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Bio-sorption of Methylene Blue by Euphorbia hirta leaves

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Abstract: *The present work study the ability of Euphorbia hirta leaves (EHL) to remove methylene blue dye from contaminated water. The optimum parameters such as contact time, particle size, absorbent dose, initial metal concentration, and pH were investigated by performing batch experiments models. The kinetics and the isotherms adsorption were evaluated by varying the initial concentration and using the optimum parameters. The optimum of contact time is 120 min and the removal capacity is* 98.39 %. *A mass of 300 mg is sufficient to reach the maximum removal of methylene blue (96.98 %). The maximum adsorption is obtained with an initial methylene blue concentration of 75 ppm (98.75%). The optimum particle size is 250 µm. The kinetics of the adsorption process are in accordance with the pseudo-second order model. Experimental values of the adsorption capacity are close proximity to the optimum values predicted by the pseudo-second order model. The Langmuir, Freundlich and Tempkin isotherms are not suitable to explain the experimental isotherm.*

Keywords: *Euphorbia hirta, methylene blue, operating parameters, kinetic, isotherm*

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I. Introduction

The contamination of natural water resources is a major problem in today's world. The textile industry is part responsible of this contamination by pouring large amount of dyes accompanied by various contaminants such as organics and bleaches [1,2]. Methylene blue is a cationic dye with a recalcitrant nature used in various domains like medical [3], textile and leather industry [4]. In the medical field, it was reported that methylene blue help improving hypotension [5], hypoxia [6] and hyper dynamic circulation in cirrhosis [7]. Use in higher dose than what recommend by the medical field, methylene blue is a toxic dye that can causes cardiac arrythmias [8,9], acute renal failure [10], with the neonates more prone to its side effects such as hyperbilirubinemia, respiratory distress, phototoxicity, and hemolytic anemia [11-13].

Finding solutions for the removal of methylene blue in wastewater is an important task both for the environment and health. It was proven that originals methods used in the treatment of wastewater are ineffective in the removal of dye in wastewater [14]. Throughout the decades several physical, chemical and microbial methods [15-18] were used in the elimination of dyes in wastewater but they are expensive and difficult to implement especially in developing countries.

The adsorption method is one of the most efficient technics used nowadays to remove dyes in wastewater. Several studies show that different adsorbent can be used such as activated carbon, clay, and peat [15,18]. Nowadays, plants are also used as adsorbent [4,19,20]. There is no intermediates issued after the adsorption because there is a direct transfer of dye molecules from solutions to adsorbent [4]. Moreover, the amounts of adsorbent used are quite low and after the adsorption the adsorbent can be stored without damage for environment.

Within this context, we selected *Euphorbia hirta* leaves (EHL) to remove methylene blue (MB) from wastewater. Different parameters will be tested such as, time, concentration of dye, adsorbent mass, etc. to understand the biosorption mechanism. Isotherm and kinetics models are also determined.

II. Material and methods

II.1 Preparation of the adsorbent

Euphorbia hirta was harvested at the UCAD botanical garden (14˚41'1.428"N, 17˚27'42.699"W). The leaves (EHL) were collected and rinsed twice with tap water first and distilled water to remove all the particles. They were shadow dried for three days. After this first process, the EHL were dried at 50°C for 48 hours. The EHL were ground using a grinder. This EHL were stored in a plastic container. The dried EHL adsorbent was again crushed and sieved to get different sized fractions, namely, 100, 250, 315, 500, 800 µm. These different fractions were stored in airtight containers for further use.

II.2 Point zero charge pH_{PZC}

The pH of the point of zero charge (pH_{PZC}) for the *Euphorbia hirta* leaves (EHL) was determined by a titration procedure. To a series of eleven 150 mL conical flasks 45 mL of a solution of KNO_3 0.01 M were added and the pH was accurately adjusted using HCl or NaOH 0.01 N solutions from pH = 2 to pH = 12 and completed with a solution KNO_3 0.01 M to 50 mL. The initial pH (pH_i) was accurately measured again. To each flask, 0.1 g of EHL was added and the flask was capped and shaken manually each 4 hours. After 48 hours, the final pH (pH_f) was measured. The $\Delta pH = pH_f - pH_i$ is plotted against pH_i. The point of intersection of the curve and the abscissa axe at ΔpH = 0 gave the pH_{PZC}.

II.3 Batch adsorption tests

All the experiments were conducted in discontinuous batch. A weighed sample of EHL was mixed with 50 mL of the methylene blue solution in 150 mL conical flasks. The mixture was stirred for a fixed time at 25°C. After this process, the liquid was separated from the adsorbent by filtration through a Whatman Filter N°1. The residual methylene blue concentration was determined using a Lambda 365 Perkin Photometer. The experimental data were used to determine the removal capacity and the quantity of methylene blue adsorbed on the EHL:

$$Removal\ \ capacity = \frac{(C_0 - C_e) \times V}{C_0} \times 100$$

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

Where C_0 and C_e are respectively the initial and the final metal concentrations (mg/L) in the liquid phase, V (L) is the volume of the liquid phase and m (g) is the adsorbent mass used.

