



## Effects of pH and ionic strength on methylene blue removal from synthetic aqueous solutions by sorption onto orange peel and desorption study

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### Abstract

The aim of this work is to study the efficiency of waste material ‘orange peel’ for the removal of methylene blue from synthetic aqueous solutions in batch conditions. The effects of initial pH and ionic strength of solution on the dye sorption kinetics has been studied at ambient temperature (25°C). A desorption tests on material, previously saturated with dye, were undertaken in distilled water at different pH values. The results showed that the sorption kinetics of the quantity of dye uptake at equilibrium depends with initial pH and the ionic strength in solution. For each parameter study, the kinetic model of pseudo-second order proved to be adequate to describe the results of sorption dye kinetics and the model of Langmuir has been found perfectly adequate to describe the equilibrium results of sorption. The maximal capacities (Q<sub>max</sub>) of methylene blue sorption decrease from 280 to 98 mg/g when the initial pH of solution decreases from 9 to 3 and from 205 to 74 mg/g when the NaCl concentration in solutions increases from 0.00 to 0.10 mol/L.

## 1. Introduction

Water treatment became nowadays a very important topic concerning environment protection. The industrial wastewaters are characterized by the presence of high quantities of organic and mineral pollutants. Among compounds dominance, we find dyes. Dyes are used extensively by several industries as: cosmetic, paper, leather, pharmacy, food industries and more especially in textile. Over  $7 \times 10^5$  tons of these dyes are produced annually worldwide. It is estimated that 10 to 15% of these chemical compounds are discharged into waste streams by the textile industry [1].

In rivers colors can affect the nature of water, reduce the penetration of light and have a derogatory effect on photosynthesis [2]. The presence of very small amounts of dyes in water is highly visible and undesirable [3]. Among the various types of dyes, methylene blue (cationic dye), is used for dyeing cotton, wool and silk [4-5]. This dye is not strongly hazardous but it can cause some harmful effects like: eye burns, nausea, vomiting, etc... [4].

Currently, there are several processes for the removal of methylene blue contained in industrial sewages. These include: flocculation-decantation, ions exchange, electrolysis, membrane separation, biologic treatment, adsorption, etc... [6-7]. Adsorption is known as the most efficient and economic method to treat these pollutants containing in water [6- 8]. Activated carbon is the more adsorbent used. However, this material is expensive and poses a problem of regeneration [8-9]. For this purpose, several researchers have been taken, during the last years, towards the investigation of new low-cost agricultural materials for the removal of methylene blue from aqueous solutions including: pine sawdust [10], coconut husk [11], tree's leaves [12], tea waste [13-14], sugarcane bagasse [15], date stones [16], cotton stalk [17], peanut husk [18], etc. Orange peel, a highly available

lignocellulosic waste, has been tested also in many studies for their efficiency to remove methylene blue from aqueous solutions [19-21]. However, few works have been taken on the effects of some experimental parameters like pH or ionic strength on dye removal by this sorbent. These parameters influence considerably on sorption phenomena and affect the dye uptake.

The aim of this work is to evaluate the sorption aptitude of orange peel for the removal of methylene blue, as a model compound of basic dyes, under different experimental conditions of solution. Firstly, the pH of the zero point charge (pH<sub>ZPC</sub>) of sorbent was measured. Then, the effects of pH, contact time and ionic strength on sorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data.

## 2. Material and Methods

### 2.1. Sorbent material

Orange peel OP (Thomson variety) was collected from the region of Mohammadia (Mascara –West Algeria). The peel was sun dried at ambient temperature (30 - 32°C) during many days, crushed with a Moulinex Easy power R68 mill and sieved with an Automatic Sieve Shaker D403 device (Controlab). Only the particle size dp:1.25-2 mm has been kept to be used in this work. In order to remove any dirty particles adhered, the material was used after the following treatment: 10 g of orange peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of  $W = 400$  rpm) by a magnetic stirrer at ambient temperature of  $25 \pm 1^\circ\text{C}$  during 4 h, filtered, washed thoroughly with distilled water until constant pH and no colour observed, then oven-dried at  $85 \pm 5^\circ\text{C}$  for 24 h. Orange peel prepared presents the following characteristics: % Holocellulose: 50.00, % lignin: 32.00, % total extractives: 15.02, total porous volume:  $732,4224 \text{ mm}^3/\text{g}$ , total porosity: 57,4 % and total specific surface area:  $10,528 \text{ m}^2/\text{g}$  [19].

### 2.2. Dye

Methylene blue MB (chemical formula:  $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$ ; molecular weight: 319.86 g/mol; maximum wavelength: 664 nm; chemical structure given in figure 1) was purchased from JANSSEN CHIMICA and used as without any purification. In single component of aqueous solutions, 1000 mg/L stock solutions of methylene blue were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions.

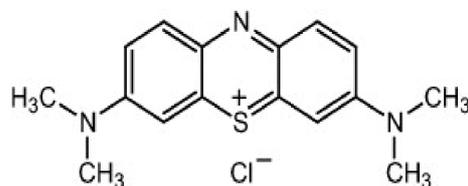


Figure 1: Chemical structure of methylene blue

### 2.3. pH zero point charge (pH<sub>ZPC</sub>) measure

The pH zero point charge (pH<sub>ZPC</sub>) of material has been measured by the electro-chemical method reported by S.Altenor and al. [22]. 50 ml of a 0.01 M NaCl solution was placed in 100 ml Erlenmeyer flasks. Then, the pH was firstly adjusted to successive initial values between 2 and 12 by using either NaOH or HCl (0.1 M), and 0.15 g of orange peel was added to the solutions. After a contact time of 48 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line pH (final) = pH (initial) is taken as the pH of the zero point charge (pH<sub>ZPC</sub>) of the OP used. The measures of pH have been made using a microprocessor pH-meter 761 (Knick-Calimatic, Germany).

