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Metal-Organic Frameworks (MIL-100 (Fe)) for commercial reactive dye effluent oxidation

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Abstract: Urgent calls for scientists' contributions towards saving eco-system from toxic deterioration. Such ever increasing urgency is leading the researchers for searching for ever greening technologies such as advanced oxidation processes for aqueous effluent elimination. This current investigation is leading to investigate the metal organic frameworks, role, MIL-100(Fe) that is prepared from reacting H_3BTC and ferric nitrate nona hydrate Also, Scanning electron microscopy is applied to set the surface shape of the synthesized substance. Subsequently, the prepared MIL-100(Fe) is used to oxidize Procion Blue MX-7RX in aqueous solution as a model textile wastewater effluent. The catalyst is applying in Fenton's oxidation system and operating parameters that affecting the system is evaluated. The experimental results revealed that 40 and 800 mgL^{-1} for MIL-100(Fe) and hydrogen peroxide, respectively at pH 3.0 that is leading to a complete dye removal (100%). Furthermore, the dye loading affects the reaction rate since its increase reduces the removal efficacy. Finally, thermodynamic parameters and kinetics of the reaction is evaluated for the scale-up purposes for real applications.

Keywords: MOF, Oxidation, Textile effluent wastewater, Modified Fenton's system

1. Introduction:

Organic dyes are frequently subjected for use in several industries such as leather and textile industries. The result is a massive amount of wastewater is produced [1]. Procion blue MX-7RX is one of the organic dyes that is embedded in wastewater from textile industry. Such effluent might cause a numerous of health problems including skin irritation, eczema, cell mutation, allergies and carcinogenic consequences [1-3]. Thus, treating such effluent is a must to deduce the deterioration in both human health and ecosystem. Currently, the global trend is treating industrial effluent prior to disposal in environmentally friendly manner. Presently, the essential requirement of engineers and academia in the whole world is to reach to sustainable wastewater treatments over the conventional technologies Numerous treatment technologies are available for management and treating industrial aqueous effluent discharge [4, 5]. Conventional wastewater management methods introduced are not efficient since due most of them are leading to imperfect and inadequate mineralization and removals and also may be results in the occurrence of unavoidable concerns such as the secondary wastes or high cost of chemicals and operating costs that makes such systems are inappropriate [6-8]. The crucial academics' goal is introducing an environmentally benign treatment technology. From this regard, presenting a photocatalytic reactions for wastewater treatment technologies showed a superior efficiency. This is due to its complete mineralization tendency for contaminants in aqueous streams [9]. Among such photocatalytic systems, iron-based catalysts which applying iron salts as a typical catalyst source, is so-called Fenton reaction that is signified with its unique activity [10]. Generally, photocatalysis is a crucial technique for treating wastewater since it may convert harmful organic molecules into harmless inorganic ones without resulting in further pollution [11]. Metal-organic frameworks (MOFs) is especially of iron-based types is one of superior photocatalytic catalysts [12].

Metal-organic frameworks (MOFs) are capable of degrading large wide of pollutants due to their unique structural, chemical, and physical properties. MOFs could be synthesized from using organic struts or linkers coordinated with metal clusters (SBUs) to generate a crystalline structure that is highly organized and porous. MOFs is signified as porous materials, possess a large surface area with a controlled pore size which makes them have a good catalytic activity [13-15]. Also, the catalytic activity might be enhanced through ligand-to-metal charge transfer. Also, MOFs is signified with their selective attack and showed a great potential in degrading various molecules. MIL-100(Fe) is one of the MOF materials that has attain a great interest among the many MOF photocatalyst due to its high specific surface area, high porosity, stability in a biological medium as well as eco-friendly nature. Furthermore, instance, MIL-100(Fe) has a surface functionalization. Also, it is selected as an iron source to be Fenton's reaction. Also, the organic linkers and transition metal centers in MOF (MIL-100(Fe)) result the different ligand-to-metal charge-transfer (LMCT) transitions which make it an efficient photocatalyst and also its great water and heat stability [16]. Furthermore, the resulting Fe-based MOFs exhibit intense visible light absorption because of the iron-oxo clusters, and iron is a metal that is abundant on Earth and very inexpensive [17].

Herein, the principle goal of this work is to assess the viability of introducing MIL-100(Fe) as an efficient MOF photocatalyst. This catalyst will be utilized as a resource of heterogeneous Fent0n system. The reaction is used to eliminate of Procion blue dye, one of the widely used textile dying. The system parameters are studied and evaluated. Various concentrations of MOF dose and H_2O_2, system pH, initial concentration of dye and temperature are investigated, also, the maximum removal efficiency is estimated.

