Removal of Methylene Blue dye solution by Fenton-like process using heat treated Laterite

Kpınsoton G. M. R.[1,2,*], Karoui H .[1], Richardson Y.[2], Koffi B. N. S .[1], Yacouba H.[3], And Collard F. X.[4]

[1]Laboratoire Eau Dépollution Ecosystème et Santé, Fondation 2iE, rue de la Science 01BP 594 Ouagadougou 01 Burkina Faso

[2]Laboratoire Biomasse Energie et Biocarburant, Fondation 2IE, rue de la Science 01BP 594 Ouagadougou 01 Burkina Faso

[3]Laboratoire Hydrologie et Ressources en eau, Fondation 2IE, rue de la Science 01BP 594 Ouagadougou 01 Burkina Faso

[4]Department of Process Engineering, Stellenbosch University, Private Bag X1, Matieland 7602, Stellenbosch, South Africa and.

*corresponding author: Gloria Murielle Rostandi KPINSOTON

e-mail: mkpinsoton@gmail.fr

Abstract

Laterite, an Iron rich soil from Dano, was heat at 800 °C and used as catalyst in methylene blue (MB) removal, a prototype of organic dye, by Heterogeneous Fenton process. The catalyst porosity was characterized through Nitrogen and MB adsorption isotherms. Nitrogen adsorption and desorption revealed that the LT-800 has a weak BET specific area, around 7m2.g-1. MB adsorption isotherms were plotted with Langmuir and Freundlich equations. The MB removal rate was of 96 % after 20 minutes of adsorption plus 80 minutes of Fenton reaction at room temperature According to the HPLC analysis results and the UV spectrum, the MB removal was based on both adsorption and degradation process. However, the degradation process was essentially heterogeneous.

Keywords: Laterite; Methylene blue Organic dyes; Heterogeneous Fenton-like process.

1. Introduction

Several synthetic dyes are produced per year in the world and most of them are non-biodegradables. Methylene blue molecules have two aromatics rings (Figure 1) which are hardly degradable and have mostly been used as prototypical dye. Advanced Oxidation Process (AOPs) are efficient for the degradation of bio-reluctant organic pollutants. Fenton process is an AOP based on the generation of hydroxyl radicals with hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}).

$$\text{(1).} H_2O_2 + Fe^{2+} \rightarrow HO° + OH^- + Fe^{3+}$$

$$\text{(2).} HO° + \text{organic pollutants} \rightarrow CO_2 + H_2O + \text{inorganics products}$$

However, in the homogeneous process, Iron sludge is generated due to the complexation of the Iron species mainly at pH up to 3. The use of solid catalyst have thus, been recommended in previous studies to get rid of these drawbacks. Zeolites (Fukuchi *et al.*, 2014), clay (Tabet *et al.*, 2006), activated carbons (Le *et al.*, 2015) are mostly used as catalysts in Fenton system. Laterite is an Iron rich soil available in tropical zones thus a stable laterite can be an attractive heterogeneous Fenton catalyst. Khataee *et al.* (2015) used an Iron rich laterite soil with mesoporous structure for the degradation of an azo dye, Acid Red 17 by heterogeneous photo Fenton. This study is focused on a formulation of heterogeneous Fenton catalyst from Dano laterite's and its capacity in methylene blue removal.

2. Materials and methods

2.1. Chemicals and materials

Laterites used in this study come from Dano, a country in Burkina Faso. In order to prepare the laterite, the raw laterite was firstly crushed. Then a crushed laterite went through a heat treatment at 800°C under air.

X-ray diffraction analysis was performed in a previous work (Kenda *et al.*, 2017). The main crystalline phases is presented in XRD pattern Figure 2 and shown some peaks which were associated quartz and hematite according to the standard powder diffraction data (JCPDS).

2.2. Characterization

Nitrogen adsorption/desorption, using a Micromeritics 3Flex, was performed to determine the porous texture of the LT-800. The specific surface area was analyzed according to the BET method. The total pore volume was taken calculated at p/po = 0.99, the highest relative pressure. The mesopore volume was estimated from the BJH plots.

The MB adsorption isotherm tests were carried out in 100 ml Erlenmeyer flasks. 1g of laterite was stirred with methylene blue solutions at initial concentrations from 20 to 80 mg L^{-1} for 15 hours. The different tests were performed at non modified pH and at room temperature.