II.4 Effect of time contact on the removal capacity

The equilibrium time was determined using a Methylene Blue solution at a concentration of 50 ppm. Each 50 mL Methylene Blue solution was treated with 0.25 g of EHL at time ranging from 10 to 120 minutes. The experiments were conducted at the same pH and the flasks contents were stirred at 500 rpm at a temperature of 25°C.

II.5 Adsorbent dose effect on the removal capacity

50 mL of a 50 ppm methylene blue solution was treated with a mass of adsorbent ranging from 0.1 to 1.0 g. The experiments were conducted at the same pH and the flasks contents were shaken at 500 rpm at temperature of 25°C for the optimal time determined previously.

II.6 Effect of solution pH on the removal capacity

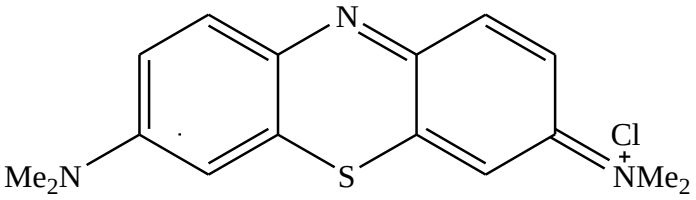
The effect of solution pH on the dyes removal capacities of the adsorbent was investigated between pH = 2 and pH = 12. The experiments were performed by adding a 0.3 g of EHL powder into six 150 mL conical flasks containing 50 mL of 50 ppm dye solutions and the pH of the solution was adjusted using 0.1 N HCl or 0.1 N NaOH. The flasks were shaken at 500 rpm and at temperature of 25°C for 120 minutes.

II.7 Effect of adsorbent particle size on the removal capacity

The ideal particle size for the adsorbent was determined by treating each category (100, 250, 315, 500 and 800 µm) with 50 ml of a 50 ppm Methylene Blue solution at the optimum pH. The flasks were shaken at 500 rpm and at a temperature of 25°C for 120 minutes.

II.8 Effect of methylene blue solution concentration on the removal capacity

The effect of dye solution on the removal capacity were determined by setting the optimum temperature, granulometry of the adsorbent, the pH of the solution and adsorbent dose and varying the methylene blue concentration between 25 to 100 ppm. The flasks contents were stirred at 500 rpm at a temperature of 25°C.



Scheme 1. Structural formulae of methylene blue.

III. Results and discussion

III.1 Fourier transforms infrared spectroscopy (FTIR) analysis

Figure 1 presents the vibrational FTIR spectrum of the pure adsorbent (EHL) and the adsorbent after the adsorption of the methylene blue (EHL-MB). For the spectra of EHL, the broad band observed at 3307 cm^{-1} is

characteristic of the presence of a hydroxyl group and the bands pointed at 2920 cm^{-1} and 2851 cm^{-1} are assigned to the stretching vibration C—H groups [21]. The peak located at 1730 cm^{-1} is due to the presence of C=O groups [4]. The presence of aromatic rings is attested by the bands pointed at 1607 and 1558 cm^{-1} [22]. The peaks at 1233 cm^{-1} and 1031 cm^{-1} attributed to C—O—C and C—O vibrations suggest the lignin structure of the adsorbent [23]. On comparison of the spectrum of EHL with the spectrum of the adsorbent after adsorption of methylene blue (EHL-MB) some changes were observed. The spectrum EHL-MB shows a new band pointed at 3671 cm^{-1}. The band due to hydroxyl group was shifted to low frequencies and pointed at 3293 cm^{-1}. The peak at 1734 cm^{-1} is attributed to the carbonyl group. For the bands attributed to C—H, the band intensity at 2920 cm^{-1} increased, and the band at 2851 cm^{-1} disappears while a new band appeared at 2988 cm^{-1}. All the changes are indicative of interactions between methylene blue and the adsorbent.

