

# Heterogeneous Photo-Fenton Oxidation of Methylene Blue Solution Using Fe(II)-Montmorillonite Calcinated Clay Catalyst <sup>†</sup>

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**Abstract:** Textile wastewaters are very problematic if released into the environment without proper treatment. Due to their recalcitrant nature, chemical treatments such as Advanced Oxidation Processes are often used. Among AOPs, Fenton-based processes presented promising results. However, considering the drawbacks associated with homogeneous Fenton, the aim of this work was to develop a heterogeneous catalyst using montmorillonite clay as the base material. After the application of an impregnation method, the Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction analysis showed the successful impregnation of iron into the montmorillonite clay. The catalyst Fe(II)-Mt was tested under different settings, and results showed that the best operational conditions (pH = 3.0, [Fe(II)-Mt 0.5M] = 1.0 g/L, [H<sub>2</sub>O<sub>2</sub>] = 4 mM, [MB] = 0.16 mM, radiation = UV-C (254 nm), time = 25 min) allowed to achieve 99.7% of Methylene blue (MB) removal. The catalyst showed great stability and was reused for three consecutive cycles. It can be concluded that Fe(II)-Mt catalyst is efficient for MB removal from aqueous solutions.

**Keywords:** FTIR; heterogeneous photo-Fenton; montmorillonite clay; X-ray diffraction



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## 1. Introduction

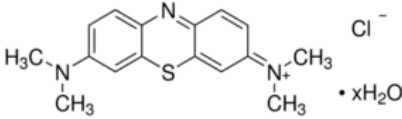
Textile dyes, such as Methylene blue (MB) are used with frequency in operations of dying and printing of natural, synthetic, man-made, and mixed textile materials such as wool, silk, nylon, polyester, acrylic, polyacetate, and polyurethane [1]. Due to the textile dye wastewater (TDW) dark color, the sunlight is blocked, which in turn hinders the life of aquatic organisms. In addition, azo dyes such as MB constitute the biggest recalcitrant category of dyes on a commercial scale, which in turn represents a serious danger to the environment [2]. To treat these types of wastewater, advanced oxidation processes (AOPs) can be applied. The AOPs are based on the production of hydroxyl radicals (HO•) with an oxidation potential of 2.80 V. These radicals are very powerful, and react quickly and unselectively [3,4]. Among the AOPs, the Fenton-based processes were observed to be effective in the degradation of textile dyes [5], however, homogeneous Fenton has several issues associated, since is strongly affected by the (1) solution pH, which needs to be kept in the acidic range, (2) temperature of the reaction, (3) oxidant and catalyst concentrations, (4) neutralization of the solution after the reaction is complete. To avoid these drawbacks, heterogeneous Fenton-type catalysts can be developed, which include the incorporation of Fe ions or Fe oxides into porous supports [6]. The aim and major novelty of this work was the development of a new catalyst using montmorillonite clay as a base material, to degrade a textile dye.

## 2. Materials and Methods

### 2.1. Reagents

The activated sodium bentonite (Na-Mt) was supplied by Angelo Coimbra & Ca., Lda, Maia, Porto, Portugal, the iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was acquired by Panreac, Castellar del Vallès, Barcelona, the hydrogen peroxide ( $\text{H}_2\text{O}_2$  30% w/w) was acquired by Sigma-Aldrich, St. Louis, Missouri, EUA and the Methylene blue (MB) was acquired by VWR Chemicals, Llinars del Vallès, Barcelona, Spain. The molecular structure of MB in non-hydrolyzed form is illustrated in Table 1. NaOH and  $\text{H}_2\text{SO}_4$  (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions. Deionized water was used to prepare the respective solutions.