The linearization of Langmuir (3) and Freundlich (4) models was used to interpret the equilibrium data.

$$\textbf{(3)}\ \frac{1}{Qe} = \frac{1}{Q_m\ K_L C_e} + \frac{1}{K_L}$$

$$\textbf{(4)}\ \ln Q_e = n\ lnCe + lnK_F$$

Where qe is the amount of MB adsorbed per mass of LT-800 [mg g^{-1}], Ce is the equilibrium concentration of MB in the solution (mg L−1), K_F and n are Freundlich's parameters, Qm and K_L are Langmui's parameters related to the adsorption capacity and to the adsorption energy.

2.3. Oxidation Fenton Tests

The MB removal experiments were performed at pH3 under magnetic stirring at ambient temperature. 3 g of the catalyst LT-800 was added to one liter of MB solution at 40 mg L^{-1}. After 20 minutes, a desired amount of H_2O_2 solution was added to initiate hydroxyls radical formation by Fenton reaction. Samples were taken at 20 minute intervals to follow the reactions. The MB concentrations, were calculated with a calibration curve and absorbance measured at the maximum wavelengths (291 and 661 nm) using an UV–vis spectrophotometer. The intermediate products were observed using a Dionex 3000 Ultimate HPLC System having a UV detector.

3. Results

3.1. Characterisation

The textural data of LT-800 are summarized in Table 1. The Laterite has weak porosity with low surface area and pore volume. The LT-800 is mainly composed of mesopores.

The values of the MB adsorption parameters for Langmuir and Freundlich models and of the correlation coefficients R2 are summarized in Table 2. The curve Qe = f (Ce) represented in Figure 3 illustrated the isotherm of MB adsorption on LT-800. According to the classification of the isotherms appearance for molecules adsorption in liquid phase made by Gilles, al (1960), the isotherm looks like type L. The MB molecules were fixed on the laterite sites until their saturation and it became difficult for the MB to find a free site. The correlation coefficient for the Langmuir and Freundlich isotherms are close to one so the MB adsorption on LT-800 fits both of the models. The value of the Freundlich constant K_F , superior to 4, could indicate that there was an affinity relatively high between the MB molecules and the LT-800 (Nouzha, 2016).

3.2. Methylene blue removal by Fenton process usingLT-800

The MB removal rate was respectively 19 and 96% in adsorption (LT-800) and in Fenton oxidation (LT-800/H2O2) for the same reaction time, as shown in Figure 4. Hydrogen peroxide can't itself remove pollutant. Therefore, these results indicate that the removal of MB in oxidation Fenton was effectively done by the hydroxyl radical produce through the Fenton reagent and not only by adsorption.

MB molecule has two aromatic rings Figure 1. Figure 5 represents the UV-Vis spectrum obtained during MB removal by adsorption and by the Fenton oxidation using LT-800. The UV-Vis spectrum of a MB solution has two main peaks: around 291 and 661 nm. It assumes that the aromatic rings are responsible of the peak at 291 nm. It has been noticed that after 100 minutes of treatment, the peaks at 291 nm 661 nm almost disappeared in case of the Fenton oxidation and just a small decrease was observe during the adsorption kinetics. The disappearance of the peak located at 291 nm can be attributed to the degradation of aromatics rings.

HPLC chromatograms in Figure 6 show the degradation. Only MB peak was observed for the first 20 minutes. News peaks, which can be attributed to the degradation products, appeared after the H_2O_2 add at t = 20min. These results are in good agreement with the spectrum UV-Vis. The concentration of the degradation products and of the MB molecules decreased gradually as the hydroxyl radicals were produced during the reaction.

In order to check the stability of the catalyst, leaching tests were carried out. The concentration of iron ions in the solution was 0.08mg L^{-1}. It can be deduced that the catalytic activity was essentially heterogeneous. The degradation was mainly due to the catalyst LT-800, and not to the leached iron ions.