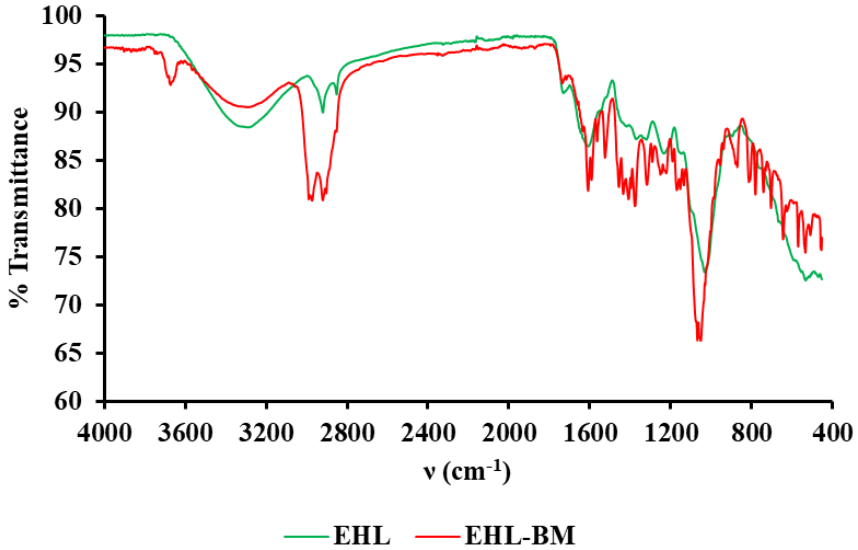


Figure 1: FTIR spectra of EH and EH-MB.

III.2 Impact of physicochemical parameters on methylene blue removal efficiency

III.2.1 Effect of contact time on the methylene blue adsorption

Figure 2 shows the effect of contact time on the adsorption efficiency of methylene blue on the defatted Adansonia seed. The concentration of methylene blue is 50 ppm and the adsorbent mass used is 250 mg. As can be observed on the figure 2, the maximum removal capacity is reached at 120 minutes with 98.39 %. The adsorption is rapid from the beginning of the experiment. After 10 minutes, 86.79 % of the methylene blue were removed. Beyond 10 minutes, the adsorption capacity continues slowly to reach its maximum at 120 min. After 120 min, a release phenomenon is observed which continues up to 180 min to give a rate of 75.5%. In order to investigate the impact of the other physicochemical parameters on the methylene blue adsorption on EHL, all the experiments were conducted with a fixed contact time of 120 minutes.

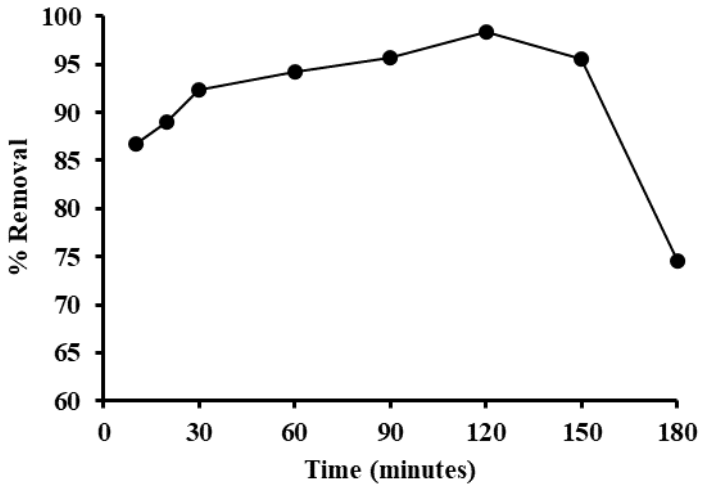


Figure 2. Effect of time contact on EHL removal capacity.

III.2.2 Effect of adsorbent dosage

The effect of initial adsorbent mass of EHL on the methylene blue removal capacity was studied using masses of adsorbent ranging from 100 mg to 1000 mg with a fixed time contact of 120 minutes and a concentration of methylene blue of 50 ppm. Figure 3 shows that the highest Methylene Blue removal capacity (96.98 %) was attained for adsorbent mass of 300 mg. From 100 mg to 200 mg, the removal capacity grows slowly from 95.00 % to 95.38 %. The removal capacity continues increasing from 200 mg to 300 mg (96.98 %) and decreases from 300 mg to 400 mg (95.65 %). For adsorbent mass higher than 400 mg, the removal capacity increases moderately until 1000 mg and reaches 96.82 %. All the next experiences were carried out with 300 mg of adsorbent and 120 minutes of contact time.