**Table 1.** Chemical structure, maximum absorbance, and molecular weight of MB [7].

Name	Chemical Structure	$\lambda_{\text{max}}$ (nm)	Molecular Weight (g/mol)
Methylene blue (azo dye)		665, 300 and 250 nm	319.85

### 2.2. Analytic Techniques

The maximum absorbance wavelength ( $\lambda_{\text{max}}$ ) of MB was found at 665 nm, and the concentration of the residual dye in solution was calculated by Beer–Lambert’s law (Equation (1)), using the optical density and molar extinction observed at the characteristic wavelength, as follows:

$$A = l\varepsilon C \quad (1)$$

where A is the absorbency, l the path length (cm),  $\varepsilon$  the molar extinction coefficient (L/mol/cm) and C the dye concentration at time t (mol/L). Dye discoloration was analyzed by Equation (2), as follows [8,9]:

$$\text{Dye concentration}(\%) = \left( \frac{1 - C_t}{C_0} \right) \times 100 \quad (2)$$

where  $C_t$  and  $C_0$  are the concentrations of dye at reaction time t and 0, respectively.

### 2.3. Catalyst Fe(II)-Mt Calcinated Clay Preparation

The Fe(II)-Mt calcinated clay was prepared by using the impregnation method [10]. A specific amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in a beaker containing distilled water. Then, the Na-Mt was added to this aqueous solution and was stirred constantly in a water bath at 100 °C until all water was evaporated. After impregnation, the sample was oven dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace. The structural characterization of the Na-Mt and Fe(II)-Mt catalyst was obtained from X-ray diffraction analysis (XRD) and Fourier-transform infrared spectroscopy (FTIR).

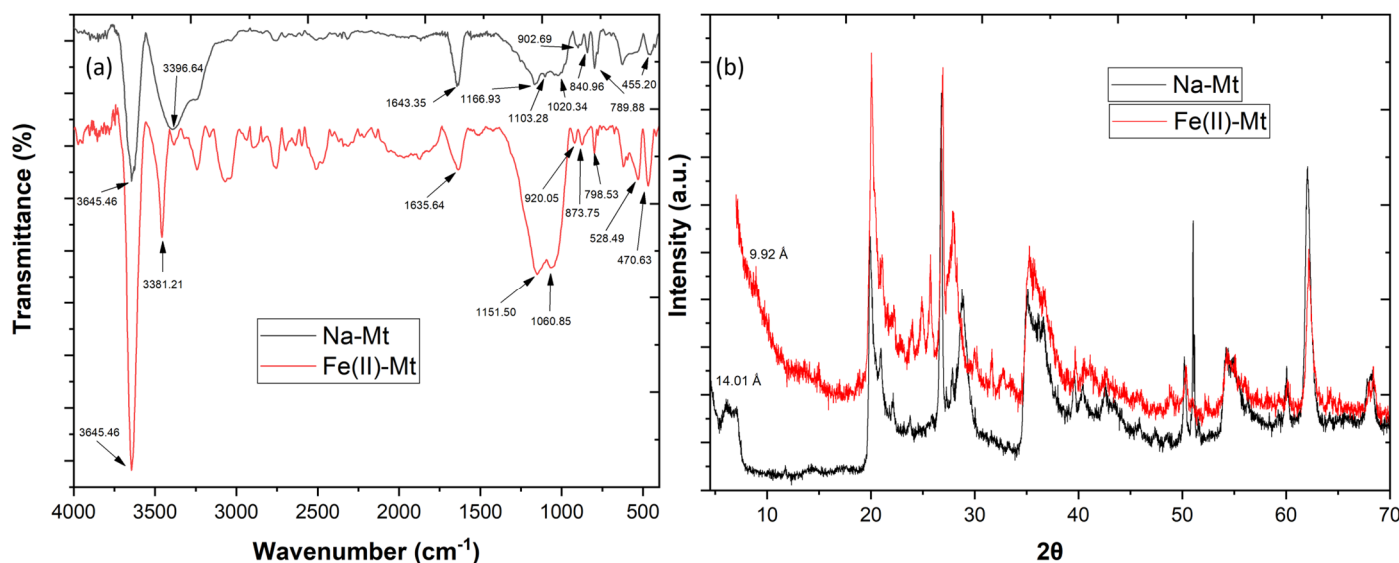
### 2.4. Heterogeneous Fenton-Based Experiments

