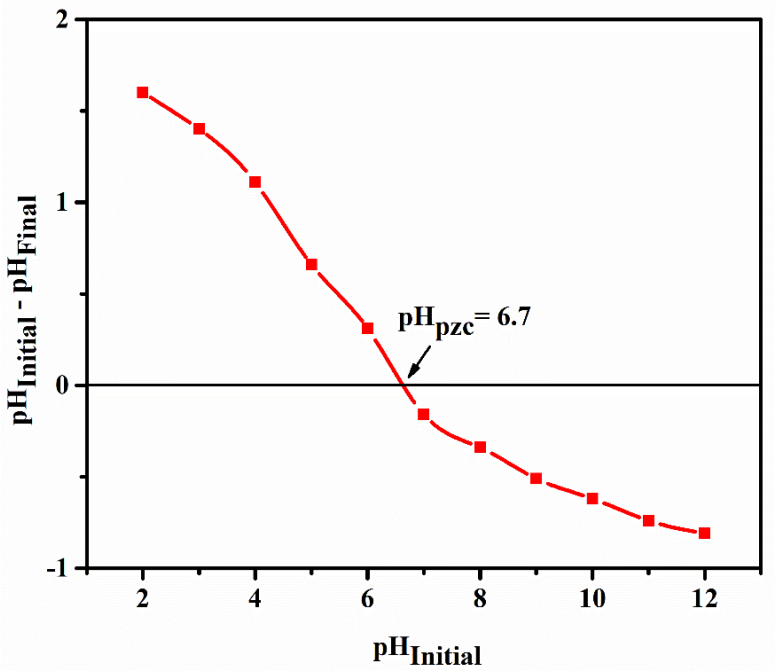

Figure S3. The point zero charce (pzc) of the Copper-Iron Phthalocyanine Metal-organic framework (Cu-FePC MOF)

References

1 Song, X.; She, Y.; Ji, H.; Zhang, Y. Highly Efficient, Mild, Bromide-Free and Acetic Acid-Free Dioxygen Oxidation of p-Nitrotoluene to p-Nitrobenzoic Acid with Metal Phthalocyanine Catalysts. *Org. Process Res. Dev.* **2005**, *9* (3), 297–301. https://doi.org/10.1021/op049810b.

2 Y. Liu, Y. Yang, Q. Sun, Z. Wang, B. Huang, Y. Dai, X. Qin and X. Zhang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7654–7658.