### 2.4. Batch sorption experiments

#### 2.4.1. Sorption kinetics

In each sorption experiment, 1L of dye solution of constant concentration (100 mg/L) was added to 1g of sorbent in a beaker agitated vigorously by a magnetic stirrer at 400 rpm and under a constant temperature  $25^\circ\text{C}$ . Samples from the clear supernatant, at appropriate time intervals, were carefully pipeted from the beaker to prevent the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (UV-2550 SHIMADZU) at  $\lambda_{\text{max}}$  664 nm previously calibrated. Figure 2 give an example of spectrophotometer calibration curves used in the effect of initial pH of solution. The amount of dye uptake  $q_t$  (mg dye/g sorbent) was determined by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

Where  $C_0$  and  $C_t$  are the initial and time dye concentration (mg/L) respectively,  $V$  is the volume of solution (mL), and  $m$  is the sorbent weight (g).

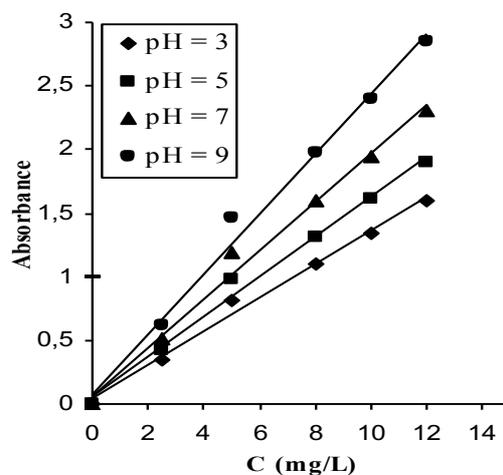


Figure 2: UV-visible spectrophotometer calibration curves at different initial pH of solution

#### 2.4.2. Sorption equilibrium

The dye equilibrium isotherms were determined by contacting a constant mass 0.25 g of each sorbent material with a range of different concentrations of dye solutions: 50-1000 mg/L. The mixture obtained was agitated in a series of conical flasks with equal volumes of solution 250 ml for a period of 24 h at a constant temperature  $25 \pm 1^\circ\text{C}$ . The equilibrium concentration of free dye in solution was determined with a UV-visible spectrophotometer. The equilibrium dye uptake  $q_e$  (mg dye/g sorbent) was determined by difference between concentrations: initial and at equilibrium respectively.

#### 2.5. Desorption study

Regeneration of materials after sorption is economically interest. This technical permits to use the material several times in the process. In these tests, methylene blue was desorbed from orange peel which was exposed previously to a concentration of 100 mg/l of this dye for 10 h and at natural initial pH of distilled water: 5.09 to 5.11. The sorption of dye by orange peel was carried out by the similar method shown previously in sorption kinetics. After equilibrium, the sorbents was filtered and oven dried during 24 h. five experiments have been taken. The amounts of methylene blue uptake by orange peel ( $Q_u$ ) vary from 84.66 to 89.73 mg/g. Every sorbent were added to 1 L of distilled water with an initial pH value (from 2-9) in a beaker vigorously agitated by a magnetic stirrer at 400 rpm and a constant temperature  $25 \pm 1^\circ\text{C}$ . The adjustment of pH values has been taken using solutions of acid hydrochloric HCl or sodium hydroxide NaOH 0.1 N (Riedel-de Haën). At appropriate time intervals, samples from the supernatant were carefully pipeted from each beacker and the dye concentrations were determined. The desorption percentages of methylene blue were calculated by the following equation:

$$\%desorption = \frac{Q_{dt} \times 100}{Q_u} \quad (2)$$

Where  $Q_{dt}$ : The amount of methylene blue desorbed from the sorbent at time  $t$  (mg/g),  $Q_u$ : The amount of methylene blue uptake by orange peel after a contact time of 24 h (mg/g).

### 3. Results and discussion

#### 3.1. pH zero point charge (pHzpc)

The pH zero point charge (pHzpc) inform on the surface charge of material (positively or negatively). The Results found for this parameter are given in figure 3. The pHpzc of orange peel has been deducted from graphs where the initial pH is equal to the final pH (intersection of curves). As shown in figure 2, the material present a surface charged negatively (pHpzc = 3.80). The surface of orange peel becomes negatively charged for a pH of solutions  $> 3.80$  and acquires a positively charge when the pH is lower 3.80. The literature report that the cations uptake is favorable to a  $\text{pH} > \text{pHpzc}$ , whereas the uptake of anions is encouraged to a  $\text{pH} < \text{pHpzc}$  of

sorbent [23]. The pHzpc has been measured in many studies of adsorption like:  $Pb^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  by kaolin [24], reactive yellow 84 dye onto animal bone meal [3] or simple aromatic compounds onto activated coal [25].

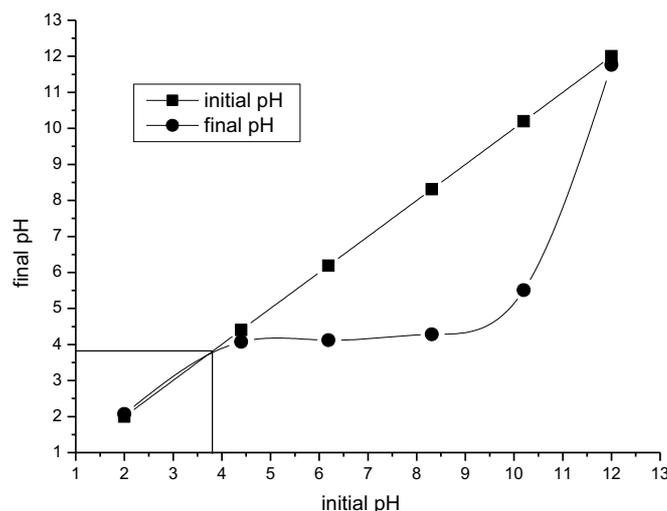


Figure 3: pHzpc for orange peel measure

### 3.2. Kinetics studies

#### 3.2.1. Effect of pH

The pH is one of the most important factors controlling the adsorption of dyes onto adsorbent. The aqueous solution pH exerts profound influence on the sorptive uptake of dyes due to its impact on the surface binding-sites of the sorbent. In this study, the effect of pH was investigated by varying the initial values of pH solution from 3 to 9. The initial pH values was adjusted by using solutions of HCl or NaOH 0.1 N (Riedel-de Haën). The results were presented in figure 4.