The photocatalytic experiments were performed in a batch cylindrical photoreactor (500 cm<sup>3</sup>), equipped with a UV-C low-pressure mercury vapor lamp (TNN 15/32)—working power = 15 W (795.8 W m<sup>−2</sup>) and  $\lambda_{\text{max}}$  = 254 nm (Heraeus, Hanau, Germany). After the reaction has started, 2 mL of dye solution was withdrawn at periodic intervals and analyzed in a UV–visible scanning spectrum 200–800 nm, using a Jasco V-530 UV-vis (Tokyo, Japan). The samples were filtrated by 0.20  $\mu\text{m}$  filter and the  $\text{Fe}^{2+}$  concentrations were analyzed by atomic absorption spectroscopy (AAS) using a Thermo Scientific iCE 3000 SERIES, Waltham, Massachusetts, EUA. All the experiments were performed in triplicate and the observed standard deviation was always less than 5% of the reported values.

### 3. Results and Discussion

#### 3.1. Characterization of Fe-BC Catalyst

The FTIR analysis (Figure 1a) showed similar peaks between the Na-Mt and Fe(II)-Mt, such as  $3645.46\text{ cm}^{-1}$  (structural O–H groups),  $1643.35\text{ cm}^{-1}$  (adsorbed water yielded),  $1103.28$ ,  $999.13$  and  $789.88\text{ cm}^{-1}$  (structural Si–O groups),  $902.69\text{ cm}^{-1}$  (structural Al–Al–OH groups) and  $883.40\text{ cm}^{-1}$  (structural Al–Fe–OH groups) [11,12]. These results mean that after calcination the montmorillonite clay kept its original structure. However, the Fe(II)-Mt revealed a significant structural change, with the disappearance of a peak at  $1103.28\text{ cm}^{-1}$  and the appearance of a new peak at  $528.49\text{ cm}^{-1}$ .