2. Experimental part:

2.1 Chemicals and reagents

Procion blue MX-7RX, Hydrogen peroxide (H_2O_2, 30%), distilled water was used in all experiments of this work.MIL-100(Fe) was synthesized by a simple modified route according to our preliminary work in the *AMSEES* lab.

2.2 Photocatalytic reaction

Initially, a synthetic model 1000-ppm stock solution of the procion blue MX-7RX (reactive 161) is prepared and then the further required dilution is done. A 100 mL of 10 ppm of procion blue MX-7RX is put into a beaker then the pH is adapted, if needed. Subsequently, specific amount of MIL-100(Fe) as a resource of Fent0n's catalyst, H_2O_2 as initiator of the reaction is added into the solution which is exposed on a magnetic stirrer and being under the UV light. After a specific time intervals (every 10 min) of illumination time, the wastewater is periodically sampled for analysis at the wavelength 570 nm until the dye removal is completely achieved. Prior analysis the samples were initially filtered by micro filters syringe (0.45 mm) and used U.V-vis spectrophotometer, Model unico U.V2100, USA, to analyze. Also, scanning electron microscope (SEM) images was applied using a SUPRA 55 with voltage of 20 kV to characterize MIL-100(Fe) catalyst. Fig. 1 illustrate the graph of the experimental setup.

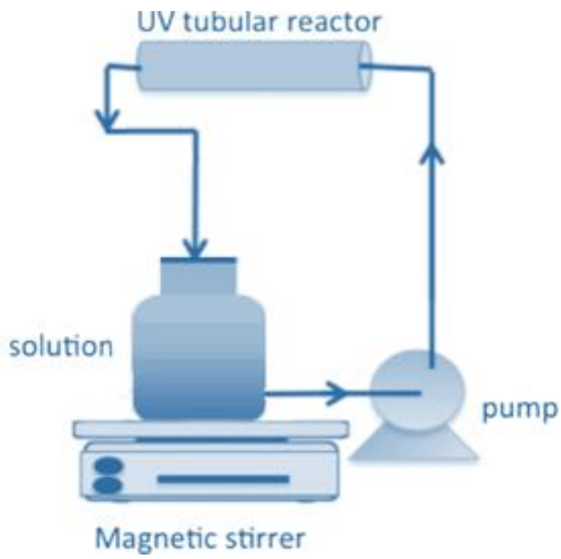

Figure 1. Laboratory scale photochemical UV reactor

3. Results and discussion

3.1 Scanning Electron Microscope (SEM)

MIL-100(Fe) sample's SEM image is displayed in Fig. 2. The MIL-100(Fe) particles' cauliflower-like morphology and the rough size of platy cleavages are visible in the SEM image.

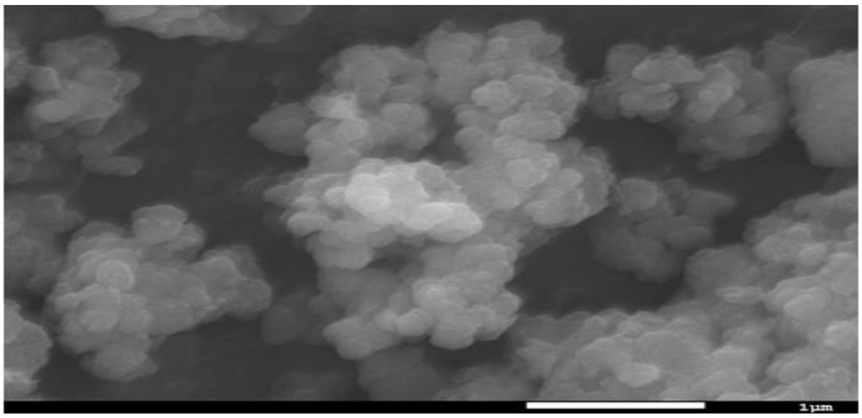

Figure 2. SEM micrographs of MIL-100(Fe)

3.2 Catalytic activity of MIL-100(Fe)

3.2.1 catalyst dose Effect: Catalyst dosage was varied from 10 to 80 mg/L of MIL-100(Fe) while the other parameters, i.e. H_2O_2= 800 mg/L and 10 ppm of dye at pH=3 are kept constant to assess the impact of the MOF dose on the dye oxidation system. The dye oxidation is improved with the increase in the catalyst dose since more active sites and higher OH radicals are achieved with the increase in the catalyst dosage from 10 to 40 mgL^{-1}. Although, further increase in the catalyst dose more than 40 mgL^{-1}, the economic dose is signified as 40 mgL^{-1} since almost the same removal rate is attained.

