

## Eco-design of heterogeneous Fenton processes using laterite and kaolinite for methylene blue degradation

*Coulibaly Sandotin Lassina<sup>1</sup>, Sangare Drissa<sup>1</sup>, Kone Tiangoua<sup>2</sup>, and Coulibaly Lacina<sup>2</sup>*

<sup>1</sup>Département Environnement et Développement Durable, UFR - Ingénierie Agronomique, Forestière et Environnementale, Université de Man, Man, Côte d'Ivoire

<sup>2</sup>Laboratoire d'Environnement et de Biologie Aquatique, UFR - Sciences et Gestion de l'Environnement, Université Nangui Abrogoua, Abidjan, Côte d'Ivoire

Copyright © 2021 ISSR Journals. This is an open access article distributed under the *Creative Commons Attribution License*, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

**ABSTRACT:** The kaolinite-coating laterite (B catalysts) was used for the efficient degradation of methylene blue (MB) from aqueous solution. Heterogeneous Fenton catalytic oxidation experiments of B catalyst were investigated by changing the effective factors such as amount of laterite and amount of kaolinite. To that end, four (4) types of B catalysts were made: (i) B0 catalyst (50% kaolinite + 50% uncalcined laterite); B1 catalyst (50% kaolinite + 50% laterite calcined at 600°C), B2 catalyst (30% kaolinite + 70 % laterite calcined at 600°C) and B3 catalyst (100 % kaolinite + Iron solution from laterite). The result showed that B2 catalyst exhibits the highest performance with a MB degradation percentage (77%) after 100 min. For analyzing the performance of B2 catalyst, the effects of B2 catalyst amount, pH, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were also studied at 100 min. Kinetic studies were also carried out in this experiment. The results indicated that more than 90% of decolorization was achieved with 60g of B2 catalyst at pH acidic (2 to 3). Moreover, higher MB degradation (≤ 90%) was reported at the presence of H<sub>2</sub>O<sub>2</sub> and B2 catalyst in the reactor. However, only 14% of MB was adsorbed in the presence of H<sub>2</sub>O<sub>2</sub> and without B2 catalyst. On the other hand, it was observed that second-order kinetics (R<sup>2</sup>>0.90) was well fitted in the MB degradation process. Considering the above, kaolinite-coating laterite (B2 catalyst) could be used as efficient, cheap, and eco-friendly catalytic oxidation material for the degradation of MB in aqueous solution.

**KEYWORDS:** Heterogeneous Fenton, Kaolinite, Kinetic parameters, Laterite, Methylene Blue.

### 1 INTRODUCTION

During the past two decades, new regulations concerning bio-recalcitrant pollutants have become necessary given the increased risks to public health and the environment [1]. The bio-recalcitrant compounds that accumulate in water and bottom sediments affect aquatic biota and the overall ecological equilibrium. Thus, several processes such as reverse osmosis precipitation/coagulation and membrane filtration have appeared in order to limit pollution. These techniques are often effective but their high cost prevents their implementation in developing countries. However, the biological processes are not applicable if the effluents to be treated contain non-biodegradable substances or substances which are inhibitory or toxic for the microorganisms and plants used. In addition, conventional physicochemical processes make it possible to compensate for these shortcomings either by completely replacing purification by biological means or by complementary treatment [2]. The Advanced Oxidation Processes (AOPs) is presented as a clean alternative technology among these physicochemical processes [1]. The research that began in the early 1970s and 1980s led to numerous AOPs as ozonation, sonolysis, photocatalysis, Fenton and photo-Fenton processes [3]. AOPs is transformed them into less toxic and/or more easily biodegradable compounds or modifying their characteristics (mobility, toxicity), before possible biological treatment [4]. Among AOPs, Fenton process and its modifications proved effective in the degradation of wide range of bio-recalcitrant compounds present in high-strength wastewater ([5], [6]). The Fenton process is a widely studied and used catalytic method based on the generation of hydroxyl radicals (HO•) from hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with iron ions acting as homogeneous catalyst at acidic pH and ambient conditions [7]. Various types of solids have been considered as heterogeneous Fenton catalysts (i.e. synthetic catalysts and natural catalysts) for the degradation of organic pollutants [8]. Both economic and environmental standpoints and scientific understanding of the complex

catalytic mechanisms underlying the heterogeneous Fenton process, the use of natural catalysts are gaining increasing attention of several researchers ([6], [9]). In this order, clays and iron minerals, like laterite have been proposed as a promising alternative to synthetic catalysts for the decontamination of sediments and wastewater effluents due to their low cost, abundance and eco-friendly nature ([6], [10]). Indeed, laterite is an important natural source of iron widely available in tropical zones ([11] and has considerably low cost, is nontoxic for the environment and exhibits a relatively high thermal and chemical stability [12]. Several researches reported that the laterite was as a source of iron for Fenton processes used for degradation of recalcitrant pollutants in wastewaters and groundwater ([6], [13], [14], [15]). However, several disadvantages arise in its practical application of the classical Fenton process, which are (i) the restricted operational pH range centered around 3 and (ii) the generation of a high amount of iron sludge ([5], ([16]). Indeed, this iron sludge limits the recycling process for further oxidation studies and it requires proper disposal technique or consolidation [17]. This can be overcome by the application of binder like kaolinite for heterogeneous Fenton processes using laterite. In this case, the aim of this study was to design the heterogeneous Fenton processes using laterite and kaolinite as binder elements consolidation (B catalysts) for Methylene Blue (MB) degradation. The first objective was to determine the best B catalyst ratio (laterite + kaolinite) for the MB degradation. Afterward, the effect of best B catalyst ratio amount, pH, and H<sub>2</sub>O<sub>2</sub> on MB degradation were also investigated. On the other hand, the kinetic parameters of MB degradation were studied.

## **2 MATERIAL AND METHODS**

### **2.1 COLLECTION AND PREPARATION OF CATALYSTS MATERIALS**

Laterites and kaolinite used in this work come from Sinematialy (North) and Bingerville (South) in Côte d'Ivoire, respectively. In order to formulate the laterite and kaolinite, these samples were crushed separately and then dried for 72 hours at room temperature. The ground materials were sieved to collect powders with a granularity of less than 250 µm, and which were used to prepare the different catalyst beds. The sieved ground materials (laterite + kaolinite) mixed in distilled water to obtain spherical pellets (B catalysts) of 1 cm in diameter, as shown in Fig. 1. Four (4) types of B catalysts were designed:

- i) B0 catalyst: 50% kaolinite + 50% uncalcined laterite;
- ii) B1 catalyst: 50% kaolinite +50% laterite calcined at 600°C;
- iii) B2 catalyst: 30% kaolinite + 70 % laterite calcined at 600° C;
- iv) B3 catalyst: 100 % kaolinite + Iron solution from laterite.