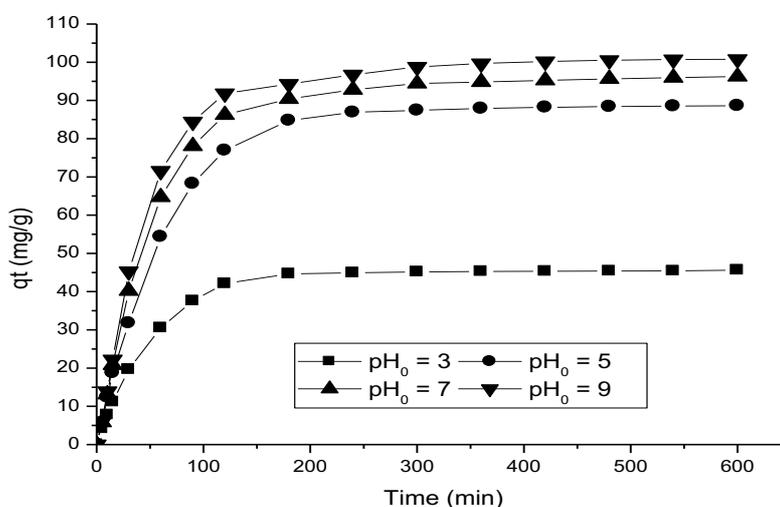


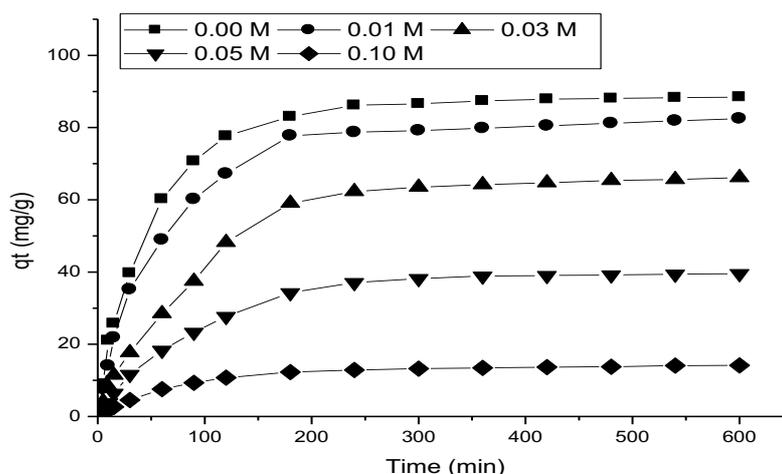
Figure 4: Effect of initial pH of solution on methylene blue sorption kinetic by orange peel ( $C_0 = 100$  mg/l,  $m/V = 1$  g/L,  $d_p = 1.25 - 2$  mm,  $w = 400$  rpm,  $T = 25^\circ C$ )

As shown in figure 4, the initial pH of solution influence considerably on the amount of dye sorbed. The amount of methylene blue sorbed at equilibrium increase from 44,90 mg/g to 98,767 mg/g with the increasing of initial pH solution from 3 to 9. Similar remarks have been observed in the sorption of methylene blue by *Posidonia oceanica* (L.) fibres [26]. The time necessary to reach equilibrium is pH depending. It is variable from 240 to 360 min when the initial pH increases from 3 to 9. These results can be explained by the value of zero point charge for orange peel measured ( $pH_{ZPC} = 3.8$ ). The literature report that at lower pH ( $pH < pH_{ZPC}$ ), the surface charge may get positively charged, thus making ( $H^+$ ) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed [27]. At higher pH ( $pH > pH_{ZPC}$ ), the material biopolymers, mainly lignin and cellulose chains, may get negatively charged, which enhances the positively charged dye cationics through

electrostatic forces of attraction. Other authors explain this phenomenon as follows: The basic dyes give positively charged ions when dissolved in water. Thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species. When the pH of dye solution increase, the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent [28]. Baybars Ali Fil et al. report that increasing in solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface [29].

### 3.2.2. Effect of ionic strength

Extensive investigations carried out on adsorption of dyes revealed that the extent of dye uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the dye-bath [30]. To study the effect of ionic strength on methylene blue sorption by orange peel, several sorption experiments were undertaken by varying the initial NaCl concentration of solution from 0.00 to 0.10 M. The results are given in figure 5.



**Figure 5:** Sorption kinetic of methylene blue by orange peel: effect of ionic strength ( $C_0 = 100$  mg/l,  $m/V = 1$  g/l,  $d_p = 1.25 - 2$  mm, initial pH of solution: 5.03 to 5.19,  $w = 400$  rpm,  $T = 25^\circ\text{C}$ )

According to the results (figure 5), the amount of dye sorbed at equilibrium, decrease from 81.51 to 14 mg/g when the ionic strength increase from 0.00 to 0.1 M. These results can be explained as follows: The surface of sorbent material becomes no easily accessible for methylene blue uptake when the quantity of NaCl salt in solution increases. As result, the amount of methylene blue sorbed decrease. Our remarks are similars to thoses observed by Slimani R. et al. [30] who studied the effect of salt NaCl presence on methylene blue adsorption by animal bone meal and reported that the dye adsorption rate decreases with the increasing chloride sodium concentration in solution. Ahsan Habib [31] reports that when a sorbent is in contact with a species of sorbat in solution, they are bound to be surrounded by a double electric diffuse layer. The thickness of this layer is much more important than the presence of salt is considerable. The presence of salts in solutions inhibits the methylene blue uptake on surface sorbent. Besides, the litterature report that when the electrostatic attraction between the adsorbent surface and adsorbate ions are attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity [32,33].

