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A New Low Cost Biosorbent for a Cationic Dye Treatment

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***Abstract*— *The aim of our study consists to investigate the adsorption of Methylene Blue from aqueous solution by a new biosorbent prepared from Papaya seed. Adsorption behavior of the cationic dye was analyzed by variation of solution pH, contact time, adsorbent dose, and temperature. Adsorption isotherms were studied according to the Langmuir and Freundlich Model, and adsorption kinetics according to pseudo first and second order. Results show that the maximum adsorption is obtained at ambient temperature with the yield of 98.82% and was reached in first 20min (pH = 10, adsorbent dose of 100 mg in 50 mL). The Langmuir isotherm shows a correlation coefficient of 99.4% higher than 95.4%obtained for Freundlich model and the adsorption kinetic model follow a pseudo-second order with a maximum adsorption capacity of 52.28 mg/g.*

Keywords*— *Methylene Blue, adsorption, Papaya seed, adsorption isotherm and adsorption kinetic.

I. INTRODUCTION

Water pollution has been generated an enormous fund input and raised worldwide concern**[1]**. Textile wastewater, generally, contains a big amount of pollutants materials like colored materials or dyes, organic compounds and heavy metals ions.These materials can affect the physicochemical and the biological properties of sea, drinking water and globally the ecosystem. In addition to the undesirable colors of textile effluents, some dyes may degrade to produce carcinogens and toxic products **[2]**. Furthermore, the colored effluents reduce light penetration and potentially prevent photosynthesis. Dyes even in very low concentrations affect the aquatic life and food chain. In the recent years, researchers are indulging their interest in wastewater treatment by various processes such as precipitation, ion exchange, reverse osmosis and adsorption **[3]**. The adsorption of colored solution has been the main point of numerous researchesas the effective process because it's easy to do, produce sludge without chemical products like conventional wastewater treatment, selective and cost-effective**[3]**.In this work, we used a new biosorbent, to treat the Methylene Blue (MB) by the batch adsorption system; the work consisted on the study of the effect of different factors which influenced the adsorption process as: pH, adsorbent dose, contact time and temperature, to deduce the adsorption thermodynamic and kinetic behavior process.

II. MATERIALS AND METHODS

2.1. Material and reagents:

Different laboratories materials are used in this work like UV visible spectroscopy (HACH LANGE DR 6000) for determination of MB concentration at a wave number of 662 nm, multi-parameter Consort C 3040 to adjust the pH values by HCl (0.1N) orNaOH (0.1N) and multi agitator.Methylene Blue(MB) ($C_{16}H_{18}ClN_3S$ see **Fig.1**), obtained from Sigma Aldrich, with a molecular weight of 319.85 g/mol. Solutions were prepared by dilution with distillated water of the stock solution of MB with the initial concentration of 1000 ppm to reach the desired concentration.

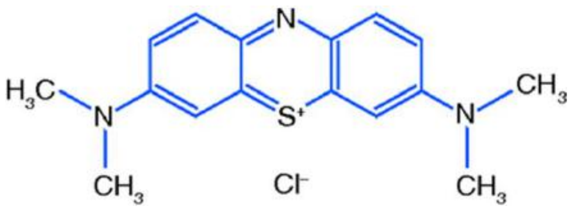

Fig.1: Methylene Blue structure

2.2. Characterization of the biosorbent:

Papaya seedare very abundant in Morocco and not valorized for any use were collected from a manufacturing process in the location of Settat- Casablanca, Morocco, washed several times to eliminate the impurities, and thencrushed to obtain a powder used as a new biosorbent. Our product was used in wastewater treatment without any chemical or physical activation treatment. The physicochemical properties of our biosorbent were determined by Langmuir and Freundlich model.

2.3. Adsorption experiments:

The adsorption experiments of MB on the biosorbent were reached after 2h of stirring at ambient temperature and

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agitation speed of 300 rpm. The suspensions were collected then centrifuged and the MB equilibrium concentrations were determined at 662 nm. The yield of adsorption and the amount of MB adsorbed at equilibrium noted R in (%) and q_e in mg·g^{-1}, respectively, were calculated by the following equations (**Eq.1 and Eq.2**):

$$R(\%) = \frac{C_0 - C_t}{C_0} . 100 \quad (1) \qquad q_e = \frac{(C_0 - C_t)V}{m} (2)$$

Where C_0 is the initial dye concentration (mg·L^{-1}), C_t is the equilibrium dye concentration (mg·L^{-1}), V is the volume of the solution and m is the mass of the adsorbent (g).