The last type of spherical powder pellets (B3 catalyst) was obtained from 100 ml of the iron solution obtained with the laterite, which was introduced into a container containing 300 g of kaolinite powder. Moreover, the spherical pellets (B3 catalyst) were calcined at 600°C in order to great accessibility of the iron oxides.



**Fig. 1.** B catalyst (spherical pellet laterite + kaolinite)

### **2.2 CATALYTIC EXPERIMENTS**

#### **2.2.1 CHARACTERISTICS OF UV-VIS SPECTRUM OF MB IN AQUEOUS SOLUTION**

In order to obtain the maximum absorbance, 150 mL of MB (8.70 mg/L) was subjected to a spectral scan from 380 to 710 nm. On the other hand, the degradation of MB in contact with laterite (50 g) was observed over time. Solutions were taken at different time intervals and analyzed with a UV-Vis spectrophotometer Hach DR 5000.

### 2.2.2 MB DEGRADATION CAPACITY OF DIFFERENT B CATALYSTS

The different experiments were performed at room temperature. MB degradation were carried out in 150 mL Erlenmeyer flasks. 50 g of each type spherical pellet (B0 catalyst, B1 catalyst, B2 catalyst, and B3 catalyst) was added with 100 mL MB solutions at concentration of 15.80 mg/L during 100 min. The different tests were performed at pH 3, ratio  $[H_2O_2] / [Fe^{2+}]$  at 15. 8 mol/L amount of 50% hydrogen peroxide (50%  $H_2O_2$ ) solution was added to initiate hydroxyls radical formation by Fenton reaction. The supernatants were taken each 25 min to monitor the variation of MB concentration. The supernatant absorbance was measured at 663 nm, using a UV–vis spectrophotometer and then, their MB concentration was calculated with a calibration curve. The MB degradation efficiency was calculated by using Equation 1:

$$R (\%) = \frac{[MB]_0 - [MB]_t}{[MB]_0} \times 100 \quad (1)$$

where  $[MB]_0$  and  $[MB]_t$  is the initial and at any time “t” concentration of MB in mg/L.

Afterward, the effect of different experimental parameters such as mass of B catalyst ratio, solution pH, and  $H_2O_2$  concentration on percentage removal of MB was also investigated. Each experiment was performed for 100 min and the samples were collected at an interval of 25 min to monitor the variation of MB concentration.

### 2.2.3 EFFECT OF AMOUNT VARIATION ON MB DEGRADATION

The effect of amount of B2 catalyst on the degradation of MB was tested by different amounts of B2 (20, 30, 50, 60, 70, 80 and 90 g), and adding 1.5 mL 50%  $H_2O_2$  and 150 mL of MB solution (8.70 mg/L) at pH 3.0, during 100 min. The initial pH of MB solutions was adjusted to 3 by using 0.1 M NaOH or 0.1M HCl solutions, and ratio  $[H_2O_2] / [Fe^{2+}] = 15$ . The BM degradation percentage was calculated according to equation 1.

### 2.2.4 EFFECT OF PH ON MB DEGRADATION

pH is an important parameter in a Fenton process: the stability of  $H_2O_2$  depends on pH. Concerning pH effect on M B degradation, the reaction medium was composed of 150 mL MB solution (8.70 mg / L), 60 g of B2 catalyst, and ratio  $[H_2O_2] / [Fe^{2+}] = 15$ . pH was varied as 2.00, 3.00, 7.00 and 10.00, respectively, using 1 N NaOH and 1 N  $H_2SO_4$  solutions. The MB degradation percentage was also calculated according to equation 1.

### 2.2.5 EFFECT OF $H_2O_2$ ON BM DEGRADATION

In a Fenton process, hydroxyl radicals are produced with the help of  $H_2O_2$  and catalyst containing iron. This experiment was carried to evaluate the effect of  $H_2O_2$  on removal of MB. In this case, three (3) tests were performed: MB solution +  $H_2O_2$  solution (E1), MB solution +  $H_2O_2$  solution + B2 catalyst (E2), and MB solution + B2 catalyst (E3). Each experiment medium was contained 8.70 mg/L of MB solution, pH at 2, and ratio  $[H_2O_2] / [Fe^{2+}] = 15$ . The removal rate of MB was calculated by using Equation 1.

### 2.2.6 KINETIC STUDIES

Two (2) kinetic models were used to apprehend the performance of the B2 catalyst and the mechanisms of the MB degradation:

- Pseudo-first (1<sup>st</sup>) order kinetics (Equation 2)

$$V = - \frac{d[MB]}{dt} = kC^1 \quad (2)$$

We obtain by integration (with  $C = C_0$  at  $t = 0$ ) only for pseudo-first order kinetics:

$$\ln \frac{C}{C_0} = -kt$$

Where  $C_0$  and C is the initial and at any time “t” concentration of MB (mg/L), and k is the rate constant ( $\text{min}^{-1}$ ).

- Pseudo-second (2<sup>nd</sup>) order kinetics (Equation 3)

$$V = -\frac{d^2C}{dt^2} = k_{app}C^2 \quad (3)$$

We obtain by integration (with  $C = C_0$  at  $t = 0$ ) that for pseudo-second order kinetics:

$$\frac{1}{C} - \frac{1}{C_0} = kt$$

Where  $C_0$  and  $C$  is the initial and at any time “ $t$ ” concentration of MB (mg/L), and  $k$  is the rate constant ( $\text{min}^{-1}$ ).