### - Sorption kinetics Modelling

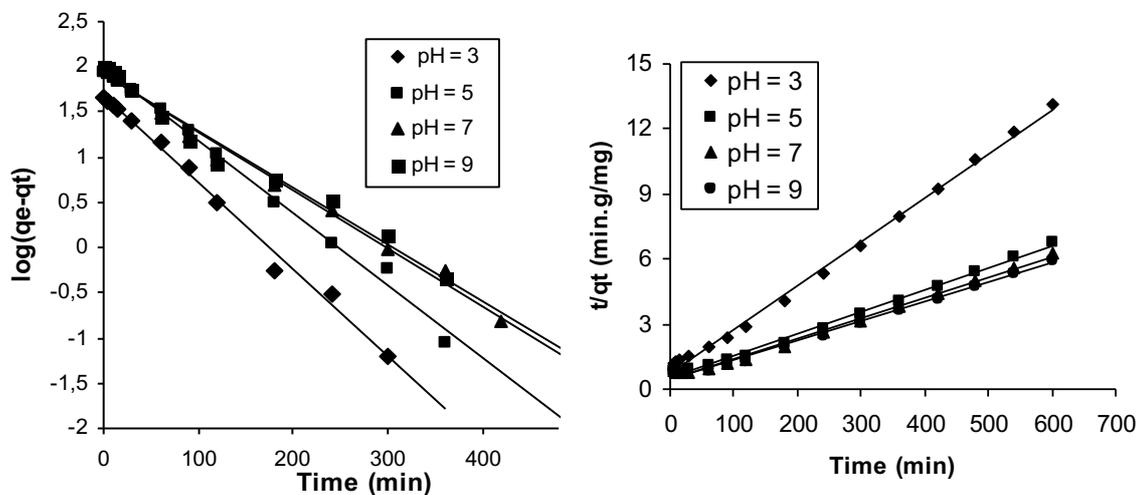
In order to analyze the kinetic data of methylene blue sorption by the orange peel under the experimental conditions tested, two common models from the literature, namely, the first-order rate model of Lagergren [34] and the pseudo second-order rate model [35- 37] were chosen and shown below as equations (2) and (3) in their linear forms:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 \times t}{2.3} \quad (3)$$

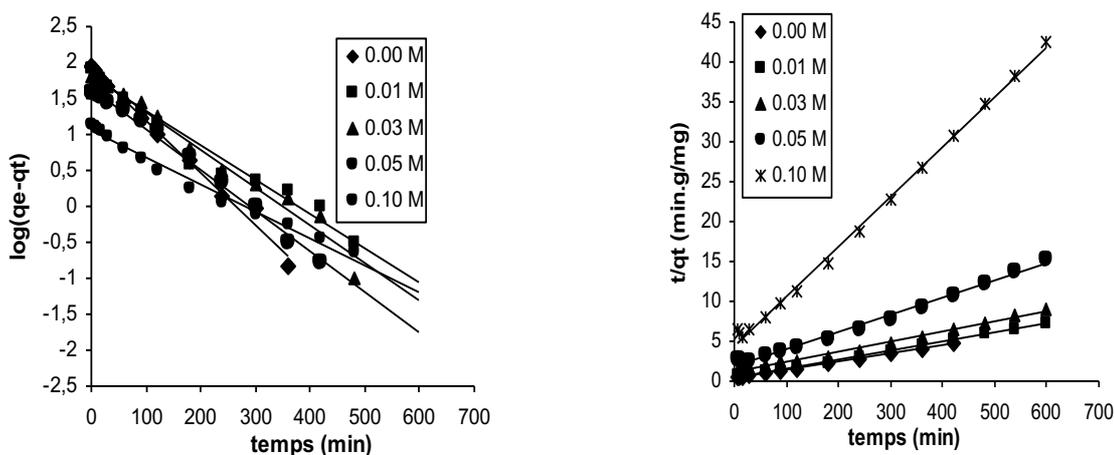
$$\frac{t}{q_t} = \frac{1}{2kq_e^2} + \frac{t}{q_e} \quad (4)$$

where:  $k_L$  is the Lagergren rate constant of sorption ( $\text{min}^{-1}$ ) and  $k$  the pseudo second-order rate constant of sorption ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ );  $q_e$  and  $q_t$  are the amounts of dye sorbed ( $\text{mg} \cdot \text{g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.

For all initial pH solution and ionic strength values studied, the different curves from the slope and intercept of linear plots of  $\log(q_e - q_t)$  versus  $t$  and  $t/q_t$  versus  $t$  are presented in figure 6 and figure 7 respectively.