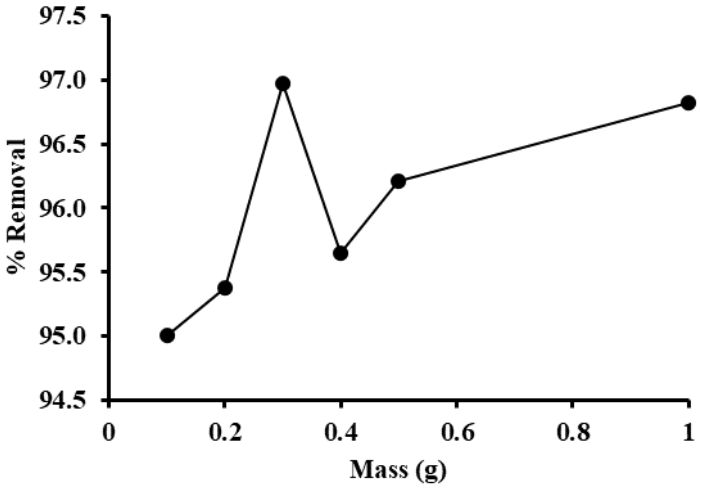


Figure 3. Adsorbent dose on removal capacity

III.2.3 Effect of solution pH on the removal capacity

Figure 4 shows the determination of the point zero charge (pH_{PZC}) of the adsorbent. The pH_{PZC} value observed of 6.72 indicates at this pH value the net surface charge of the adsorbent is zero. For pH values smaller than the pH_{PZC}, the functional groups are protonated, and the absorbent present a positive surface charge and can easily interact with negatively charged species. For pH values higher than the pH_{PZC}, the functional groups are deprotonated, and the absorbent present a negative surface charge and can adsorb easily positively charged species [24]. So, the varying pH of solutions changes the concentration of the functional groups of the adsorbent. So, increasing the pH from 4 to 11, the methylene blue uptake is raised (Figure 4b) and the maximum capacity removal (95.07 %) is reached at pH = 9. In fact, methylene blue is a cationic species, thus at pH=9, the negatively charged surface of the adsorbent can interact easily with the cation yielding a better removal capacity. For lower pH values competition between hydrogen ions and the cationic methylene blue species is won by hydrogen ions.

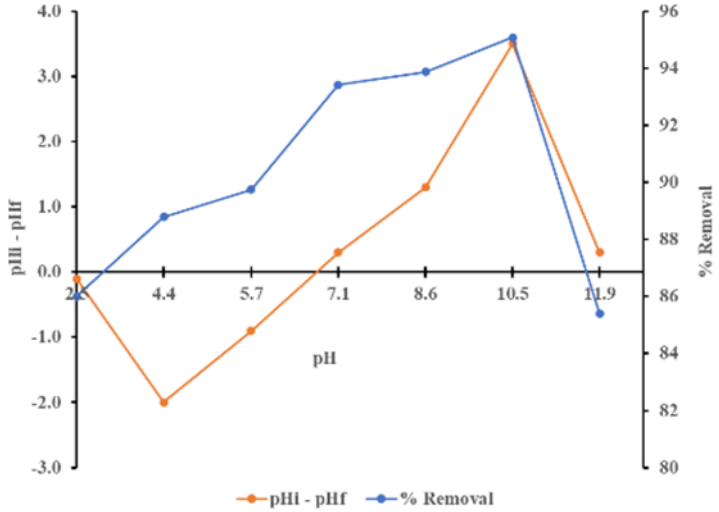


Figure 4: pH_{PZC} and optimum pH determination.

III.2.4 Effect of particle size.

The adsorption process is highly dependent on the specific surface area of the adsorbent [25]. The finer the particles, the higher the specific surface area. The percent removal of methylene blue decreases when the particle size of EHL increases as shown in Figure 5. The maximum rate of elimination of methylene blue is reached for particles of 250 µm with a value of 97.55%. When the particle size increases the removal rate decreases slightly to reach 95.30% at 800 µm. Indeed, the larger surface/volume ratio of small particles increases their adsorption capacity. In the rest of the work, particle size of 250 µm of EHL were used.

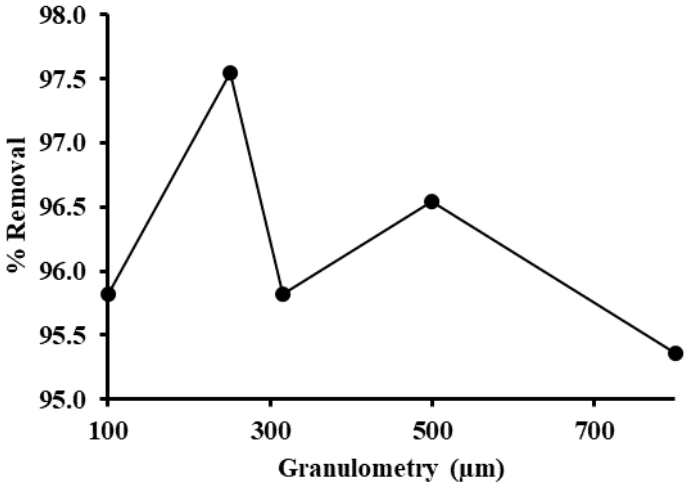


Figure 5. Particle size of adsorbent onto removal capacity.