### 3 RESULT AND DISCUSSIONS

#### 3.1 UV-VIS SPECTRUM OF MB IN AQUEOUS SOLUTION

Fig. 2 depicts the spectral evolution of the MB solution during Fenton oxidation using raw laterite. The dye spectrum is characterized by one band in the visible region located at 600 and 700 nm, with a maximum located at 663 nm. [18] also reported that similar band in the visible region was observed at 664 nm originating from an extended chromophore, comprising aromatic ring during Fenton-like degradation of MB using paper mill sludge-derived magnetically separable heterogeneous. The absorbance peaks in the visible region is due to the chromophore-containing azo linkage [19]. On the other hand, this disappearance indicates the destruction of the chromophoric groups responsible for the color conjugated system) and the UV absorption ([6], [20]). Besides, the degradation intensity of the dye MB solution decreased with time in the presence raw laterite as catalyst. Moreover, the maximum MB degradation was observed at 100 min reaction time (Fig. 2b). Then, 100 min reaction time was used for the following experiments of MB degradation process in this study.

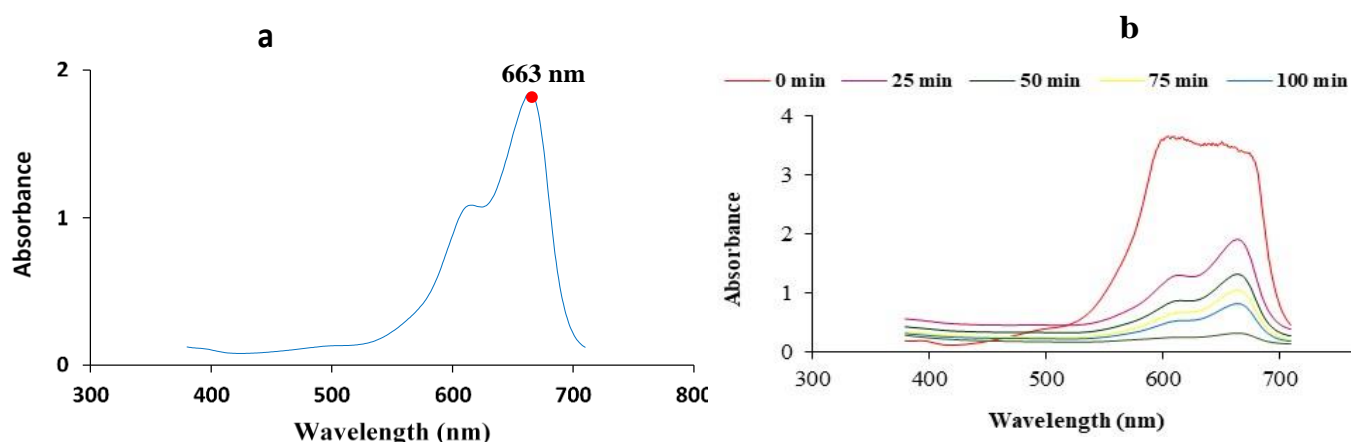


Fig. 2. (a) UV-Vis absorption spectra of MB solution; (b) UV-Vis absorption spectra during MB Fenton degradation using raw laterite

#### 3.2 DEGRADATION CAPACITY OF DIFFERENT B CATALYSTS

The performance of different B catalysts (spherical pellets laterite + kaolinite) on the MB degradation are presented in Fig. 3. After 100 min reaction time, the MB degradation rate was 77%, 76 %, 73%, and 51 % for B2 catalyst, B0 catalyst, B1 catalyst and B3 catalyst, respectively. The result showed that B2 catalyst (30% kaolinite + 70% laterite calcined at 600° C) exhibits the highest performance with a MB degradation rate of 77% after 100 min of treatment at room temperature. It can be explained due the increase the amount of free iron oxides available at the surface of the catalyst during the raw laterite calcination. Indeed, the calcination is an option to improve the catalytic activity of every solid catalyst, as clays [21], and laterite [6]. In addition, this experiment showed that the best ratio spherical powder pellets for MB degradation was B2 catalyst (30% kaolinite + 70 % laterite calcined at 600° C), which was considered in the subsequent experiments to optimize other parameters.

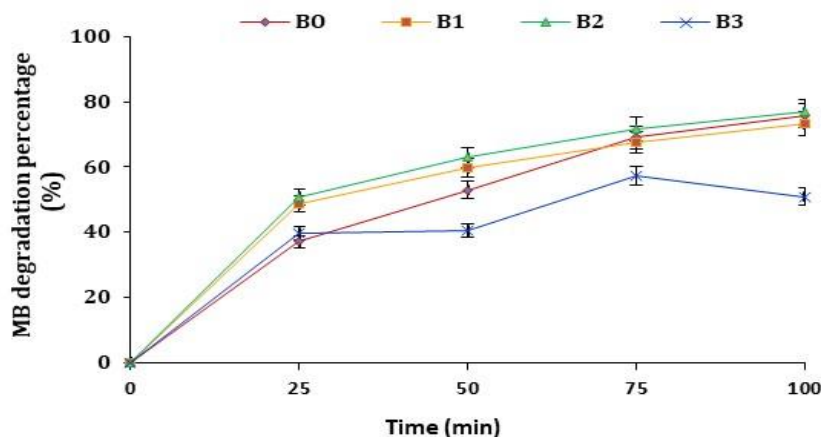


Fig. 3. MB degradation on different B catalysts. [MB solution (8.40 mg/L);  $[H_2O_2] / [Fe^{2+}] = 15$ ; pH 3;  $T = 25^\circ C$ ; reaction time = 100 min]

### 3.3 EFFECT OF B2 CATALYST AMOUNT VARIATION ON MB DEGRADATION

Fig. 4 depicts the effect of amount on MB degradation percentage. The result showed that MB removal efficiency increased B2 catalyst mass increase. With the increase in the amount of B2 catalyst from 20 to 90g, the removal efficiency of MB increased to 96.81%. This is due to the increase of the catalytic active sites on the surface of the catalyst and the associated generated free hydroxyl radicals [22] and availability of more iron-active sites for the decomposition of  $H_2O_2$  [23]. This result showed that more than 96% of decolorization was achieved with 60g of B2 catalyst, and a further increase of the of B2 catalyst mass slightly affects the MB degradation due to agglutination of the adsorbent particles. It can be concluded that 60g of B2 catalyst has excellent potency for MB degradation among other B2 catalysts. However, when the amount of B2 catalyst increased over 60g, the degradation efficiency did not change so much. This phenomenon is attributed to the scavenging effect of  $HO^\bullet$  radicals during unwanted side reactions over the B2 catalyst surface, resulting in a reduction of the availability of  $HO^\bullet$  and MB degradation efficiency ([6], [24]). This inhibition effect caused by excess catalyst playing a role as a scavenger of OH radicals [18]. The optimized B2 catalyst amount was found to be 60g, which was considered for subsequent experiments to optimize other parameters.