**Figure 6:** Sorption kinetic Modelling of methylene blue by orange peel: effect of initial pH of solution  
 a) First-order rate model b) Pseudo-second-order rate model  
 ( $C_0=100 \text{ mg/l}$ ,  $m/V = 1 \text{ g/l}$ ,  $dp=1.25 - 2 \text{ mm}$ ,  $w= 400 \text{ rpm}$ ,  $T = 25^\circ\text{C}$ )



**Figure 7:** Sorption kinetic Modelling of methylene blue by orange peel: effect of ionic strength  
 a) First-order rate model b) Pseudo-second-order rate model  
 ( $C_0=100 \text{ mg/l}$ ,  $m =V 1 \text{ g/l}$ ,  $dp=1.25 - 2 \text{ mm}$ , initial pH of solution: 5,03 to 5,19,  $w= 400 \text{ rpm}$ ,  $T = 25^\circ\text{C}$ )

Besides the values of models rate constants obtained for each model are summarized in the table 1 and table 2

**Table 1:** Models rate constants for MB sorption kinetics by orange peel: effect of initial pH of solution

Pseudo-second-order rate model			First-order rate model				$\text{pH}_0$
$R^2$	$k \cdot 10^{-4}$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )	$q_{e,cal}$ ( $\text{mg/g}$ )	$R^2$	$k_L \cdot 10^{-3}$ ( $\text{min}^{-1}$ )	$q_{e,cal.}$ ( $\text{mg/g}$ )	$q_{e,exp.}$ ( $\text{mg/g}$ )	
0.9999	36.56	46.00	0.9883	22.08	47.50	45.217	3
1	13.67	89.85	0.9983	18.38	94.02	87.997	5
1	7.36	98.42	0.9818	15.78	87.28	95.398	7
0.9999	6.46	103.52	0.9536	15.09	85.55	100.108	9

**Table 2:** Models rate constants for MB sorption kinetics by orange peel: effect of ionic strengt

Pseudo-second-order rate model			First-order rate model				
$R^2$	$k \cdot 10^{-4}$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )	$q_{e,cal}$ ( $\text{mg/g}$ )	$R^2$	$k_L \cdot 10^{-3}$ ( $\text{min}^{-1}$ )	$q_{e,cal}$ ( $\text{mg/g}$ )	$q_{e,exp}$ ( $\text{mg/g}$ )	[NaCl] (M)
1	9.72	90.17	0.9973	16.86	80.73	87.546	0.00
0.9997	5.10	85.32	0.9718	11.94	65.27	81.506	0.01
0.9998	4.58	80.45	0.9921	11.64	66.45	76.282	0.02
0.9999	5.62	68.87	0.9954	13.41	73.30	65.460	0.03
0.9997	6.01	53.79	0.9917	11.48	51.29	50.648	0.04
0.9998	10.13	41.19	0.9933	11.75	40.88	39.215	0.05
0.9996	14.63	15.18	0.9765	8.86	11.70	14.003	0.10

As shown in figure 6, figure 7 and tables 1 and 2, the data obtained at different values of initial pH solution or ionic strength, were only fitted to the pseudo-second-order rate equation indicating that the process follows a pseudo-second-order kinetics. The regression coefficients are around  $R^2 = 1$  ( $R^2 = 0.999 - 1$ ). The values of  $q_e$  obtained from the fitting to the pseudo-second-order reaction rate model are very near to the experimental values obtained from the sorption kinetics at equilibrium. These confirm that the kinetic data obtained follow the pseudo-second kinetic model.

These results are in good agreement with many researches carried out on MB sorption on cellulosic substrates which is well described by a pseudo-second order model [14, 26, 38-39].

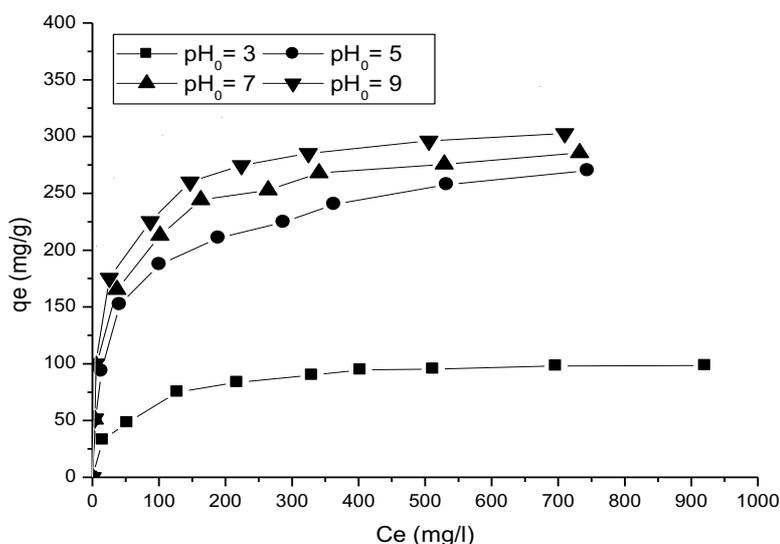
### 3.3. Equilibrium study

#### 3.3.1. Sorption isotherms

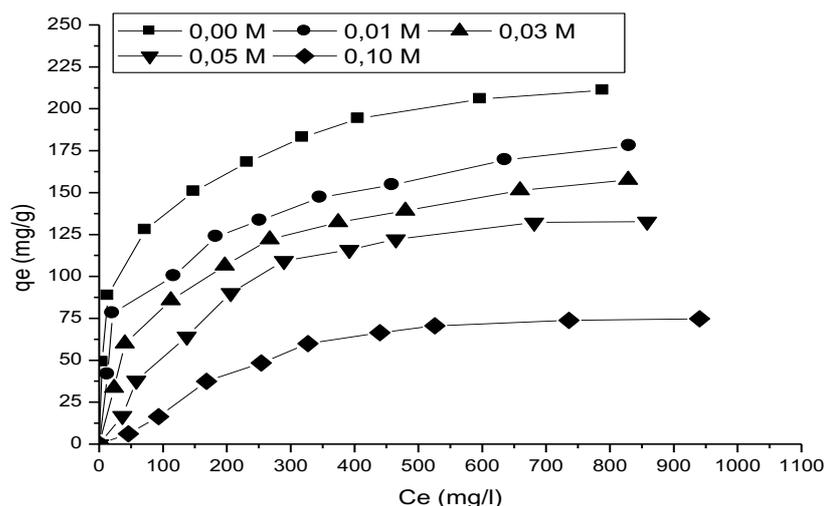
Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. These data provide information on the capacity of the sorbent or the amount required to remove a unit mass of pollutant under the system conditions. Figure 8 and figure 9 shows the methylene blue sorption isotherm, ( $q_e$  versus  $C_e$ ) by orange peel, for different values of initial pH solutions and ionic strength respectively. As shown in figure 8 and figure 9, isotherm curves are similar to L type according to the classification of Giles et al. [40] for liquid-solid adsorption. The maximal capacities ( $q_{max}$ ) of methylene blue sorption decrease from 280 to 98 mg/g when the initial pH of solution decrease from 9 to 3 (figure 8) and from 205 to 74 mg/g when the NaCl concentration in solutions increases from 0.00 M to 0.10 M (figure 9).

