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RESEARCH ARTICLE

PHOTOCHEMICAL REMOVAL OF METHYLENE BLUE IN AQUEOUS SOLUTION

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ABSTRACT

Methylene blue (MB) is a synthetic dye widely used in textile industries. This work describes the application of solar radiation to direct photolysis degradation of methylene blue in aqueous solution. Experiments were conducted at room temperature to study the effects of exposure time, solution volume and MB concentration on dye degradation rates. The results show that the maximum amount of methylene blue removed is 6.8 mg/L, obtained at an initial concentration of 10 mg/L, volume of 50 mL and exposure to solar radiation for 5 hours. These results also point to an increased efficacy of direct photolysis of methylene blue as the dye concentration increases. Kinetic model analysis indicates that the absorption of methylene blue follows a first-order kinetics, with a constant velocity $k = 1,3 \times 10^{-3} \text{ min}^{-1}$. Direct photolysis by solar radiation is an effective method for degrading or even eliminating methylene blue in water.

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INTRODUCTION

Environmental pollution and environmental problems are gaining increasing attention worldwide. The problems of pollution have become an unavoidable reality that threatens the present and future life of man. Human activities produce various forms of pollution on the environment that can lead to harmful effects on fauna, flora and humans themselves [1]. The areas that are generally affected are: air, soil and water. The problem of water pollution is undoubtedly one of the most worrying aspects of the degradation of the natural environment by contemporary civilization [2]. Some of the pollutants used are dyes that, once dissolved in water, will sometimes be difficult to treat because the dyes have a synthetic origin and complex molecular structure that makes them more stable and difficult to biodegrade [3] may therefore constitute factors of risk to our health and nuisances for our environment. Indeed, these wastes contain mostly acid or basic dyes, trace metal elements (ETM, salts, solid suspensions recognized as proven sources of environmental pollution and water quality degradation [4]. In Côte d'Ivoire, the situation is much more worrying due to the lack of effluent treatment systems in artisanal dyers and the poor state of operation of wastewater collection networks. The effluent from these dyeing plants is thus discharged in its raw state into sewers, alleys and pipes to result in surface water and groundwater pollution [5]. The presence and fate of dyes in the environment, even at low concentrations, is a concern for the scientific community given the large number of publications and writings on these chemical compounds called "emerging pollutants".

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This study is concerned with the removal of methylene blue dye by direct photolysis under solar radiation. The monitoring of photodegradation of methylene blue allows to systematically evaluate the rates of abatement in relation to physico-chemical parameters such as exposure time to the sun, volume of the solution and concentration of pollutant. The photodegradation of this molecule was modelled by the Langmuir-Hinshelwood equation, from which the speed constant k and the adsorption equilibrium constant K were evaluated.

MATERIAL AND METHODS

Material: The chemicals and equipment used for this work are: OHAUS/Scout Pro analytical balance (accuracy 0.01g), spectrophotometer UV-Visible absorption of type Hach DR 3900 and digital heating magnetic stirrer of LBX H20D, Methylene blue (C₁₆H₁₈N₃SCl) as a dark green powder, commonly used in the dyeing of cotton, wood and paper (Mehmet *et al.*, 2007). Methylene blue is sensitive to light, so the standard solutions are placed in vials wrapped in aluminum foil.



Spectrophotometer UV-Visible Hach DR 3900



Bottle of methylene blue



BM standard solutions sheltered from light

Optimization method for methylene blue degradation

Factor screening and modelling of a first-degree polynomial: A comprehensive factor plan has been developed to screen factors that may influence the amount of methylene blue. To do this, a number of quantitative factors equal to three are used, namely the time of exposure to the sun, the volume of the solution and the concentration of the solution. This choice is motivated by the fact that the complete factorial plan is one of the simplest plans used in experimental research methodology. To conduct interpretations of the isolated effects and interactions of experimental factors on the responses studied. For a two-level, three-factor factorial plane, there are 23 combinations, or 8 tests performed to optimize the amount of methylene blue removed. Table 1 summarizes the characteristics of the problem to be studied. This experimental approach allows an overview of the impact of factors, regardless of their qualitative or quantitative nature. It also provides the possibilities for statistical processing of data taking into account the nature of these factors. The experimental conditions of the 8 trials are presented in the general experimental design in Table 2. The experimental responses (Y_i) represent the resolutions obtained.