III.2.5 Effect of initial methylene blue concentration

The effect of the initial concentration of methylene blue on EHL was studied by varying the concentration from 25 to 100 ppm as shown in Figure 6. The equilibrium adsorption rate of methylene blue by EHL increases with the initial concentration between 25 and 75 ppm to reach a rate of 98.75%. Above 75 ppm, the adsorption rate remains almost constant. Between 25 and 75 ppm, there is a high driving force between the EHL adsorbent and the methylene blue solution. This has the consequence of increasing the efficiency of the adsorption of methylene blue by EHL. The quasi-constant removal rate observed when the initial concentration increases from 75 ppm to 100 ppm can be explained by the saturation of the EHL adsorption sites reached more quickly. These observations are reported by several authors for various dyes and adsorbents [22].

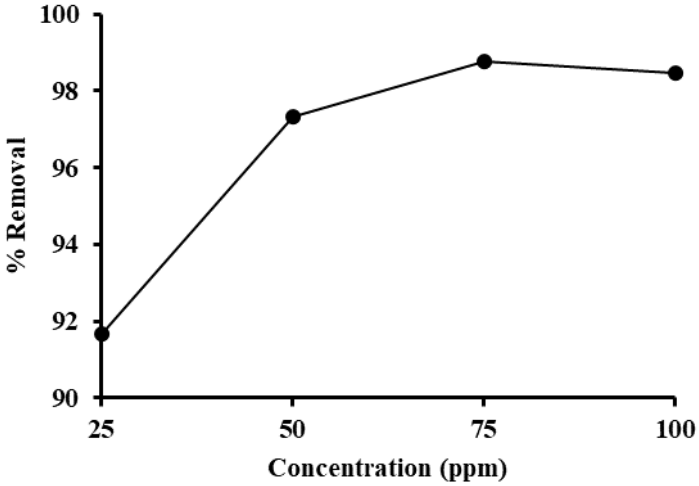


Figure 6. Optimum initial concentration determination.

III.3 Adsorption isotherms

Equilibrium adsorption isotherms are among the most important data for understanding the mechanism of adsorption. Therefore, the adsorption of methylene blue on EHL is determined as a function of the equilibrium of the methylene blue concentration (C_e) and the isotherms of the corresponding adsorption are plotted in Figure 7. Parameters and correlation coefficients obtained from plots according to Langmuir, Freundlich, Temkin and Harkin-Jura models are listed in Table 1. The values of R^2 that are important for

estimating the fit of the model are all far from unity. Langmuir's model cannot be correlated with the experimental data and gives a very low R^2 value of 0.105.

Table 1. Adsorption isotherms parameters.

Langmuir isotherm			**Freundlich isotherm**		
$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{1}{Q_0} C_e$			$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$		
Q_0 (mg/g)	K_L (L/mg)	R^2	$\frac{1}{n}$	K_F	R^2
9.597	3.473	0.105	−0.245	2.651	0.008
Temkin isotherm			**Harkin-Jura isotherm**		
$q_e = \frac{RT}{b_t} \ln K_T + \frac{RT}{b_t} \ln C_e$			$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log C_E$		
b_t (J/mol)	K_T (L/mole)	R^2	A_{HJ}	B_{HJ}	R^2
−412.374	0.149	0.060	17.123	0.467	0.041

The Temkin model is also very far from correlating with the experimental data with a R^2 value of 0.06, while the Freundlich model, which is the worst, gives an R^2 value of 0.008. Harkin-Jura model does not fit the experimental data with a low R^2 value of 0.041. These data suggest that neither the Langmuir model, nor the Freundlich model, nor the Temkin model nor the Harkin-Jura model are not suitable for describing the adsorption of methylene blue on EHL.