#### - Equilibrium data modelling

In order to optimize the design of a sorption system to remove pollutant from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely: Langmuir and Freundlich.



**Figure 8:** Isotherms of methylene blue sorption by orange peel at 25 °C: effect of initial pH of solution ( $m/V = 1$  g/l,  $d_p = 1.25$ -2 mm,  $w = 400$  rpm,  $t_{eq} = 24$  h)



**Figure 9:** Isotherms of methylene blue sorption by orange peel at 25 °C: effect of ionic strength (m/V= 1 g /l, dp= 1.25- 2 mm, initial pH of solution: 5,03 to 5.19, w= 400 rpm, teq = 24 h)

-The model of Langmuir is based on the hypothesis that the surface of adsorbent is uniform with an absence of interactions between molecules adsorbed. The enthalpie of adsorption doesn't depend on the rate of recovery. This model considers that the adsorption operates by the formation of an adsorbat monocouche [41]. The linearised Langmuir model has the following form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \times q_m} \quad (5)$$

with  $q_e$  is the amount of dye sorbed at equilibrium per g of sorbent (mg/g),  $q_m$  is the maximal dye sorption capacity of sorbent material (mg/g),  $C_e$  is the equilibrium dye concentration in the solution (mg/L) and  $K_L$  is a constant of equilibrium (L/mg) depending on temperature and the applied conditions. The constants  $q_m$  and  $K_L$  will be obtained from the intercepts and slopes of the system of coordinates  $C_e/q_e = f(C_e)$ . This modelling permits us to determine the maximal capacity ( $q_m$ ) of sorption.

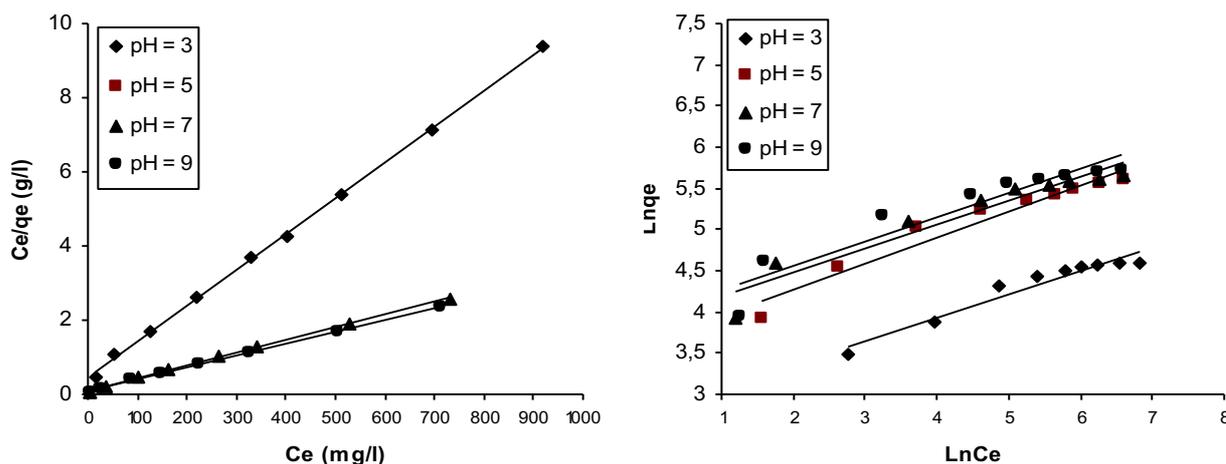
- The model of Freundlich is based on an empiric equation that translates a variation of adsorption energies with the quantity adsorbed. This distribution explains by heterogeneity of adsorption sites. Contrary to the model of Langmuir, this model admits the existence of interactions between molecules adsorbed [42]. The linearised Freundlich model has the following form:

$$\text{Ln } q_e = \text{Ln } K_F + n \text{ Ln } C_e \quad (6)$$

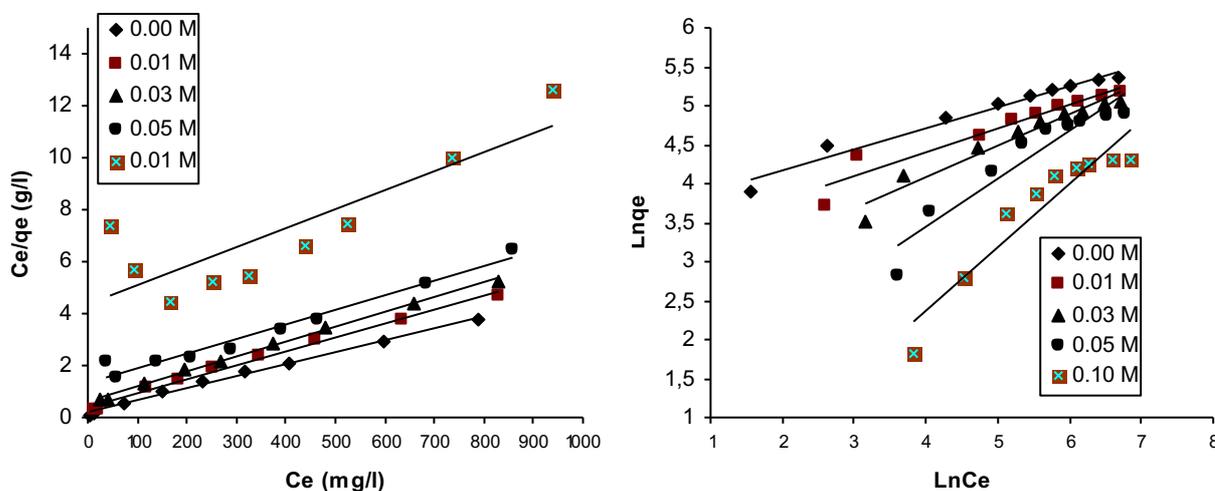
where  $q_e$  and  $C_e$  are as described before,  $K_F$  and  $n$  are positive constants depending on the nature of system solute- sorbent and temperature,  $n < 1$ . From the system of coordinates  $\text{Ln } q_e = f(\text{Ln } C_e)$ , the slope and the intercept to the origin give the values of constants  $n$  and  $K_F$  respectively.