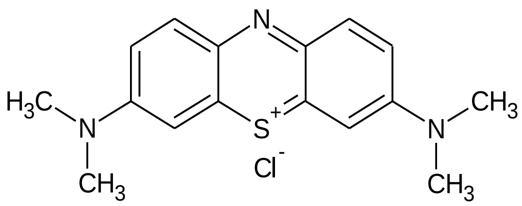

Figure 1: Chemical structure of Methylene blue**.**

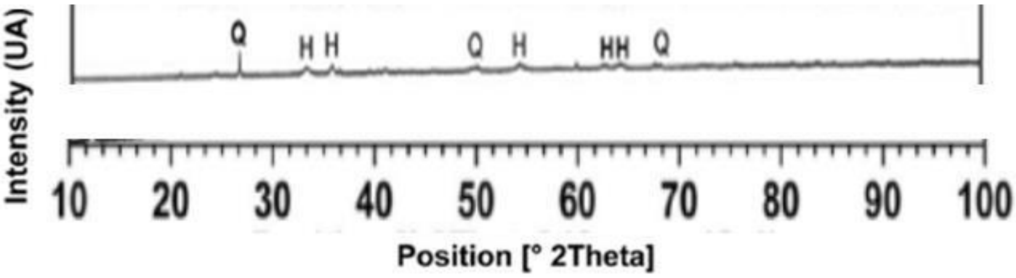

Figure 2: XRD pattern of Laterite from Dano heat treated at 800°C adapted from

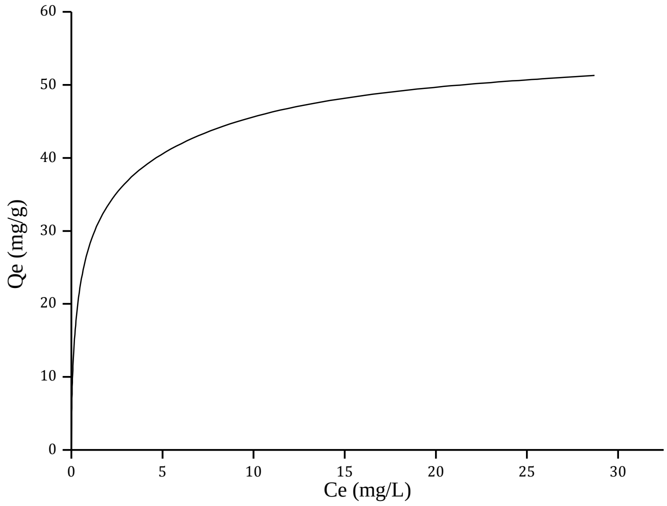

Figure 3: MB Adsorption Isothermes of MB on LT 800

Table 1: Porosity characteristics of LT-800

Textural property	**Value**
Surface Area [m² g]	7
Pore Volume [cm³ g-1] at p/po = 0.99	0.047
BJH mesopore volume [cm3 g–1]	0.024
Average pore size diameter [nm]	25.6

Table 2. Langmuir and Freundlich models parameters

Freundlich			**Langmuir**		
1/n	**KF**	**R2**	**Qm**	**KL**	**R2**
0.16	31.77	0.99	46.44	9.71	0.99

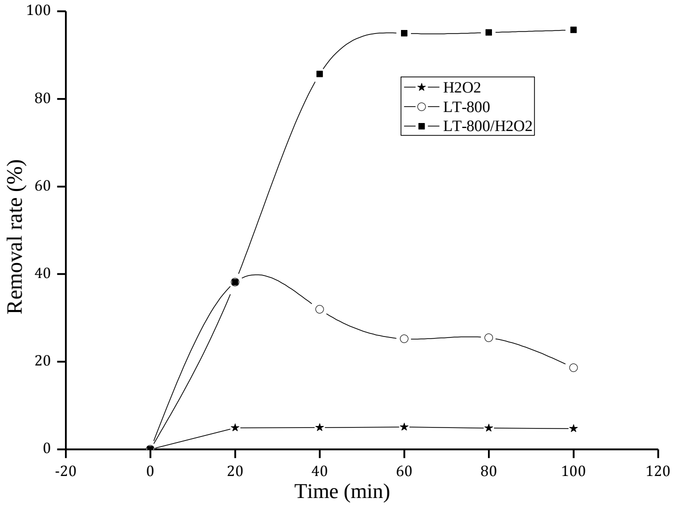

Figure 4: Comparison of MB removal kinetic by adsorption and Fenton oxidation using the catalyst LT-800