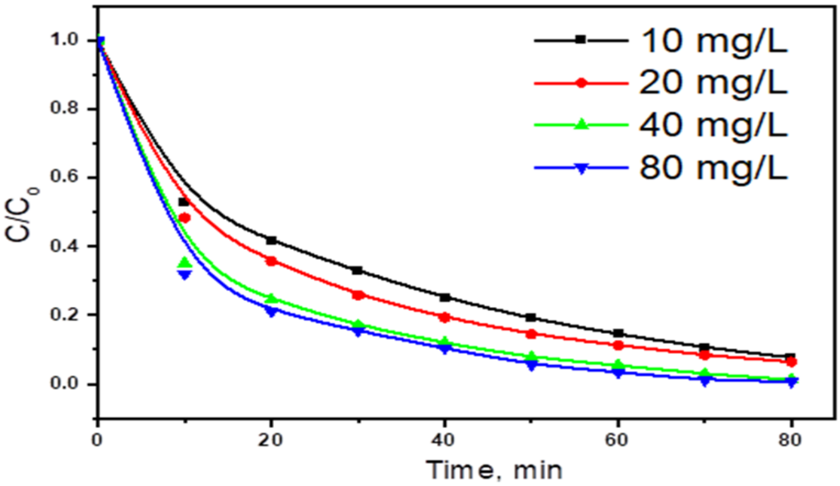

Figure 3. Catalyst dose Effect on the photo Fenton's system

3.2.2 Initial dye load Effect: For a real practical application, the effect of the initial dye load on the Fenton's photo-catalytic oxidation efficiency was studied. The findings are displayed in Fig. 4. A dye concentration is adjusted between 5 to 40 ppm while 40 mg L^{-1} of MIL-100(Fe) and 800 mg L-1 H_2O_2 were employed at pH. The data revealed from the results displayed in Fig. 4 show that the rate of the reaction increased with a decrease in the initial load of dye after 60 minutes of UV light and the removal percentages were varied from 91, 90.97, 75.6 and 45.4% of the corresponding initial concentrations of dye 5, 10, 20 and 40 ppm, respectively. Such phenomena could be explained by the decline in the rate of dye removal with initial concentration of dye, is associated with as the wastewater increased, the color creates a shadowing effect that makes the UV light could not effectively reach the aqueous solution. Thus, the •OH radicals' yield is not enough to the dye oxidation in high loads of concentration. Additionally, the unoccupied active surface of MOF sites is not enough for adsorbing high load of procion blue dye. Furthermore, the MOF active sites become crowded with the dye on the high loads that consequences in reduce the active •OH radicals' quantity. Similar data is previously explained and illustrated in literature [17] using oxidation system. As a result, there were decreasing in hydroxyl radicals which in turn caused the total reaction rate to decrease.

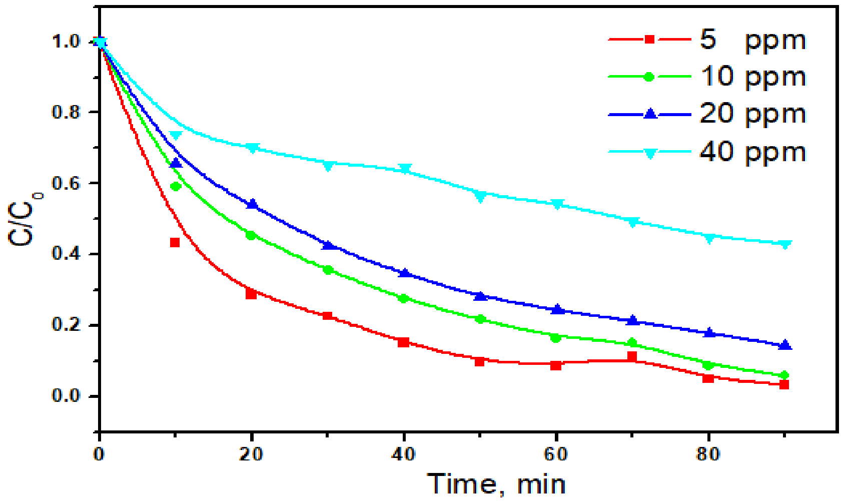

Figure 4. Dye load Effect on the photo Fenton's system.