Table 1. Characteristics of the studied's problem

Coded variables	Factors (units)	Experimental field	
		Low level (-1)	High level (+1)
X1	Solution volume (mL)	20	20
X2	Solution concentration (mg/L)	5	10
X3	Exposure time (h)	3	5

Table 2. Experience matrix

N° test	X1	X2	X3	Responses
1	-1	-1	-1	Y1
2	1	-1	-1	Y2
3	-1	1	-1	Y3
4	1	1	-1	.
5	-1	-1	1	.
6	1	-1	1	.
7	-1	1	1	.
8	1	1	1	Y8

Significance of coefficients: A coefficient is considered to be statistically equal to zero and the factor is not taken into account in the model if, in absolute value, this coefficient is less than twice the experimental standard deviation ($|a_i| < 2 \times \sigma_e$). Conversely, a coefficient is considered to be statistically different from zero and the factor is taken into account in the model if $|a_i| > 2 \times \sigma_e$. Interpretation of the coefficients is based on the determination of the magnitude σ_e , representing the experimental standard deviation, calculated using the relation $\sigma_e = \frac{\sigma}{\sqrt{n}}$.

In this relation, σ is the standard deviation calculated from n repetitions of the test at the centre when all factors are quantitative, or from any test where there is at least one qualitative factor. The calculation of σ is done using the relation $\sigma = \sqrt{\frac{\sum_1^n (x_i - \bar{x})^2}{n-1}}$.

Data processing and the different diagrams from the experiment plan were made using Minitab 19 software.

Conditions for carrying out the tests: The tests were carried out by exposing a known volume of MB of known concentration to solar radiation for a well-defined time. The solutions are then recovered and analyzed for residual concentrations using the UV-Visible spectrophotometer.

Determination of the degradation kinetics: The experiments were conducted by exposing a known volume of BM dye solution, with a specified concentration, to solar radiation for a set period of time. The solutions are then recovered and analyzed for residual concentrations using molecular absorption spectrophotometry. The discoloration kinetics was determined using the UV-Visible spectrophotometer at 650 nm wavelength which is in the visible part of the electromagnetic spectrum. This kinetics of degradation of methylene blue involves the determination of the constant speed k , necessary for the determination of the order of the reaction.

The BM bleaching balance equation is written:



The equation of a first-order kinetics is written :

$$V = -\frac{d[BM]}{dt} = k * [C]$$

The integration of this first-order kinetic equation is written:

$$\ln\left(\frac{C_0}{C}\right) = -k * t$$

The speed constant k is determined graphically. Half-life time is obtained by the formula:

$$t_{1/2} = \frac{\ln 2}{k}$$

When the dye is degraded, it is assumed that the order is equal to 1 if the correlation coefficient of the line is very close to 1. Note that t is obtained graphically on the plot of the curve:

$$\ln\left(\frac{C_0}{C}\right) = f(t).$$

The following formula was used to calculate the yields or degradation rates of the dye:

$$\text{Rate} = \frac{[BM]_{\text{initial}} - [BM]_{\text{final}}}{[BM]_{\text{initial}}} \times 100$$

Influence of initial MB concentration: To determine the influence of the initial concentration of methylene blue on photolysis, 50 ml of solution at different concentrations (5 mg/L; 10 mg/L; 20 mg/L; 25 mg/L and 30 mg/L) were exposed to solar radiation for 5 hours. The solutions are then recovered and analyzed for residual concentrations

using the UV-Visible spectrophotometer. Table 3 provides an estimate of the coefficients of the factors. According to Boutaghane & Mekhzem [6], positive sign coefficients contribute to increased adsorption capacity and negative sign coefficients reduce it. In the case of this study, it appears from the table that exposure time positively influences the response, while MB concentration and volume of solution positively influence the response. Thus, for a better elimination of MB in this experimental field, it is necessary to have volumes and concentrations of MB made and a long exposure time to solar radiation.