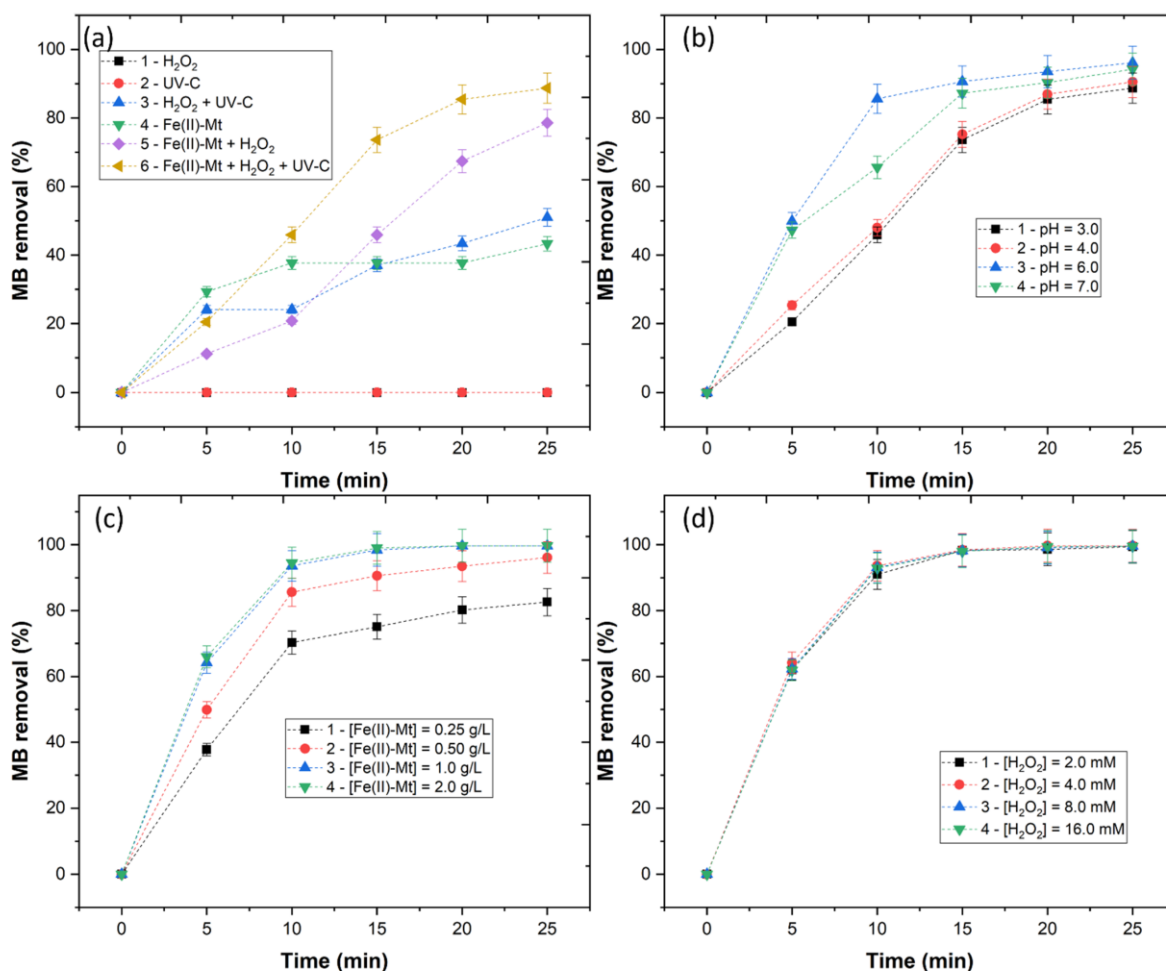


**Figure 1.** Analysis of Na-Mt and Fe(II)-Mt by (a) FTIR and (b) X-ray diffraction.

The XRD patterns of both Na-Mt and catalyst Fe(II)-Mt are shown in Figure 1b, and the crystallographic parameters were evaluated by measuring the basal reflections in the plane  $d_{hkl}$  001. It was observed that Na-Mt exhibits a diffraction peak at the  $d_{001}$  plane at  $2\theta = 6.18^\circ$  which corresponded to a basal spacing of  $14.01\text{ Å}$ , a characteristic peak of montmorillonite clays. The data revealed a significant shift associated with the reflection  $d_{001}$ , from  $14.01\text{ Å}$  to  $9.92\text{ Å}$ , confirming the structural modifications that occurred on the Fe(II)-Mt after the calcination.

#### 3.2. MB Degradation by Heterogeneous Fenton-Based Processes

In the previous section, the successful impregnation of iron into the Na-Mt clay was shown. Before the application of the Fe(II)-Mt catalyst, it is necessary to understand the effect of the different AOPs in MB removal. In Figure 2a, six different processes were tested, with the following conditions:  $\text{pH} = 3.0$ ,  $[\text{Fe(II)-Mt } 0.5\text{M}] = 0.5\text{ g/L}$ ,  $[\text{H}_2\text{O}_2] = 4\text{ mM}$ ,  $[\text{MB}] = 0.16\text{ mM}$ , radiation = UV-C ( $254\text{ nm}$ ), time = 25 min. The application of UV-C and  $\text{H}_2\text{O}_2$  had the lowest MB removal ( $<0.5\%$ ), since these processes were not capable of producing hydroxyl radicals ( $\text{HO}^\bullet$ ). With the combination of  $\text{H}_2\text{O}_2 + \text{UV-C}$ , MB removal achieved a removal of  $51.0\%$ , due to the direct photolysis of  $\text{H}_2\text{O}_2$  by the UV radiation, which lead to the generation of  $\text{HO}^\bullet$  radicals [13]. The application of Fe(II)-Mt reached  $43.3\%$  MB removal. This removal evidences the Fe(II)-Mt adsorption capacity, which is similar to works such as Flores et al. [14], who observed that heterogeneous catalysts have adsorption capacity. Finally, heterogeneous Fenton and photo-Fenton were applied, with results showing an MB removal of  $78.6$  and  $88.7\%$ . Clearly, the catalyst can convert the  $\text{H}_2\text{O}_2$  and generate  $\text{HO}^\bullet$  radicals. This effect is enhanced by the application of UV radiation, thus heterogeneous photo-Fenton was selected as the best AOP.