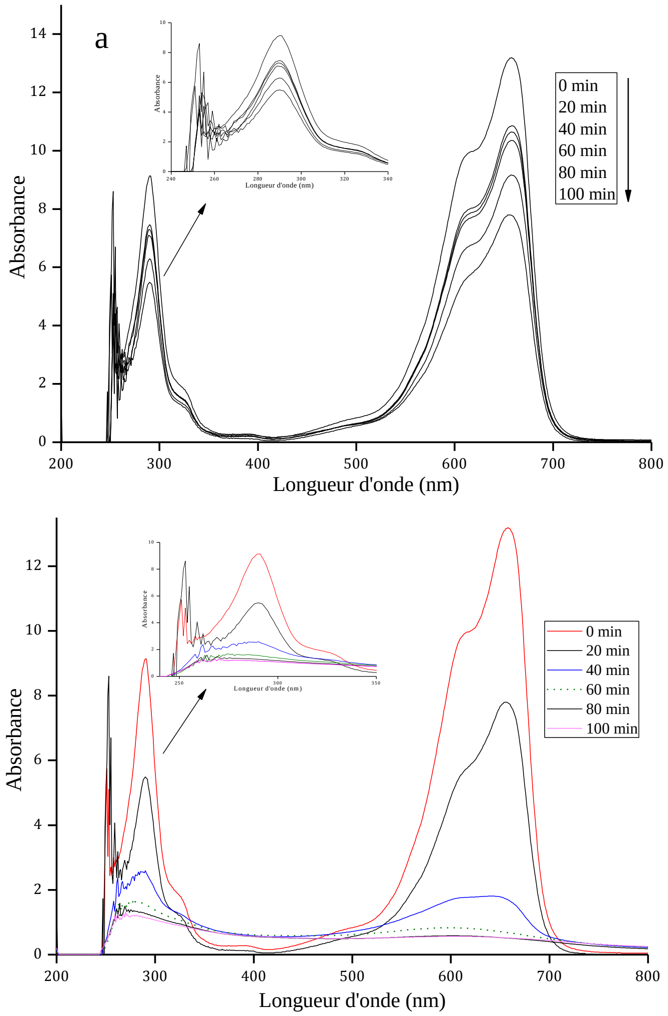

Figure 5: Spectrum UV / Visible MB treatment by a. adsorption b. Fenton process using LT-800

Operationg conditions:[BM] 0 = 40 mg.L^{-1}, [LT-800] = 3 g.L-1, [H_2O_2] = 25 mg.L-1, pH= 3, T = 25°C, Speed stirring =230 trs/min

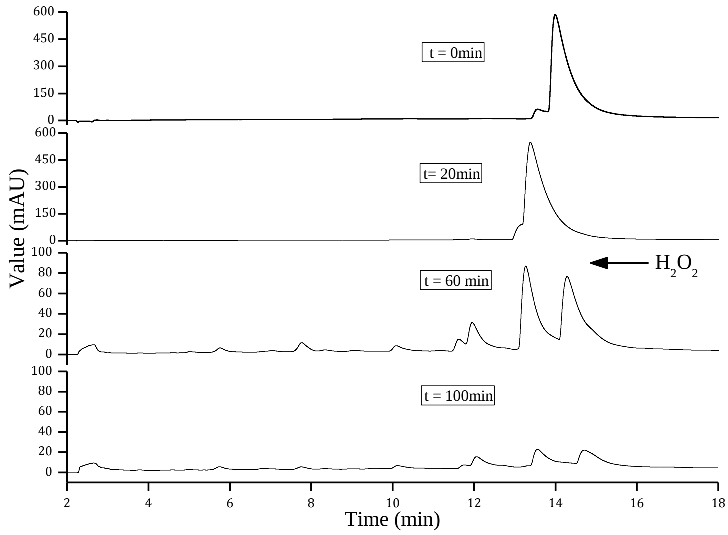

Figure 6: HPLC chromatograms at 291 nm during MB removal by Fenton process using LT-800
Operationg conditions:[BM] 0 = 40 mg.L-1, [Latérites] = 3 g.L-1, [H2O2] = 25 mg.L-1, pH= 3, T = 25°C, Speed stirring =230 trs/min

References

Fukuchi, S., Nishimoto, R., Fukushima, M., and Zhu, Q. (2014). Effects of reducing agents on the degradation of 2,4,6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite. Appl. Catal. B Environ. 147, 411–419.

Kenda, E.S., Py, X., N'Tsoukpoe, K.E., Coulibaly, Y., and Sadiki, N. (2017). Thermal Energy Storage Materials Made of Natural and Recycled Resources for CSP in West Africa. Waste Biomass Valorization 1–15.

Khataee, A., Salahpour, F., Fathinia, M., Seyyedi, B., and Vahid, B. (2015). Iron rich laterite soil with mesoporous structure for heterogeneous Fenton-like degradation of an azo dye under visible light. J. Ind. Eng. Chem. 26, 129–135.

Le, S.T.T., Ngo, T.T., Khanitchaidecha, W., and Nakaruk, A. (2015). Synthesis of iron/GAC catalyst for wastewater treatment using heterogeneous Fenton reaction. Bull. Mater. Sci. 38, 1039–1042.

Nouzha, B. (2016). Elimination du 2-Mercaptobenzothiazole par voie photochimique et par adsorption sur la bentonite et le charbon actif en poudre.

Tabet, D., Saidi, M., Houari, M., Pichat, P., and Khalaf, H. (2006). Fe-pillared clay as a Fenton-type heterogeneous catalyst for cinnamic acid degradation. J. Environ. Manage. 80, 342–346.