The first degree model is explained by the equation:

$$Q = 4,63 - 0,84X1 + 0,71X2 - 0,52X3$$

Table 3. Estimation of factor coefficients

Factors	Constant	X1	X2	X3
Coefficients	a ₀	a ₁	a ₂	a ₃
Coefficient values	4,63	-0,841	0,714	-0,529

RESULTS AND DISCUSSION

Optimization of methylene blue removal

Experimental results of the factorial plan : The experiment plan was conducted with eight (2³) trials. The experimental matrix and the experimental results of the quantities eliminated are reported in Table 4. For an initial dye concentration of 10 mg/L and 20 mg/L, the quantities of dyes removed vary between 2.20 mg/L and 6.66 mg/L, representing a yield of 11% to 49.2%, depending on the experimental range chosen. This variation indicates that at least one factor has an influence on the amount of BM removed.

Table 4. Experimental results

Tests	Volume (mL)	Concentration (mg/L)	Time (h)	Quantities disposed (mg/L)	Degradation rate (%)
1	50	10	3	4,92	49,2
2	100	10	3	3,20	32
3	50	20	3	6,49	32,5
4	100	20	3	6,03	30,2
5	50	10	5	3,82	38,2
6	100	10	5	3,73	37,3
7	50	20	5	6,66	33,3
8	100	20	5	2,20	11,0

Pareto diagram : The Pareto diagram of normalized effects (Figure 2) was used to qualitatively identify factors and interactions that influence the effect. This diagram reflects the contribution of each factor in the model [7]. All effects beyond the baseline are significant. According to the Pareto diagram below, the factors that have a significant influence are the volume of the solution (X1) and the time of exposure to the sun (X2). Nevertheless, the concentration of the solution (X3) is almost at the reference line, we considered it as an important factor in the chosen experimental field. Thus, all factors studied in this study are considered to have a significant influence on the amount of MB eliminated. Since the interactions between the different factors do not influence the quantity of MB eliminated, the interaction diagrams were not studied further. The Pareto diagram made it possible to know qualitatively the contribution of the factor studied in the elimination of MB by direct photolysis. However, it does not provide any information on how these factors influence the response.

Main effects diagram: The diagram reflecting the contribution of each factor taken separately in the elimination of MB is given in Figure 3. The average of the quantities of MB eliminated using 50 mL as the volume of the solution is 5.47 mg/L while that obtained using 100 mL is 3.79 mg/L. We therefore observe a drop in the quantity eliminated by 30% when the injection volume increases from 50 mL

to 100 mL. Which demonstrates the strong influence of the volume of the solution on the elimination of MB.