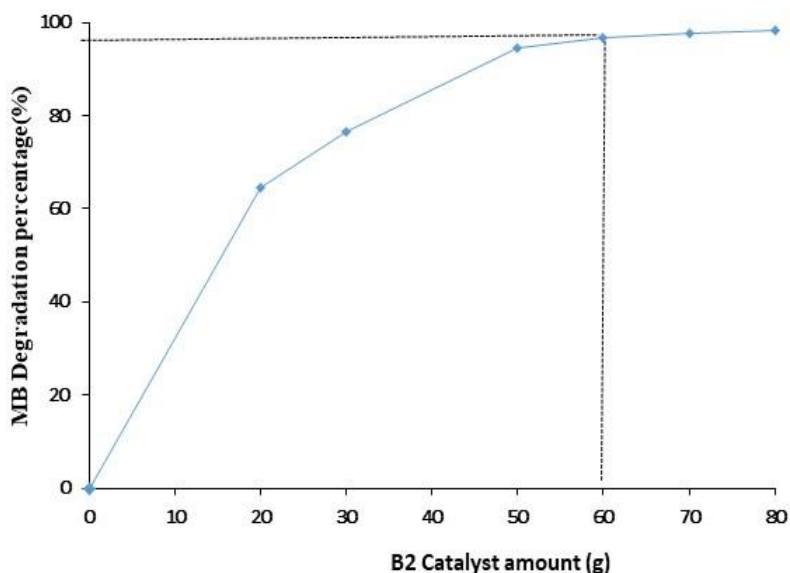


Fig. 4. Effect of mass variation on MB degradation using B2 catalyst. [MB solution (8.40 mg / L);  $[H_2O_2] / [Fe^{2+}] = 15$ ;  $T = 25^\circ C$ ; reaction time = 100 min]

### 3.4 EFFECT OF PH ON MB DEGRADATION

Fig. 5 shows the effect of varying pH from 2 to 10 on the degradation of MB. The result indicates that the MB removal efficiencies were higher than 90% with acidic pH (2.0 to 3.0), and reached at neutral pH (7.0). Interestingly, MB removal (95 %) at pH 2.0 was the

most efficient heterogeneous Fenton process in this present study. The high degradation rate at acidic pH is related to producing high amount of hydroxyl radicals in solution. This finding is in broad agreement with earlier works ([25], [26]), which indicating maximum performance of MB removal at acidic pH. However, their studies showed that high MB removal efficiency was found at pH 3.0. In contrast, the less efficiency for MB degradation was observed at alkaline solution (pH=10.0). In this condition, the oxide ion (O<sup>-</sup>) formation usually occurs instead of hydroxyl radicals [27], which reduces the removal efficiency. Furthermore, this removal rate inhibition occurred due to the formation of negatively charged dye molecules and radicals ([25], [28]). On contrary, [24] reported that the maximum degradation efficiency of MB is 100% in the pH region of 9–12 on laterite-coating manganese dioxide nanoparticle material. Based on the obtained results while varying the pH values, pH 2 was considered as the most favourable pH for the removal of MB using B2 catalyst.

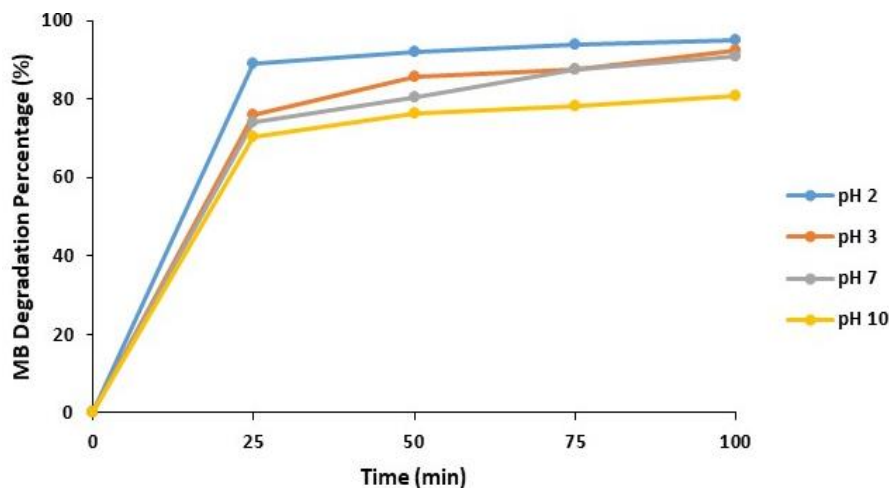


Fig. 5. Effect of pH on BM degradation using B2 catalyst. [B2 catalyst = 60g; MB solution (8.40 mg / L); [H<sub>2</sub>O<sub>2</sub>] / [Fe<sup>2+</sup>] =15; T=25°C; reaction time= 100 min]

### 3.5 EFFECT OF H<sub>2</sub>O<sub>2</sub> ON MB DEGRADATION

The effect of the without and/or presence H<sub>2</sub>O<sub>2</sub> on MB degradation after 100 min is shown in Fig. 6. The result indicates that only 14.30% of MB was adsorbed after 100 min in the presence of H<sub>2</sub>O<sub>2</sub> and without B2 catalyst (E1). The lower MB degradation confirm that H<sub>2</sub>O<sub>2</sub> itself cannot oxidize MB. This result is in good agreement with [6] for their experiment performed in the presence of H<sub>2</sub>O<sub>2</sub> and without catalyst resulted in nearly no MB removal. This may be due to the fact that H<sub>2</sub>O<sub>2</sub> was stable at room temperature, and the reaction rate was extremely slow without the presence of catalysts [18]. However, the MB efficiency degradation increased to reach 74.0 % with the addition B2 catalyst and without H<sub>2</sub>O<sub>2</sub> (E3). This MB degradation increase is correlated with the increase of the adsorption sites provided by B2 catalyst in this test (E3). Interestingly, the experiment (E2) performed in the presence of H<sub>2</sub>O<sub>2</sub> and B2 catalyst resulted in higher MB degradation (91.40%). Higher MB degradation (91.40%) can be explained due of the boost HO<sup>•</sup> generated by H<sub>2</sub>O<sub>2</sub> over the B2 catalyst surface [6]. Indeed, hydroxyl radicals are produced with the help of H<sub>2</sub>O<sub>2</sub> and catalyst containing iron in a Fenton process.

