

Proceeding Paper

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

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**Abstract:** The textile dye wastewaters are very dangerous if released into the environment without proper treatment. Due to their recalcitrant nature, chemical treatments such as Fenton based processes are more appropriated. Considering the drawbacks associated with homogeneous Fenton, the aim of this work was to develop a heterogeneous catalyst using a montmorillonite clay as based 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 AOPs and results showed that under 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) it was achieved 99.7% MB removal. The catalyst showed great stability and was reused for 3 consecutive cycles. It is concluded that the catalyst Fe(II)-Mt is efficient for MB removal from aqueous solution.

**Keywords:** FTIR; Heterogeneous photo-Fenton; Montmorillonite clay; X-ray diffraction

## 1. Introduction

Textile dyes, such as methylene blue (MB) are use with frequency in operations of dyeing 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, the 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<sup>•</sup>) with an oxidation potential of 2.80 V. These radicals are very powerful, react quickly and unselectively [3,4]. Among the AOPs, the Fenton based processes were observed to be effective in the degradation of textile dyes [5,6], however, homogeneous Fenton has several issues associated, since is strongly affected by the (1) solution pH, which needs to be kept in acidic range, (2) temperature of the reaction, (3) oxidant and catalyst

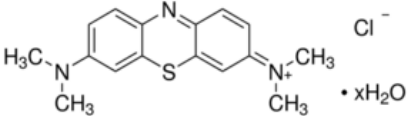
concentrations, (4) neutralization of the solution after the reaction is complete. To avoid these drawbacks, it can be developed heterogeneous Fenton-type catalysts, which includes the incorporation of Fe ions or Fe oxides into porous supports [7]. The aim and major novelty of this work was to develop a new catalyst using a 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 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 [8].

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:

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

where A is the absorbency, l the path length (cm),  $\epsilon$  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 [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 calcinations 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 vapour 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]. 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  $\text{cm}^{-1}$ .

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 reflexions 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  $\text{\AA}$ , which was observed to be a characteristic peak of montmorillonite clays. The data revealed a significant shift associated with the reflection  $d_{001}$ , from 14.01  $\text{\AA}$  to 9.92  $\text{\AA}$ , confirming the structural modifications that occurred on the Fe(II)-Mt after the calcination.