**Figure 2.** Removal of MB by (a) variation of processes, (b) variation of pH (3.0–7.0) with  $[\text{Fe(II)-Mt}] = 0.5 \text{ g/L}$ ,  $[\text{H}_2\text{O}_2] = 4 \text{ mM}$ ,  $[\text{MB}] = 0.16 \text{ mM}$ , radiation = UV-C (254 nm), time = 25 min (c) variation of Fe(II)-Mt 0.5M catalyst concentration (0.25–2.0 g/L), with pH = 3.0,  $[\text{H}_2\text{O}_2] = 4 \text{ mM}$ ,  $[\text{MB}] = 0.16 \text{ mM}$ , radiation = UV-C (254 nm), time = 25 min and (d) variation of H<sub>2</sub>O<sub>2</sub> concentration (2.0–16.0 mM) with pH = 3.0,  $[\text{Fe(II)-Mt}] = 1.0 \text{ g/L}$ ,  $[\text{MB}] = 0.16 \text{ mM}$ , radiation = UV-C (254 nm), time = 25 min.

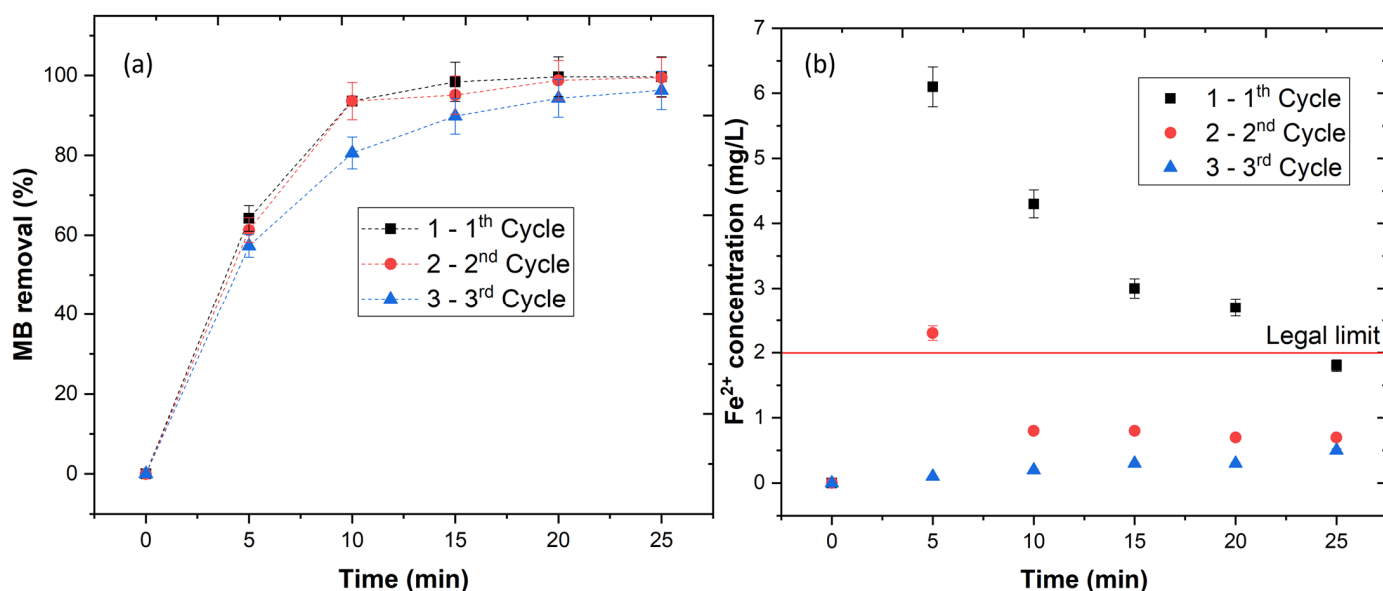
One of the major limitations regarding homogeneous Fenton is the precipitation of the catalyst at alkaline pH. Thus, the pH varied from 3.0 to 7.0 (Figure 2b). Results showed an MB removal of 88.7, 90.5, 96.1, and 94.2%, respectively, for pH 3.0, 4.0, 6.0, and 7.0. The increase in efficiency observed at pH 6.0 was similar to the work of Guimarães et al. [15], who applied pillared catalysts to treat winery wastewater. In addition, Portuguese legislation demands the final water pH to be between 6–9, and a further neutralization process is avoided, thus reducing additional costs.