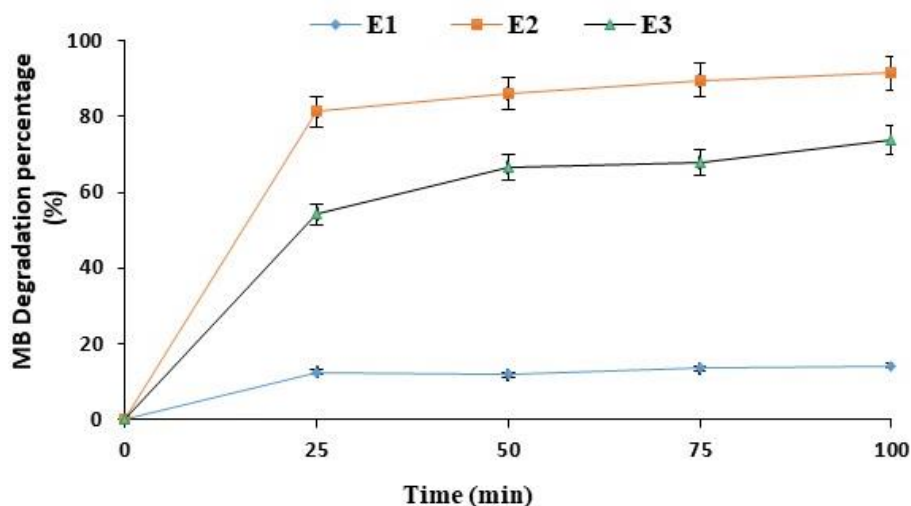


Fig. 6. Effect of  $H_2O_2$  on the heterogeneous Fenton process with B2 catalyst. [B2 catalyst = 60g; MB solution (8.40 mg/L);  $[H_2O_2] / [Fe^{2+}] = 15$ ; pH 2,  $T=25^\circ C$ ; reaction time= 100 min, E1 (MB +  $H_2O_2$ ); E2 (MB +  $H_2O_2$  + B2 catalyst); E3 (MB + B2 catalyst)]

### 3.6 MATHEMATICAL MODELING OF MB DEGRADATION KINETICS

#### 3.6.1 EFFECT OF B2 CATALYST AMOUNT

indicates the pseudo-first order and pseudo-second order kinetics parameters showing kinetics improvement with the increase of B2 catalyst amount. Fig. 7 a b demonstrates that, the correlation coefficient  $R^2$  values of  $\leq 0.9000$  (e.g.  $R^2 = 0.8963$  to  $0.8457$ ) for 1<sup>st</sup> order model, and for the 2<sup>nd</sup> order model is  $\geq 0.9000$  (e.g.  $R^2 = 0.9675$  to  $0.9947$ ). It clearly indicates that the 2<sup>nd</sup> order degradation kinetics model was best fitted than 1<sup>st</sup> order model. The rate constants are also significantly increased from  $0.0014$ - $0.0340 \text{ min}^{-1}$ . The good agreement of the data with the pseudo-second-order kinetics model suggested that chemisorptions could be the dominant mechanism that rules the MB degradation by B2 catalyst. Contrary phenomenon has been observed in the MB degradation on laterite calcined by [6], and which 1<sup>st</sup> order degradation kinetic was best than fitted than 2<sup>nd</sup> order.

Table 1. Parameters of pseudo first order kinetic and pseudo-second kinetic model related to B2 catalyst mass for MB degradation

B2 catalyst amount (g)	Pseudo-first order kinetic		Pseudo-second order kinetic		MB degradation percentage (%)
	$k_1 (\text{min}^{-1})$	$R^2$	$k_2 (\text{min}^{-1})$	$R^2$	
20	0.0064	0.8963	0.0014	0.9675	64.42
30	0.0092	0.8802	0.0025	0.9817	76.41
50	0.0187	0.9229	0.0127	0.9869	94.68
60	0.0231	0.7846	0.0227	0.9939	96.81
70	0.0246	0.8190	0.0293	0.9944	97.11
80	0.0254	0.8457	0.0340	0.9947	98.21

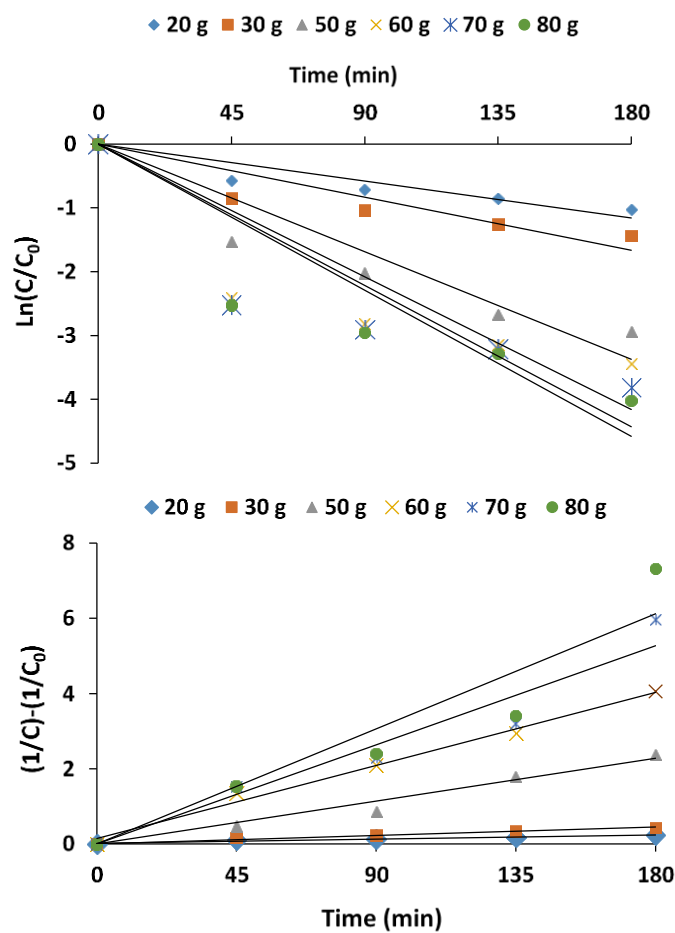


Fig. 7. Plots of kinetics degradation of MB according to pseudo-first-order (a) and pseudo-second order (b) related to B2 catalyst amount

### 3.6.2 EFFECT OF PH ON MB DEGRADATION

summarizes the pseudo-first order and pseudo-second order kinetics parameters showing kinetics improvement with acidics pH (2-3). The high value of the linear coefficient of determination (e.g.  $R^2 = 0.9762$  to  $0.9923$ ) as shown in Fig. 8ab and also summarized in This result confirmed that the pseudo-second order kinetic model is best fitted than the pseudo-first order kinetic for evaluate the effect of pH on MB degradation. On the other hand, the highest kinetic constant ( $K_2 = 0.0248 \text{ min}^{-1}$ ,  $R^2 = 0.9762$ ) of heterogeneous Fenton reaction over the B2 catalyst was achieved at pH 2 with 95.14% MB degradation.