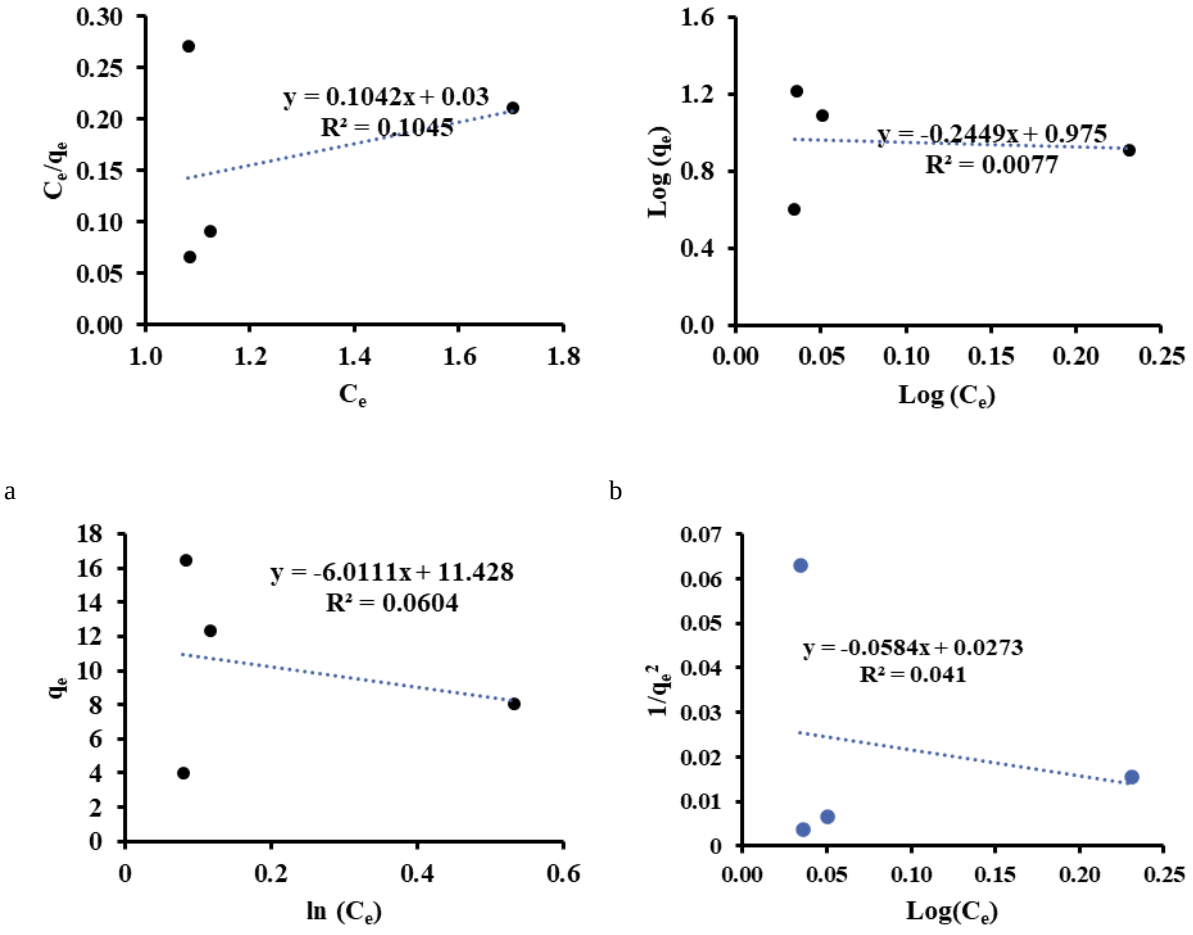


Figure 7. Methylene blue adsorption isotherms : Langmuir (a), Freundlich (b); Tempkin (c), Harkin-Jura (d).

III.4 Adsorption kinetics

Pseudo-first, pseudo-second order kinetic models, intra-particles diffusion model and Elovich equation were used to study the adsorption processes of methylene blue on EHL and the potential rate limiting the adsorption.

$\ln(q_e - q_t) = \ln q_e - k_1 t$ Pseudo-first order model (Equation 1)

$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ Pseudo-second-first order model (Equation 2)

$q_t = k_i t^{1/2} + I$ Intra-particle diffusion model (Equation 3)

$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t$ Elovich model (Equation 4)

where k_1 is the rate constant of sorption (min^{-1}), k_2 the pseudo-second-order rate constant of sorption (g mg^{-1} min^{-1}), k_i the intra-particle diffusion rate constant (g mg^{-1} min^{-1}), q_e and q_t are the amounts of metal adsorbed (mg g^{-1}) at equilibrium and at time t, respectively. α represents the initial sorption rate (mg g^{-1} min^{-1}) and β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

The plots of Equation 1 (Figure 8) give the values of the adsorption rate constant k_1 for the methylene blue on EHL as the slopes ($-k_1$) and the intercepts give the ln (q_e). The large differences of $q_{e,exp}$ and $q_{e,cal}$ and the low values of the correlation coefficient R^2 (Table 2) indicated that the pseudo-first order model does not fit the adsorption of methylene blue on EHL (Figure 8).