The curves of equilibrium data modeling are presented in figure 10 and figure 11, respectively, for effect of initial pH and effect of ionic strength.

Besides, table 3 and table 4 gives the parameter results determined for the models. From results obtained (figure 10 and figure 11) and the model parameters determined and presented in table 3 and table 4, it appears that, and for each parameter studied, the Langmuir model is better to describe the experimental equilibrium results over the experimental dye concentration range with good coefficients of regression ( $R^2 > 0.98$ ). According to coefficients of correlation ( $R^2 > 0.89$ ) obtained, the model of Freundlich is not adequate for modeling the isotherm of dye sorption by orange peel tested in all the domain of studied concentrations. The maximal capacity ( $q_{\text{max}}$ ) of MB sorption by orange peel increases (table 3) with the increasing of initial pH of solution (from 103.95 mg/g at  $\text{pH}_0 = 3$  to 309.60 mg/g at  $\text{pH} = 9$ ). However, we can observed from results in table 4, the maximal capacity ( $q_{\text{max}}$ ) of MB sorption by orange peel decreases with increasing of the ionic strength from 218.82 mg/g at 0.00 M to 94.97 mg/g at 0.10 M. These results confirm those found previously in kinetic studies.



**Figure 10:** Equilibrium data modelling for methylene blue sorption by orange peel: effect of initial pH of solution **a)** Langmuir Model, **b)** Freundlich Model ( $m/V = 1 \text{ g/l}$ ,  $dp = 1.25\text{-}2 \text{ mm}$ ,  $w = 400 \text{ rpm}$ ,  $T = 25^\circ\text{C}$ ,  $teq = 24 \text{ h}$ )



**Figure 11:** Equilibrium data modelling for methylene blue sorption by orange peel: Effect of ionic strength **a)** Langmuir model, **b)** Freundlich model ( $m/V = 1 \text{ g/l}$ ,  $dp = 1.25\text{-}2 \text{ mm}$ , natural pH of solution,  $w = 400 \text{ rpm}$ ,  $T = 25^\circ\text{C}$ ,  $teq = 24 \text{ h}$ )

**Table 3:** Parameters of Langmuir and Freundlich models for MB sorption Isotherm by orange peel: effect of initial pH of solution

Freundlich model			Langmuir model			pH <sub>0</sub>
R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>	K <sub>L</sub> (L/mg)	q <sub>max</sub> (mg/g)	
0.9376	0.282	16.530	0.9993	0.0208	103.95	3
0.9447	0.313	38.758	0.9954	0.0239	277.78	5
0.9195	0.290	49.542	0.9983	0.0374	291.54	7
0.8912	0.294	53.016	0.9991	0.0444	309.60	9

**Table 4:** Parameters of Langmuir and Freundlich models for MB sorption Isotherm by orange peel: effect of ionic strength

Freundlich model			Langmuir model			[NaCl] (M)
R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>	K <sub>L</sub> (L/mg)	q <sub>max</sub> (mg/g)	
0.9675	0.271	37.78	0.9944	0.022	218.82	0.00
0.9256	0.307	23.84	0.9895	0.013	187.97	0.01
0.9485	0.403	11.73	0.9965	0.009	175.13	0.03
0.9054	0.621	2.63	0.9924	0.006	165.29	0.05
0.8962	0.819	0.46	0.9859	0.005	94.97	0.10

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter,  $R_L$  [43], which is defined as follow (equation 6):

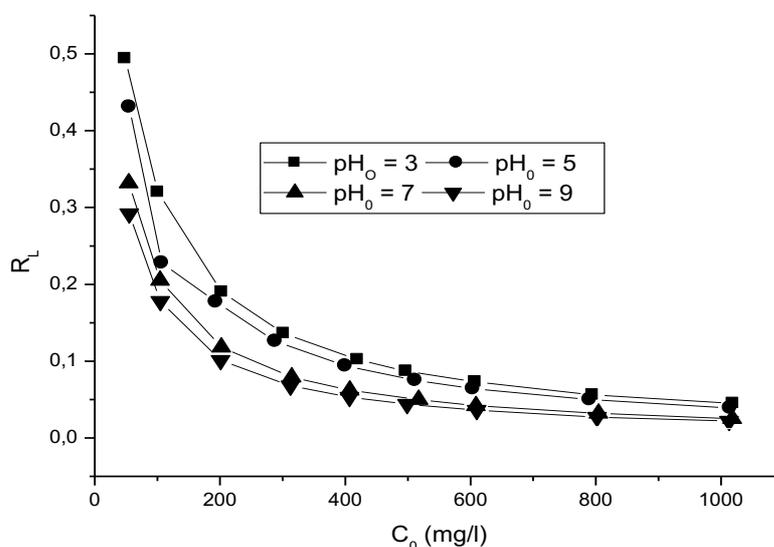
$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (7)$$