Table 2. Parameters of pseudo first order kinetic and pseudo-second kinetic model related to pH values for MB degradation using B2 catalyst

pH	Pseudo-first order kinetic		Pseudo-second order kinetic		MB degradation percentage (%)
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{min}^{-1}$ )	$R^2$	
2.00	0.0370	0.7587	0.0248	0.9762	95.14
3.00	0.0292	0.8832	0.0135	0.9800	92.45
7.00	0.0127	0.9069	0.0113	0.9923	90.82
10.00	0.0203	0.7325	0.0058	0.9258	80.96



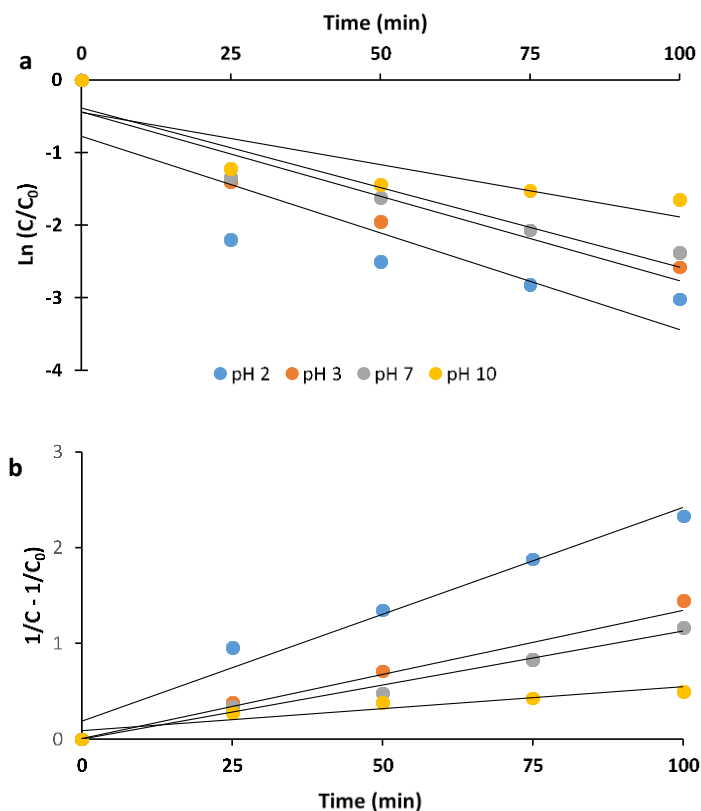


Fig. 8. Plots of kinetics degradation of MB according to pseudo-first-order (a) and pseudo-second order (b) related to pH values using B2 catalyst

### 3.6.3 EFFECT OF H<sub>2</sub>O<sub>2</sub> ON MB DEGRADATION

summarizes the pseudo-first order and pseudo-second order kinetics parameters showing an actual kinetics improvement with the presence simultaneous of H<sub>2</sub>O<sub>2</sub> and B2 catalyst in reactor. Similar to previous experiments, Fig. 9 a b shows that, the correlation coefficient R<sup>2</sup> values of  $\leq 0.8500$  (e.g. R<sup>2</sup><sub>E1</sub> = 0.6351; R<sup>2</sup><sub>E2</sub> = 0.8023; R<sup>2</sup><sub>E3</sub> = 0.8502) for 1<sup>st</sup> order model, and for the 2<sup>nd</sup> order model is  $\geq 0.9000$  (e.g. R<sup>2</sup><sub>E1</sub> = 0.9623; R<sup>2</sup><sub>E2</sub> = 0.9771; R<sup>2</sup><sub>E3</sub> = 0.9559). It clearly indicates that the 2<sup>nd</sup> order degradation kinetics model was best fitted than 1<sup>st</sup> order model. Moreover, the experiment performed in the presence of H<sub>2</sub>O<sub>2</sub> and B2 catalyst (E2) has highest rate constant ( $k_2 = 0.0130 \text{ min}^{-1}$ ) and highest MB degradation percentage (91.41%). It confirms that degradation of MB may be due to the hydroxyl radicals are produced with the help of H<sub>2</sub>O<sub>2</sub> and B2 catalyst containing iron in heterogeneous Fenton process.

Table 3. Parameters of pseudo first order kinetic and pseudo-second kinetic model related to H<sub>2</sub>O<sub>2</sub> for MB degradation

Experiments	Pseudo-first order kinetic		Pseudo-second order kinetic		MB degradation percentage (%)
	$k_1 (\text{min}^{-1})$	R <sup>2</sup>	$k_2 (\text{min}^{-1})$	R <sup>2</sup>	
E1	0.0019	0.6351	0.0002	0.9623	14.29
E2	0.0296	0.8023	0.0130	0.9771	91.41
E3	0.0156	0.8502	0.0034	0.9559	73.77

E1 (MB + H<sub>2</sub>O<sub>2</sub>); E2 (MB + H<sub>2</sub>O<sub>2</sub> + B2 catalyst); E3 (MB + B2 catalyst)