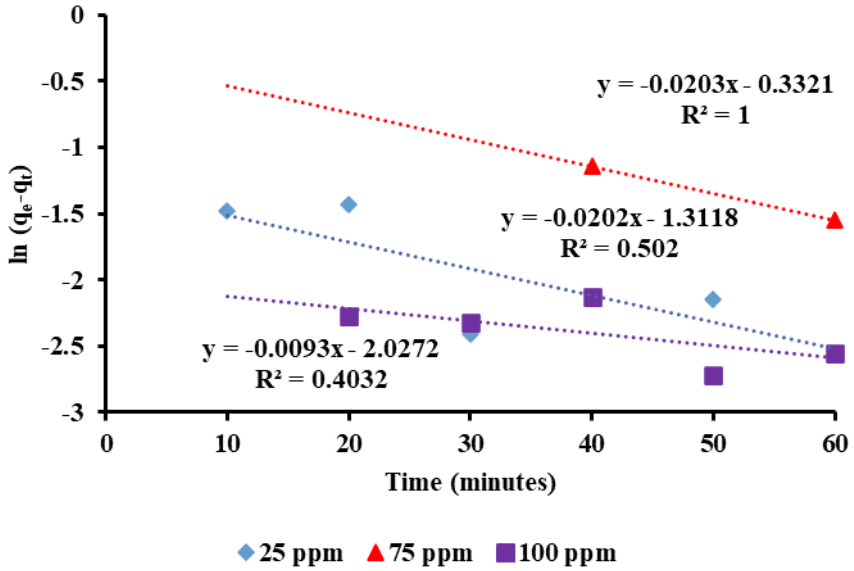


Figure 8. Pseudo-first order model kinetic.

The plots of the pseudo-second order Equation 2 gives the best-fitted model according to the linear regression coefficient values, R^2. As shown in table 2, R^2 values are very close to unity for all the initial concentrations (0.999 ~ 1.000). The $q_{e,exp}$ and $q_{e,cal}$ values are close proximity for each initial concentration. These results show clearly that the kinetic of the adsorption of methylene blue on EHL is achieved through the use of pseudo-second order model (Figure 9).

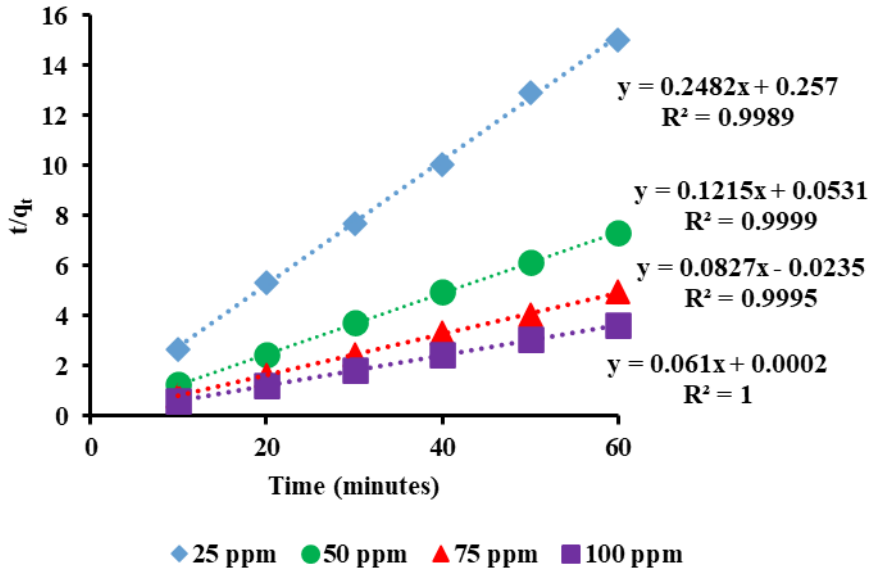


Figure 9. Pseudo-second order model kinetic.

Apart from adsorption on the outer surface of the adsorbent, there is also a possibility for the adsorbate to enter the pores of the adsorbent. It is intra-particle diffusion process that can be studied by plotting q_t as a function of $t^{1/2}$, according to Equation 3, in which q_t is the quantity of methylene blue adsorbed at time t in mg/g, t is the contact time (min) and k_i is the intra-particle diffusion constant (mg/g $min^{1/2}$). Based on the theory proposed by Weber and Morris [26], the plot of the above equation gives a straight line which pass through the origin if intraparticle diffusion is involved.

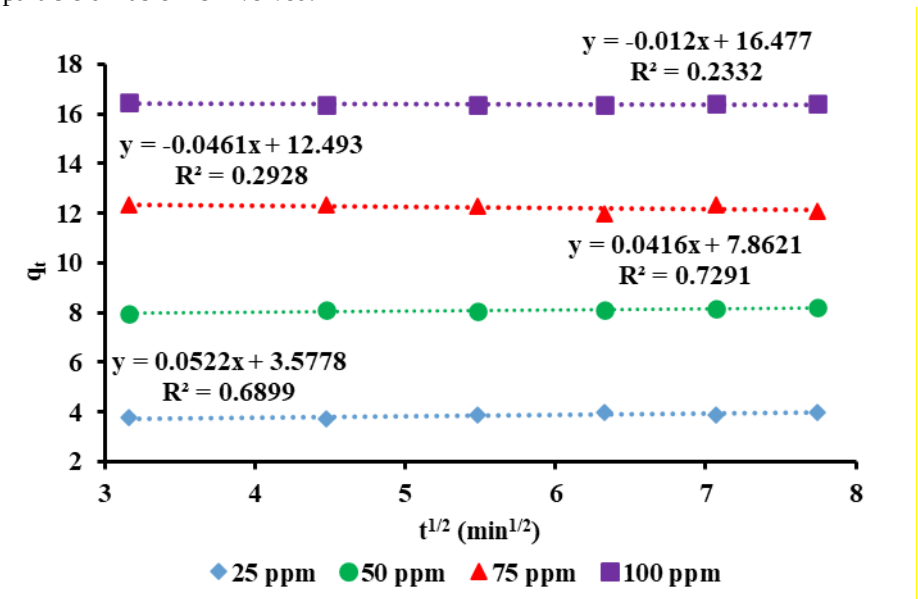


Figure 10. Intraparticle diffusion model kinetic.