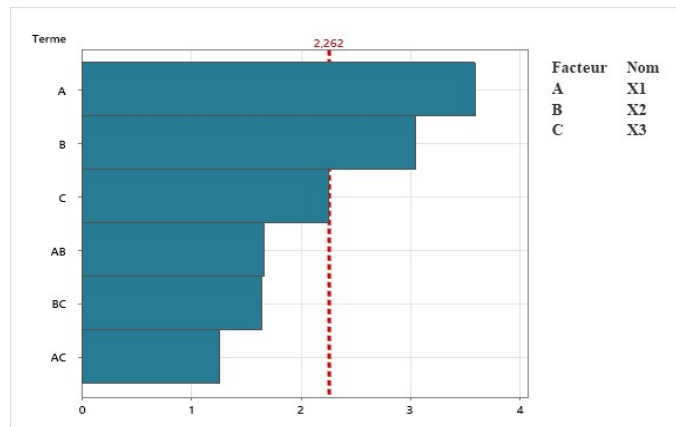


Figure 2. Pareto diagram of the factors studied

Regarding the exposure time, it should be noted that the average quantity of MB eliminated by exposing the sample to the sun for 3 hours is 3.91 while that obtained with an exposure time of 5 hours is 5.34, an increase of 36% when the exposure time increases from 3 hours to 5 hours. As for the concentration of MB solution, its increase results in a decrease in the quantity of MB eliminated. The average quantity of MB removed using a 10 mg/L solution is 5.71 mg/L, while the concentration of MB at 20 mg/L is 4.10 mg/L, which is a 28% decrease when the solution concentration increases from 10 mg/L to 20 mg/L.

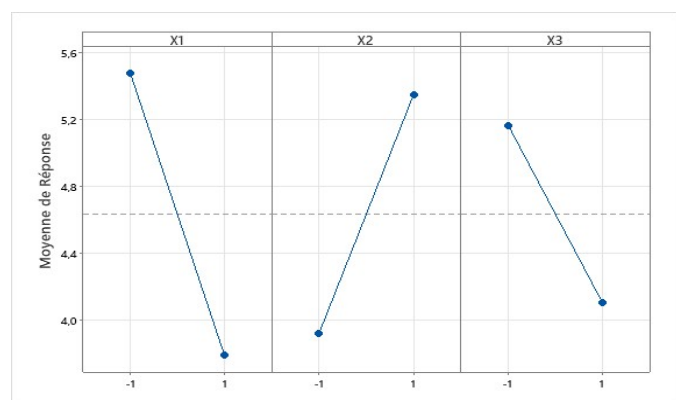


Figure 3. Main effects diagram

Optimisation of the quantity eliminated: The values of the quantity of MB, eliminated, predicted by the model, are recorded in table 5. The adjusted (or expected) value for these factors is 7.19. All estimates also have some degree of uncertainty because they use sample data. The 95% confidence interval is the range of probable values for average resolution. For example, exposing 50 ml of a 10 mg/L BM solution for 5 hours is 95% certain that the resolution is between 5.75 mg/L and 8.60 mg/L. These results are confirmed by the contour diagram below (Figure 4). This figure shows that for a concentration set at 10 mg/L, maximum elimination is achieved for low volume and longer exposure time.

Table 5. Model prediction

Variables	Configurations			
X1	-1			
X2	1			
X3	-1			
Responses	Adjusted value	ErT ajust	95% confidence interval	
Resolutions	7,19	0,62	(5,75; 8,60)	

Kinetics of direct photolysis

Determination of half-life and elimination rate: Figure 5 shows the kinetics of photolysis of degradation of methylene blue dye in

aqueous solution under irradiation from solar radiation. After 6 hours, or 360 minutes of irradiation, 49% of the dye was degraded. This result shows that this molecule is hardly degraded by direct photolysis under solar radiation. This finding was made by Diarra et al. [8], after studying the degradation of the dye Red 6 by direct photolysis under monochromatic lamp of wavelength 285 nm whose radiations are comparable to solar radiation. Indeed, Kouadio [9], following the kinetics of degradation of norfloxacin, ciprofloxacin and meclofenamic acid both under exposure of monochromatic and polychromatic lamp and solar, showed very low removal of these molecules under solar irradiation. The low degradation of molecules observed during exposure to the sun could be due to some unforeseeable. Indeed, most photochemical processes leading to photodegradation take place with UV radiation located in the near UV (from 290 to 400 nm). This spectral zone is subject to strong intensity variations according to latitude, altitude, air pollution, season etc [9]. The semi-logarithmic curve shown in Figure 6 shows that the rate of disappearance of the methylene blue dye under these experimental conditions obeys a kinetic law of first-order. The rate constant and half-life of the methylene blue degradation are recorded in Table 6.