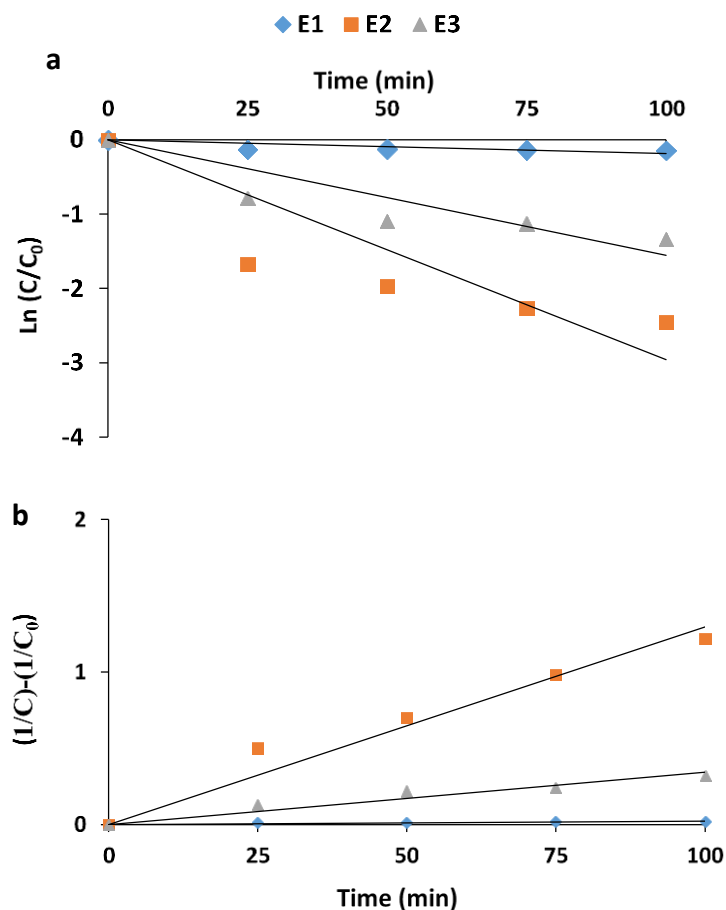


Fig. 9. Plots of kinetics degradation of MB according to pseudo-first-order (a) and pseudo-second order (b) related to  $H_2O_2$

#### 4 CONCLUSION

The heterogeneous Fenton catalytic oxidation experiments of kaolinite-coating laterite (B catalysts) were investigated by changing the effective factors such as amount of laterite and amount of kaolinite for Methylene Blue (MB) degradation. The results showed that B2 catalyst (30% kaolinite + 70 % laterite calcined at 600° C) exhibits the highest performance with a MB degradation rate (77%) after 100 min at room temperature conditions. Afterward, the effects of B2 catalyst amount, solution pH, and hydrogen peroxide ( $H_2O_2$ ) were also studied at 100 min for analyzing the performance of B2 catalyst. The results demonstrate that more than 90% of decolorization was achieved with 60g of B2 catalyst at pH acidic (2 to 3). Moreover, higher MB degradation ( $\leq 90\%$ ) was reported at the presence of  $H_2O_2$  and B2 catalyst in the reactor. On contrary, only 14% of MB was adsorbed in the presence of  $H_2O_2$  and without B2 catalyst. On the other hand, the MB degradation kinetics were performed for both pseudo-first order and second-order, it was observed that second-order kinetic ( $R^2 > 0.90$ ) was well fitted in the treatment process. Besides, mathematical models were also built for the correlation of the kinetic constants with the pH value,  $H_2O_2$ , and B2 catalyst mass. Based on these catalytic performances, kaolinite-coating laterite (B2 catalyst) could be used as efficient, cheap, and eco-friendly catalytic oxidation material for the degradation of MB in aqueous solution.