According to the results recorded in Table 2 and Figure 10, the values of *I* give an idea of the thickness of the boundary layer. Indeed, the higher is the value of *I*, the greater the boundary layer effect. The calculated parameters in Table 2 indicate that intra-particle diffusion is not rate-controlling step [27].

Table 2. Kinetic parameters of the adsorption of methylene blue on EHL.

C_0 (ppm)	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		$\ln(q_e - q_t) = \ln q_e - k_1 t$			$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
25	3.986	0.202	0.269	0.502	0.240	4.029	0.999
50	8.049	n/a	n/a	n/a	0.278	8.230	0.999
75	12.313	0.020	0.717	1.000	−0.270	12.092	0.999
100	16.486	0.009	0.132	0.403	18.605	16.393	1.000
C_0 (ppm)	$q_{e,exp}$ (mg/g)	Intraparticle diffusion			Elovich		
		$q_t = k_i t + I$			$q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ln t$		
		k_i (mg/g min)	I	R^2	β (g/mg)	α (mg/min)	R^2
25	3.986	0.052	3.578	0.690	7.524	2.05×10^{10}	0.680
50	8.049	0.042	7.862	0.729	26.596	4.05×10^{90}	0.722
75	12.313	−0.046	12.493	0.293	−8.584	-9.97×10^{-49}	0.284
100	16.486	−0.012	16.477	0.233	−26.954	-1.02×10^{-195}	0.341

The Elovich Equation 4 was plotted. The correlation coefficients are far from the unity (Figure 11 and Table 2) indicating that the Elovich model is the worst kinetic model in this case.
From these findings the adsorption kinetics of methylene blue by EHL is exclusively described by the pseudo-second order model and that only one adsorption mode takes place during this process.

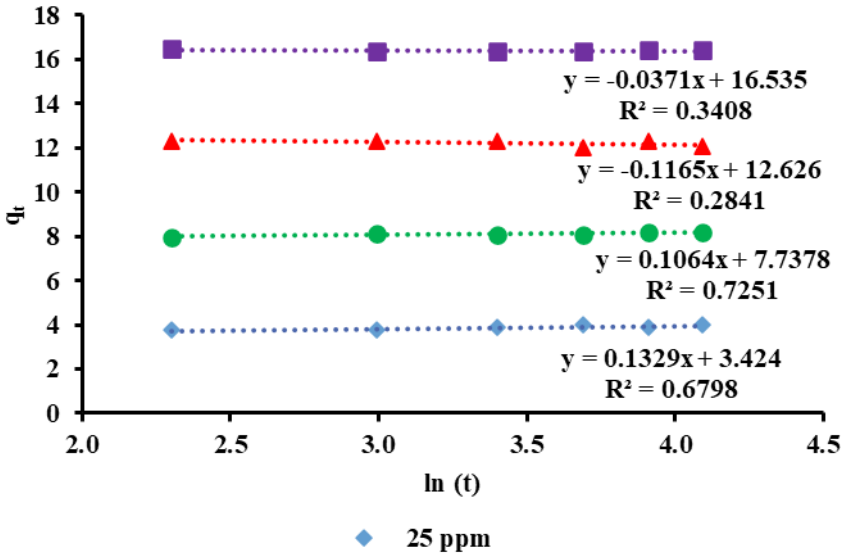


Figure 11. Elovich model kinetic.

IV. Conclusion

The leaves of *Euphorbia hirta* studied in this article is an excellent alternative for purifying effluents contaminated with methylene blue. After the preparation and characterization by FTIR of the plant material with the demonstration of functional groups allowing the adsorption process, the material is used as an adsorbent to eliminate methylene blue from laboratory effluents. The different parameters that can influence the adsorption capacity are optimized. After establishing the best adsorption conditions related to pH, contact time, adsorbent dose, particle size and initial MB concentration to saturate the available sites located on the adsorbent surface , four kinetic models were used to adjust the adsorption. The pseudo second order was the best kinetic model to describe the MB adsorption phenomenon on EHL. Three types of isotherms are studied (Langmuir, Freundlich and Temkin models) and none of them is suitable to describe the adsorption of MB on EHL.

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