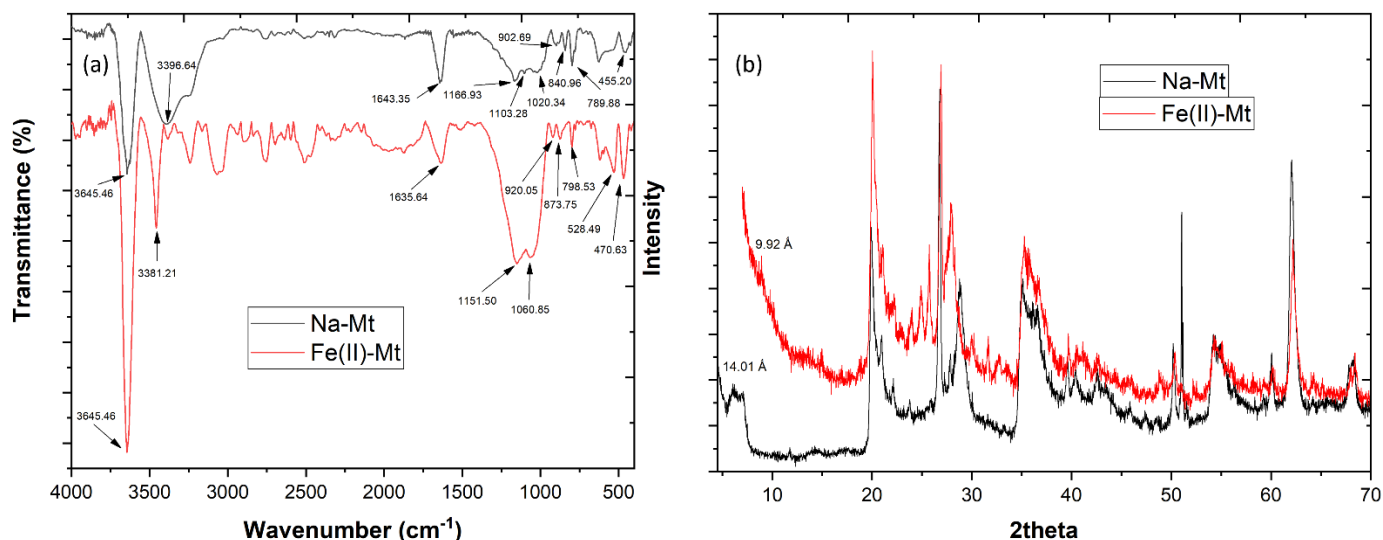


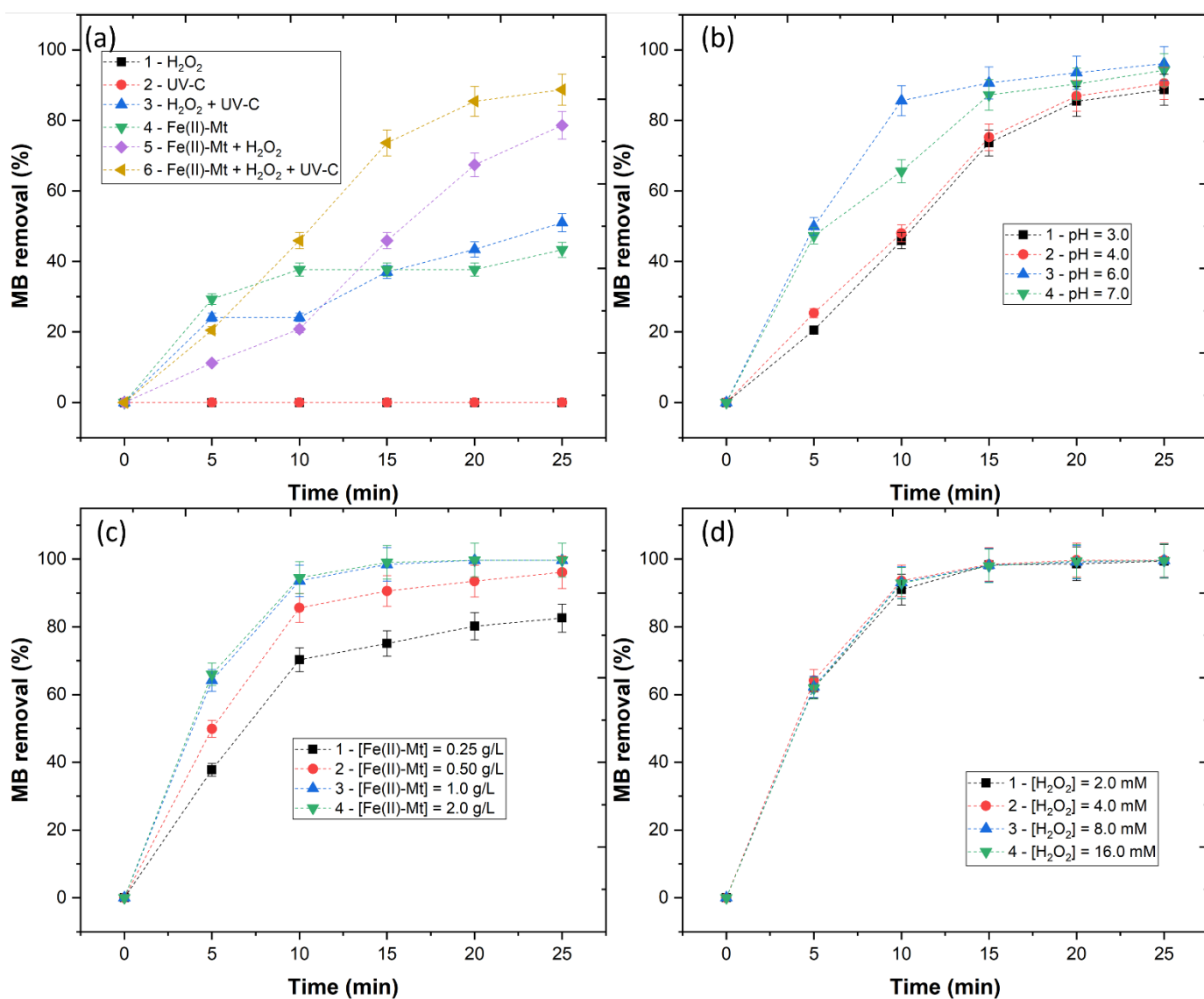
Figure 1. Analysis of Na-Mt and Fe(II)-Mt by (a) FTIR and (b) X-ray diffraction.

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

In the previous section it was shown the successful impregnation of iron into the Na-Mt clay. 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 AOPs 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 nm), time = 25 min. The application of UV-C and  $\text{H}_2\text{O}_2$  had the lowest MB removal (0.5% <), due to the fact that these AOPs were not capable of producing hydroxyl radicals ( $\text{HO}^\bullet$ ). With application of  $\text{H}_2\text{O}_2 + \text{UV-C}$ , MB removal achieved 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 [12]. 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., [13], who observed that heterogeneous catalysts have adsorption capacity. Finally, heterogeneous Fenton and photo-Fenton were applied, with results showing a MB removal of 78.6 and 88.7%. Clearly, the catalyst can convert the H<sub>2</sub>O<sub>2</sub> and generate HO<sup>•</sup> radicals. This effect is enhanced with the application of UV radiation, thus heterogeneous photo-Fenton was selected as the best AOP.

One of the major limitations regarding the homogeneous Fenton is the precipitation of the catalyst at alkaline pH. Thus, the pH was varied from 3.0 to 7.0 (Figure 2b). Results showed a 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 of efficiency observed at pH 6.0 was similar to the work of Guimarães et al., [14], who applied pillared catalysts to treat winery wastewater. In addition, the Portuguese legislation demands the final water pH to be between 6–9 and also it is avoided a further neutralization process, thus avoiding additional costs.