3.2.3 pH Effect: The effect of pH possesses a defined role on the Fenton's oxidation reaction as pH has a major impact on the formation of OH. Thus, it is regarded as a crucial parameter in the photo Fenton's reaction. In this view, its efficacy is evaluated and the pH (initial) of dye wastewater is changed from 3-8 at 40 mg/L of MIL-100(Fe) and H_2O_2 were added to be 800 mg/L to several samples of wastewater under 150 min of UV irradiation. The results illustrated in Fig. 5 showed that a strong acidic pH system is preferred.

It is important to cite that the removal rate of Procion blue which dependent on inital pH of the solution was highly, as illustrated in Fig. 5. The reaction removal rate was increased to 100% by decreasing pH value. Also, neutral and alkaline wastewater resulted in 99.9 and 96%, respectively. This possibly related to the ideal pH range effects on the degradation if hydrogen peroxide as well as the iron particle's hydrolytic speciation [18-20].

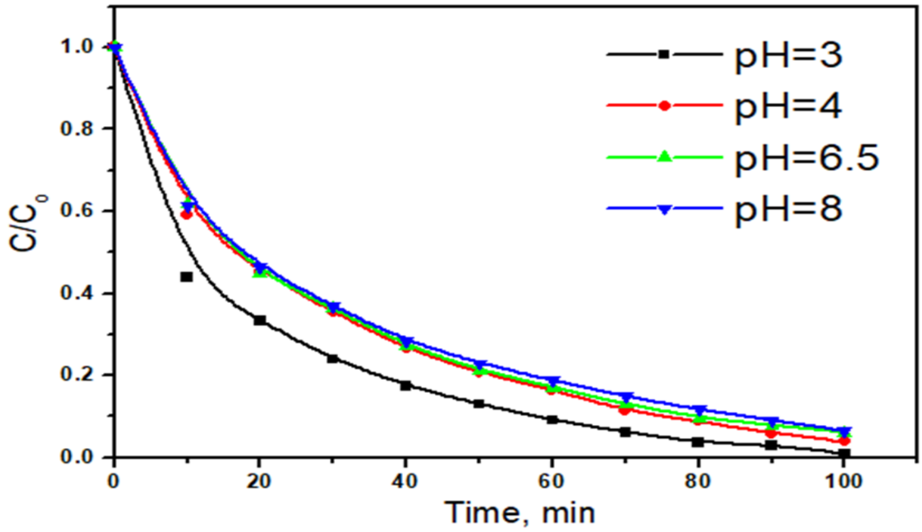

Figure 5. pH Effect on the photo Fenton's system.

3.2.4 H_2O_2 concentration Effect: Hydrogen peroxide is playing a crucial role in producing the hydroxyl free radicals on the Fenton's system and it is represented as the horsepower of the oxidation system. The affects of different hydrogen peroxide doses that are ranged from 100 to 3600 mgL^{-1} are showcased in Fig 6. Such test is evaluated while all other parameters are maintained at their constant levels of pH 3.0 and 40 mgL^{-1} MIL-100(Fe). After 80 minutes of UV illumination reaction time, the results in Fig. 6 revealed a notable elevation in the rate of the removal by increasing hydrogen peroxide reagent. Although H_2O_2 was checked at high concentration such as 800, 1600 and 3600 mgL^{-1} and high concentration attain high removal rate, the economic amount was 800 mgL-1 is selected. This is due to the removal rate at this stage is signified a complete dye removal. This is not considered too high where solo H_2O_2 was tried and the oxidation rate was less than H_2O_2 augmented with catalyst (MIL-100(Fe)). This means that the oxidation reaction was regarding to Fenton's reaction not regarding to hydrogen peroxide only. Such results could be illustrated since the concentration of H_2O_2 was a critical element that noticeably impacted the radicals' formation, such increase in rate of the reaction was related to the hydroxyl radicals produced. On the other hand, the total reaction yield dropped when the hydrogen peroxide concentration above 800 mgL^{-1}, the ideal value, since the extra H_2O_2 interacted with the hydroxyl free radicals alternatively generating them. As a result, there were less accessible OH radicals in the reaction medium to cause the organic molecules to break down. Moreover, the hydroxyl radicals were replaced by per hydroxyl radicals, which are weak and trivial for oxidation in comparison to the hydroxyl radicals' species. Consequently, the overdose hydrogen peroxide concentration had a so-called scavenging effect on the reaction oxidation rate [6].