## REFERENCES

- [1] M. Azri and D. Zeroual, "Traitement d'effluents pétrochimiques par procédés Electro-Fenton. Étude électrochimique sur la réaction de réduction d'oxygène pour la génération du peroxyde d'hydrogène," *Revue des Energies Renouvelables*, vol. 16, no. 1, pp. 11-22, 2013, <https://www.asjp.cerist.dz/en/article/121005>.
- [2] R. Gallay, *Etude de la dégradation de composés récalcitrants par le procédé photo-Fenton couplé à une biomasse immobilisée*. Mémoire de Master, Ecole polytechnique Fédérale de Lausanne, Suisse, p.89, 2006.
- [3] N. Kulik, M. Trapido, A. Goi, Y. Veressinina, and R. Munter, "Combined chemical treatment of pharmaceutical effluents from medical ointment production," *Chemosphere*, vol.70, no. 8, pp. 1525-1531, 2008, doi: 10.1016/j.chemosphere.2007.08.026.
- [4] V. Flotron, *La réaction de Fenton comme procédé de réhabilitation dans le traitement des eaux: application à la dégradation des hydrocarbures aromatiques polycycliques dans les eaux et les boues résiduelles*. Thèse de Doctorat. Institut National Agronomique Paris-Grignon. Paris. France. p.355, 2004.
- [5] M. Trapido, T. Tenno, A. Goi, N. Dulova, E. Kattel, D. Klauson, and M. Viisimaa, "Bio-recalcitrant pollutants removal from wastewater with combination of the Fenton treatment and biological oxidation," *Journal of Water Process Engineering*, vol.16, pp. 277–282, 2017, doi: 10.1016/j.jwpe.2017.02.007.
- [6] G.M.R. Kpinsoton, H. Karoui, Y. Richardson, B.N.S. Koffi, H. Yacouba, J. Motuzas, and A. Lawane Gana, "New insight into the microstructure of natural calcined laterites and their performance as heterogeneous Fenton catalyst for methylene blue degradation. Reaction Kinetics, Mechanisms and Catalysis," vol.124, no.2, pp. 931–956, 2018, doi: 10.1007/s11144-018-1406-0.
- [7] H.J.H. Fenton, "Oxidation of tartaric acid in presence of iron," *Journal of the Chemical Society, Transactions*, vol. 65, pp. 899–910, 1894, doi.org/10.1039/ct8946500899.
- [8] P.V. Nidheesh, "Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review," *RSC Advances*, vol. 5, pp. 40552–40577, 2015, <https://doi.org/10.1039/C5RA02023A>.
- [9] E.G. Garrido-Ramirez, B.K. Theng, and M.L. Mora, "Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions-a review," *Applied Clay Science*, vol. 47, pp.182–192, 2010, <https://doi.org/10.1016/j.clay.2009.11.044>.
- [10] A. Khataee, F. Salahpour, M. Fathinia, B. Seyyedi, and B. Vahid, "Iron rich laterite soil with mesoporous structure for heterogeneous Fenton-like degradation of an azo dye under visible light," *Journal of Industrial and Engineering Chemistry*, vol. 26, pp. 129–135, 2015, <https://doi.org/10.1016/j.jiec.2014.11.024>.
- [11] L.S. Coulibaly, *Abattement des phosphates des eaux usées par adsorption sur des géomatériaux constitués de Latérite, Grès et schistes ardoisiers*. Thèse de Doctorat. Université Lorraine, France/Université Nangui Abrogoua, Abidjan. Côte d'Ivoire, p. 233, 2014.
- [12] L. Zhang, S. Hong, J. He, F. Gan, and Y.S. Ho, "Adsorption characteristic studies of phosphorus onto laterite," *Desalination and Water Treatment*, vol. 25, no.1-3, pp.98–105, 2011, <https://doi.org/10.5004/dwt.2011.1871>.
- [13] B. Manu, and Mahamood, "Degradation of paracetamol in aqueous solution by Fenton Oxidation and Photo-Fenton Oxidation processes using Iron from Laterite soil as catalyst," *International Journal of Earth Sciences and Engineering*, vol.4, no.6, pp. 1103–1110, 2011.
- [14] T. Koottatop, V.H.N. Phong, S.K. Chapagain, A. Panuvatvanich, C. Polprasert, and K.H. Ahn, "Potential of laterite soil coupling fenton reaction in acetaminophen (ACT) removal in constructed wetlands," *Water Air and Soil Pollution*, vol. 228, no.8, 283, 2017, <https://doi.org/10.1007/s11270-017-3454-x>.
- [15] R.D. Ouedraogo, C. Bakouan, B. Sorgho, B. Guel, and L.D. Bonou, "Characterization of a natural laterite of Burkina Faso for the elimination of arsenic (III) and arsenic (V) in groundwater," *International Journal of Biological and Chemical Sciences*, vol.13, no. 6, pp. 2959-2977, 2019. DOI: 10.4314/ijbcs.v13i6.41.
- [16] S. Karthikeyan, A. Titus, A. Gnanamani, A.B. Mandal, and G. Sekaran, "Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes," *Desalination*, vol. 281, pp.438–445, 2011, <https://doi.org/10.1016/j.desal.2011.04.011>.
- [17] S. Sangami, and B. Manu, "Catalytic efficiency of laterite-based FeNPs for the mineralization of mixture of herbicides in water," *Environmental Technology*, pp. 1–13, 2018, doi: 10.1080/09593330.2018.144989.
- [18] G. Zhou, Z. Chen, F. Fang, Y. He, H. Sun, and H. Shi, "Fenton-like degradation of Methylene Blue using paper mill sludge-derived magnetically separable heterogeneous catalyst: Characterization and mechanism," *Journal of Environmental Sciences*, vol. 35, pp. 20–26, 2015, <http://dx.doi.org/10.1016/j.jes.2015.01.026>.
- [19] C. Bauer, P. Jacques, and A. Kalt, "Photooxidation of an azo dye induced by visible light incident on the surface of TiO<sub>2</sub>," *Journal of Photochemistry and Photobiology A: Chemistry*, vol.140, pp. 87-92, 2001, [https://doi.org/10.1016/S1010-6030\(01\)00391-4](https://doi.org/10.1016/S1010-6030(01)00391-4).
- [20] J.H. Ramirez, C.A. Costa, L.M. Madeira, G. Mata, M.A. Vincent, M.L. Rojas-Cervantes, and R.M. Martin-Aranda, "Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay," *Applied Catalysis B Environmental*, vol. 71, no.1, 44-56, 2007, DOI: 10.1016/j.apcatb.2006.08.012.
- [21] N. Duwal, S. Joshi, and J. Bhattarai, "Study on the Removable of Methylene Blue by Calcined Kamerotar Clays as an Eco-Friendly Low Cost Adsorbent," *International Journal of Advanced Research in Chemical Science*, vol.3, no.11, pp. 1-8, 2016, DOI: <http://dx.doi.org/10.20431/2349-0403.0311001>.

- [22] M.E. Becerra, A.M. Suarez, N.P. Arias, and O. Giraldo, "Decomposition of the methylene blue dye using layered manganese oxide materials synthesized by solid state reactions," *International Journal of Chemical Engineering*, pp.1-11, 2018, DOI: 10.1155/2018/4902376.
- [23] Z. Sun, C. Xiao, and F. Hussain, "Synthesis of stable and easily recycled ferric oxides assisted by Rhodamine B for efficient degradation of organic pollutants in heterogeneous photo-Fenton system," *Journal of Cleaner Production*, vol. 196, pp. 1501–1507, 2018. DOI: 10.1016/j.jclepro.2018.06.122.
- [24] T.-H. Le, T. H. A. Ngo, V. T. Doan, L. M. T. Nguyen, and M. C. Le, "Preparation of Manganese Dioxide Nanoparticles on Laterite for Methylene Blue Degradation," *Journal of Chemistry*, pp. 1–9, 2019, doi: 10.1155/2019/1602752.
- [25] A. R. Khataee, and S. G. Pakdehi, "Removal of sodium azide from aqueous solution by Fentonlike process using natural laterite as a heterogeneous catalyst: Kinetic modeling based on nonlinear regression analysis," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no.5, pp. 2664-2672, 2014, <https://doi.org/10.1016/j.jtice.2014.08.007>.
- [26] S. Punathil, D. Ghime, T. Mohapatra, C. Thakur, and P. Ghosh, "Fixed Bed Reactor for Removal of Methylene Blue Dye Using Heterogeneous Fenton Catalyst," *Journal of Hazardous, Toxic, and Radioactive Waste*, vol. 24, no.4, 04020037, 2020.
- [27] K., Gaddam, and H. M. Cheung, "Effects of pressure, temperature, and pH on the sonochemical destruction of 1, 1, 1-trichloroethane in dilute aqueous solution," *Ultrasonics Sonochemistry*, Vol.8, no.2, pp.103–109, 2001, [https://doi.org/10.1016/S1350-4177\(00\)00032-8](https://doi.org/10.1016/S1350-4177(00)00032-8).
- [28] Y. Yavuz, A. S. Kopalal, A. Artik, and U. B. Ögütveren, "Degradation of C.I. basic Red 29 solution by combined ultrasound and Co<sup>2+</sup>-H<sub>2</sub>O<sub>2</sub> system," *Desalination*, vol. 249, no.2, pp. 828–831, 2009, <https://doi.org/10.1016/j.desal.2008.10.036>.