The catalyst concentration was varied (0.25–2.0 g/L), to study its effect on MB removal. The results in Figure 2c showed an MB removal of 82.6, 96.1, 99.7, and 99.7%, respectively, for 0.25, 0.50, 1.0, and 2.0 g/L. As the catalyst concentration increased from 0.25 to 1.0 g/L, the production of HO• radicals increased, due to a higher content of Fe<sup>2+</sup> present in the solution. However, as the catalyst concentration increased further than 1.0 g/L, no significant changes were observed in MB removal. These results suggest that an excess of catalyst concentration may increase the solution turbidity hampering the UV radiation penetration and decreasing the MB removal efficiency.

Finally, the H<sub>2</sub>O<sub>2</sub> concentration was varied from 2.0 to 16.0 mM to access the effect of the oxidant concentration in heterogeneous photo-Fenton (Figure 2d). The results showed an MB removal of 99.4, 99.7, 99.6, and 99.5%, respectively. The results showed that the

removal of MB does not change for  $\text{H}_2\text{O}_2$  concentrations higher than 2.0 mM. These results are in agreement with the work of Silva et al. [16], who observed that the concentration of  $\text{H}_2\text{O}_2$  had no effect on the degradation of textile dyes by heterogeneous photo-Fenton.

The results showed that Fe(II)-Mt catalyst is very efficient in the degradation of textile dyes, however, in order to reduce the operational costs in actual wastewater treatment plants (WWTP), the catalyst should be recovered and reused. Therefore, three consecutive cycles were performed. The results in Figure 3a showed an MB removal of 99.7, 99.5, and 96.3%, respectively, for the first, second and third cycles, respectively. These results showed that the catalyst releases the iron to the aqueous solution taking place the photo-Fenton process. Afterwards, the catalyst reabsorbs the iron at the end of the reaction and reuse it again for three cycles. In order to prove this idea, the leaching concentration was determined during the three cycles (Figure 3b). These results showed a high  $\text{Fe}^{2+}$  release during the first 5 min, decreasing its concentration from 5 to 25 min, clearly showing the absorption of iron back to the catalyst. In addition, the final  $\text{Fe}^{2+}$  concentration values were observed to be far below the legal limits for the discharge of treated waters— $2 \text{ mg L}^{-1}$  [16].



**Figure 3.** (a) Catalyst stability, (b)  $\text{Fe}^{2+}$  leaching concentration for 3 consecutive cycles. Experimental conditions: pH = 3.0, [Fe(II)-Mt 0.5M] = 1.0 g/L, [ $\text{H}_2\text{O}_2$ ] = 2.0 mM, [MB] = 0.16 mM, radiation = UV-C (254 nm), time = 25 min.

#### 4. Conclusions

Based on the FTIR and X-ray diffraction analysis, it can be concluded that calcination of montmorillonite clays does not affect their structural integrity and allows the incorporation of  $\text{Fe}^{2+}$ . Therefore, heterogeneous photo-Fenton is an efficient process for MB degradation and it is affected by the solution pH, concentration of catalyst and  $\text{H}_2\text{O}_2$ . Finally, the catalyst can be reused for, at least, three consecutive cycles, decreasing the treatment costs.

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