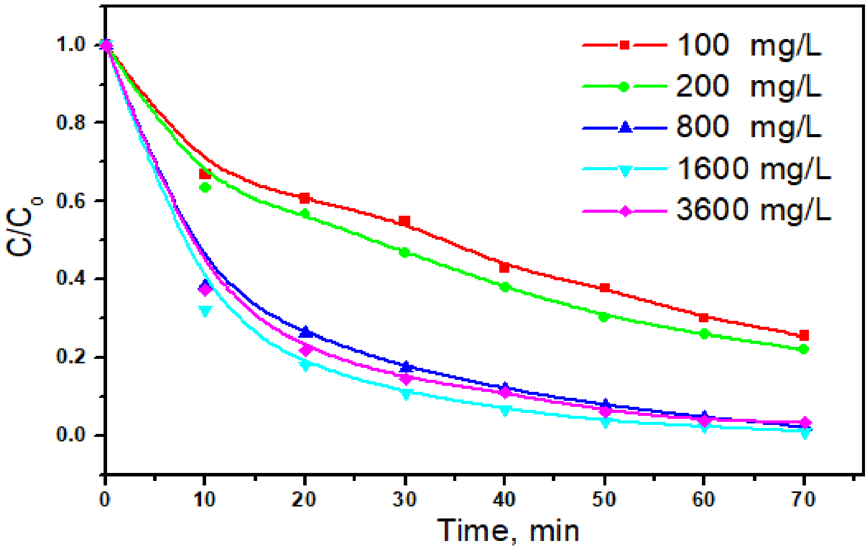

Figure 6. H_2O_2 Effect on photo Fenton's system.

3.2.5 Temperature Effect: Wide temperature range investigation is essential to widen the process real application. The temperature of the wastewater effluent is signified to be a crucial parameter influencing the photo-Fenton reactions. To assess such parameter, varied solution temperatures affecting the photo Fenton reaction, this reaction was conducted at 25, 40, 50, and 60 °C. The Fenton's reaction rate increased slightly as temperature rose, as Fig. 7 illustrates. When the temperature was raised from 26 to 40 °C, the maximum dye removal efficiency was 100%. This demonstrates the endothermic nature of the photo-oxidation Fenton reaction on the Procion blue dye. With rising temperatures, the dye removal increased and reached 100% in one hour of irradiance time. Consequently, the reason for the temperature-dependent increase in the removal rate was most likely the rise in the frequency of molecular collisions in the solution at higher temperatures. According to this finding, the reaction kinetics were even more accelerated by a rise in temperature. At these high temperatures, H_2O_2 may have broken down into O_2 and H_2O, which would have decreased the concentration of OH radicals [7]. The research suggests that low temperature range is signified as more effective working temperatures for the Fenton's reaction.

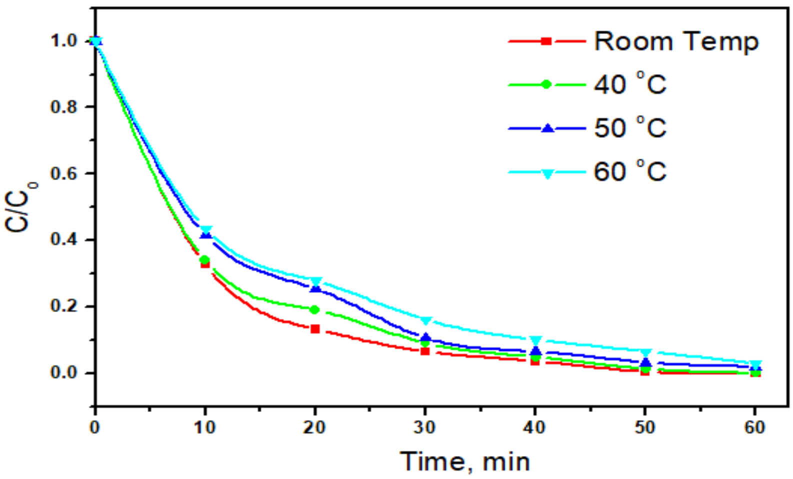

Figure 7. Temperature Effect on photo Fenton's system.

4. Conclusion

In the current study MOF MIL-100(Fe) based Fenton system is applied as a photo-oxidation system to remove Procion Blue MX-7RX. The system parameters are evaluated, i.e. optimal pH value found was 3 and H_2O_2 and MOF MIL-100(Fe) were noted at 800 and 40 mg/L, respectively. A complete dye removal was achieved (100% removal) when optimal conditions were applied. The dye removal potential followed a second order kinetic rate. The oxidation of Procion dye, depended on temperature, was also recorded and the thermodynamic parameters were calculated and showed that the reaction is endothermic. Thus, the results from this work is suggesting MOF is superior source of Fenton's reagent which may be then applied as a solar photocatalyst for more cost-efficient real applications.

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