According to the value of  $R_L$ , the isotherm shape may be interpreted as follows:

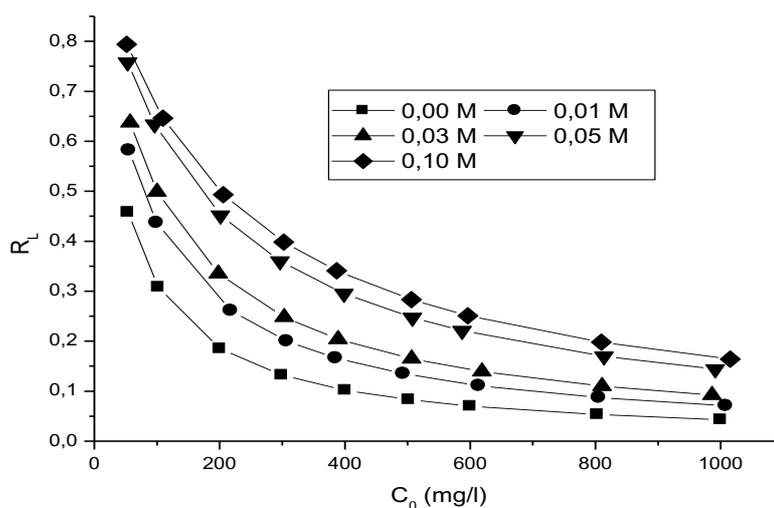
**Table 5:** Significance of the separation factor of Langmuir  $R_L$

Type of adsorption	Value of $R_L$
Unfavorable	$R_L > 1$
Linear	$R_L = 1$
Favorable	$0 < R_L < 1$
Irreversible	$R_L = 0$

The calculated  $R_L$  value versus MB initial concentration at 25°C, was represented in figure 12 for effect of initial pH solution and in figure 13 for effect of ionic strength.



**Figure 12:** Separation factor for methylene blue sorption by orange peels at 25°C: effect of initial pH of solution

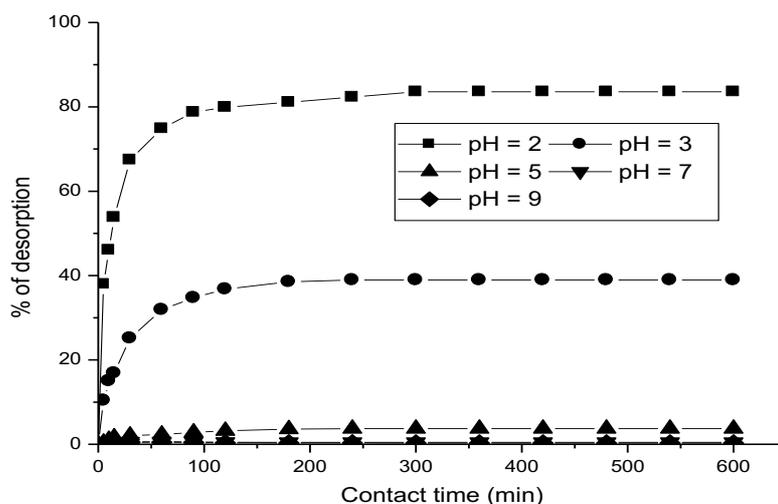


**Figure 13:** Separation factor for methylene blue sorption by orange peels at 25°C: effect of ionic strength

For all parameters studied, the values of  $R_L$  (figure 12 and figure 13) are between 0 and 1, ( $0 < R_L < 1$ ), which indicates that the sorption process of methylene blue by orange peel is favorable.

### 3.4. Desorption kinetics of methylene blue

The desorption study were undertaken in distilled water at different values of initial pH ranging from 2 to 9. The results are presented in figure 14.



**Figure 14:** MB kinetics desorption from orange peel previously saturated: effect of initial pH of distilled water ( $m/V = 1\text{g/l}$ ,  $dp=1.25\text{-}2\text{ mm}$ ,  $w= 400\text{ rpm}$ ,  $T= 25^\circ\text{C}$ )

As shown in figure, an acidic pH is very favorable for methylene blue desorption. More than 80 % of the dye previously sorbed on orange peel was pass through solution of water distilled at  $\text{pH}_0 = 2$ . The desorption rate decrease of more than 50 % at  $\text{pH} = 3$ , and became negligible (less 0.5 %) at neutral or basic pH. A contact time of 4 hours was be found necessary to reach the equilibrium of dye desorption (figure 14). Over this time, no variation in the desorption rate has been observed.

### Conclusion

The present study shows that orange peel can be efficiently used as sorbent for removal methylene blue from synthetic aqueous solutions. The results showed that the quantity of dye uptake at equilibrium is contact time, initial pH and ionic strength of the solution depending. The amount of methylene blue sorbed at equilibrium increase from 44,90 mg/g to 98,76 mg/g with the increasing of initial pH solution from 3 to 9. The amount of dye sorbed at equilibrium, decrease from 81.51 to 14 mg/g when the ionic strength increase from 0.00 to 0.1 M. The maximal capacities ( $q_{\text{max}}$ ) of methylene blue sorption decrease from 280 to 98 mg/g when the initial pH of solution decreases from 9 to 3 and from 205 to 74 mg/g when the NaCl concentration in solutions increases from 0.00 M to 0.10 M. An acidic pH ( $\text{pH} = 2$ ) is very favorable for a good desorption of dye in distilled water (more than 80 %). A contact time of 4 hours was be found necessary to reach the equilibrium of dye desorption. The pH value of solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence on adsorption capacity. Initial pH value may enhance or depress the dye uptake. This is attributed to the charge of the sorbent surface with the change in pH value.

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