**Figure 2.** Removal of MB by (a) variation of AOPs, (b) variation of pH (3.0–7.0), (c) variation of Fe(II)-Mt catalyst concentration (0.25–2.0 g/L) and (d) variation of H<sub>2</sub>O<sub>2</sub> concentration (2.0–16.0 mM).

The catalyst concentration was varied (0.25–2.0 g/L), to study its effect in MB removal. The results in Figure 2c showed a 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<sup>•</sup> radicals increased, due to a higher content of Fe<sup>2+</sup> present in 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, decreasing the MB removal efficiency.

Finally, the  $\text{H}_2\text{O}_2$  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 a MB removal of 99.4, 99.7, 99.6 and 99.5%, respectively. The results showed that the removal of MB was independent from the concentration of  $\text{H}_2\text{O}_2$ . These results are in agreement with the work of Silva et al., [15], 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 the Fe(II)-Mt catalyst is very efficient in the degradation of textile dyes, however, in order to be economic for wastewater treatment plants (WWTP), the catalyst should be recovered and reused. Therefore, 3 consecutive cycles were performed. The results in Figure 3a showed a MB removal of 99.7, 99.5 and 96.3%, respectively for the 1st, 2nd and 3rd cycles. These results showed that the catalyst is able to release the iron to perform the photo-Fenton process, reabsorb the iron in the end of the reaction and reuse it again for 3 cycles. In order to prove this idea, the leaching concentration was determined during the 3 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 European Economic Community standards for discharge of treated waters—2 mg  $\text{L}^{-1}$  [15].

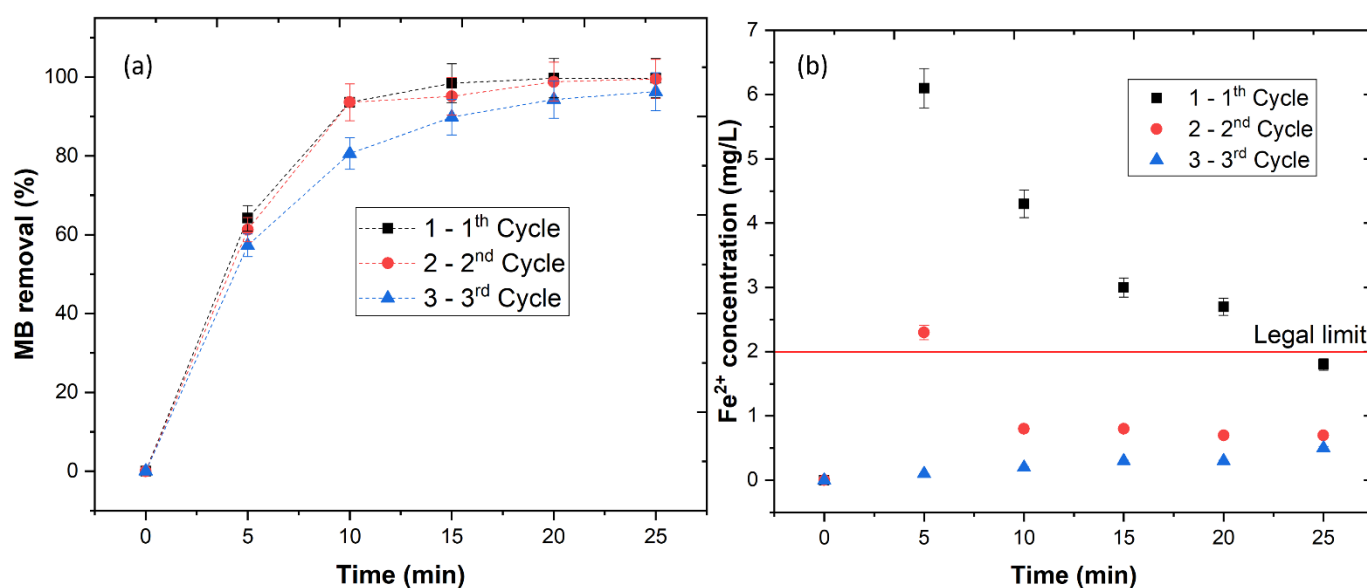


Figure 3. (a) Catalyst stability, (b)  $\text{Fe}^{2+}$  leaching concentration for 3 consecutive cycles.

#### 4. Conclusions

Based on the FTIR and X-ray diffraction analysis, it is concluded that calcination of montmorillonite clays does not affect their structural integrity and allows the incorporation of  $\text{Fe}^{2+}$ . It is concluded that heterogeneous photo-Fenton is the most efficient process in MB degradation and that this process is affected by the solution pH, concentration of catalyst and  $\text{H}_2\text{O}_2$ . Finally, it is concluded that the catalyst can be reused for 3 consecutive cycles, decreasing the treatment costs and the iron is reabsorbed after each cycle.

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