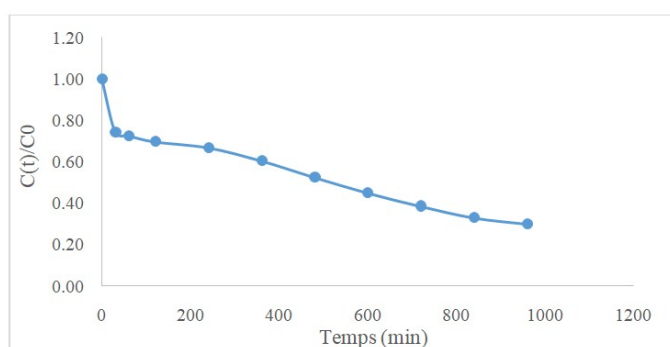


Figure 5. Kinetics of methylene blue degradation by direct photolysis

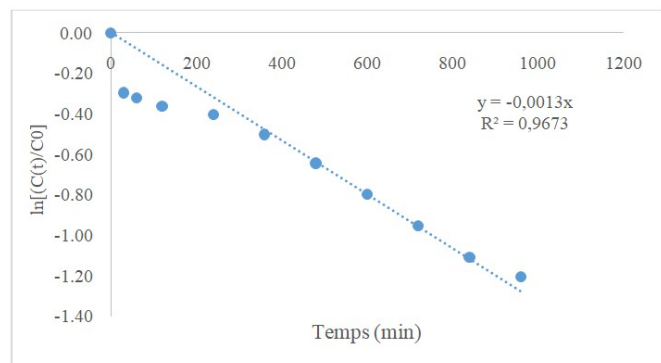


Figure 6. Semi-logarithmic graph of dye degradation

Table 6. Speed constants, and half-life times of methylene blue degradation kinetics

Apparent speed found	Half-life
$k = 1,3 \times 10^{-3} \text{ min}^{-1}$	$t_{1/2} = 533,19 \text{ min}$

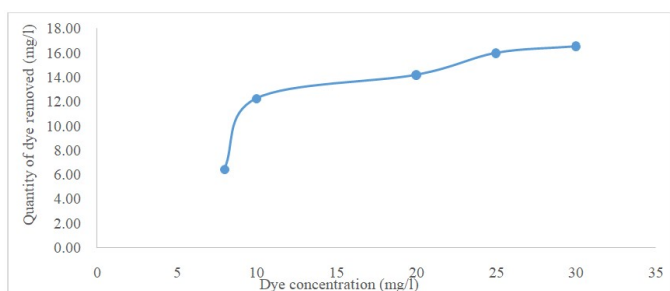


Figure 7. Influence of the dye concentration on photolysis

Influence of concentration on elimination: The results of the study of the influence of methylene blue concentration on photolysis are shown in Figure 7 below. The results in Figure 7 show that the elimination of BM by photolysis depends on its initial concentration. This was also found by Diarra et al. [8] after studying the influence of the initial concentration of the dye on photocatalysis. The higher the initial concentration, the lower the rate of degradation. This influence of the initial concentration on the kinetics is due to the fact that the length of the path of the photonic field through the solution decreases by screen effect when the concentration of the dye increases.

CONCLUSION

This study was conducted to remove methylene blue (MB), a synthetic dye found in textile industry effluents. The degradation of this dye was effected by the solar radiation produced in the medium to be treated. The experimental results showed that the maximum amount of MB removed is 6.8 mg/L and is obtained at a concentration of 10 mg/L, volume of 50 mL and exposure time to solar radiation equal to 5 hours. These results also showed a high efficiency of direct photolysis of the MB when the dye concentration increases. Kinetic model analysis revealed that the absorption of methylene blue follows a kinetics of order 1 with a velocity constant $k = 1,3 \times 10^{-3} \text{ min}^{-1}$. Direct photolysis by solar radiation is an effective method to degrade or even remove methylene blue dye in water.

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