2.3.1. Kinetic study:

Adsorption kinetic experiments were carried out using batch model. All of the dye solution was prepared with distilled water. Kinetic experiments were carried out by agitating 100 ml of solution of a constant dye concentration with 60 mg of MB at a constant agitation speed, ambient temperature and pH = 2. Agitation was made from 5 to 120 min.The experimental data will fitted by the pseudo-first-order and pseudo-second-order equation **[4]**

$$\mathrm{Ln}\,(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

Where:

K_1: the rate constant of the pseudo-second order model (min^{-1}); q_t and q_e are the amounts of dye adsorbed on biosorbent in mg/g at time t and in the equilibrium respectively;

k_2 is the pseudo-second order kinetic model rate constant in g/mg. min

3.3.2. Isotherm study:

Different isotherm models provide us several information about the adsorption mechanism, the surface properties of the sorbent and the affinities between the sorbent and sorbate. In this work, two of the most used isotherms namely Langmuir and Freundlich, were used to fit the equilibrium experimental data of MBadsorption into our biosorbent. Langmuir theory assumes the existence of finite number of identical sites homogeneously distributed over the adsorbent surface, the linear form of this model is represented in the Eq.(**5**):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} (5)$$

Where:

q_e: the equilibrium dye concentration on the adsorbent (mg.g^{-1}); C_e: the equilibrium dye concentration in the solution (mg.L^{-1}); q_{max}: the maximum adsorption capacity of the adsorbent (mg.g^{-1}); K_L: the Langmuir adsorption constant (L.mg^{-1})

When the Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction betweenthe adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that asthe adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increasesand, correspondingly, the sorption energy exponentially decreases. The well-known expression for the Freundlich model is given by the linear equation (**Eq.6**):

$$\mathrm{Log}\,q_e = \log K_f + \frac{1}{n_F} . \log C_e \qquad (6)$$

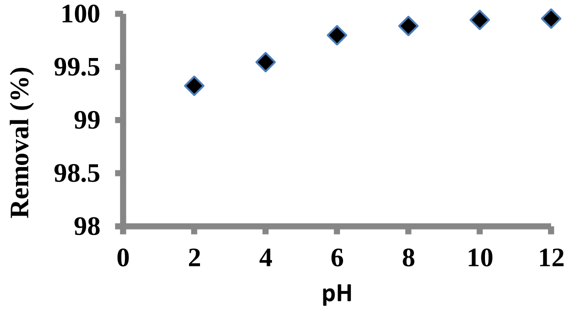
Where

q_e: the equilibrium dye concentration on the adsorbent (mg.g^{-1}); C_e: the equilibrium dye concentration in the solution (mg.L^{-1}); K_F: Proportionality constant for Freundlich equation [(mg.g^{-1})(L.mg^{-1}) $^{1/n}$]; 1/n_F: the adsorption intensity.

III. RESULTS AND DISCUSSIONS

3.1. Effect of pH on adsorption process:

In general, initial pH value may enhance or depress the uptake of solute. ThepH of adsorption medium influences not only the surface charge of adsorbent, but also, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent and the solution dye chemistry**[5]**.The effect of pH on MBremoval was analyzed over the pH range from 2-12. The pH was adjusted using 0.1 N (NaOH) or 0.1 N (HCl) solutions. In this work, 50 mL of dye solution was agitated with200mg of our biosorbentfor 120 min then the sample was centrifuged and analyzed using a spectrophotometer by measuring the absorbance changes at a wavelength of maximum absorbance 662nm. The **Fig.3**shows the effect of pH on Methylene Blue elimination, it's can be seen from the figure that the percentage removal of Methylene Blue by our biosorbent was optimum at basicpH =10, It could be as a result of the attraction between the positives charges of the cationic dye and the negatives of the sorbent. **Hassan et al., (2013)[6]**were obtained the similar basic adsorption (pH=8) of MB onto Haloxylonrecurvum plant stems



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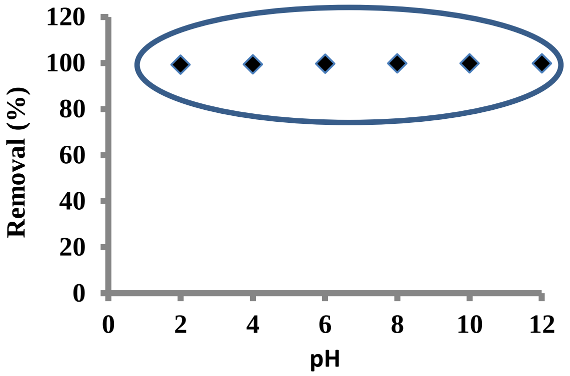


Fig.1: Effect of pH on Methylene Blue adsorption (V=50mL, t=2H, m = 200 mg)

3.2. Effect of adsorbent dose:
Adsorbent dose is a very important factor that influences the sorption process. Thebiosorbent product at various doses was added to 50 mL of MB solution with initial concentration of 100 ppm at optimal pH of 10 and atambient temperature.

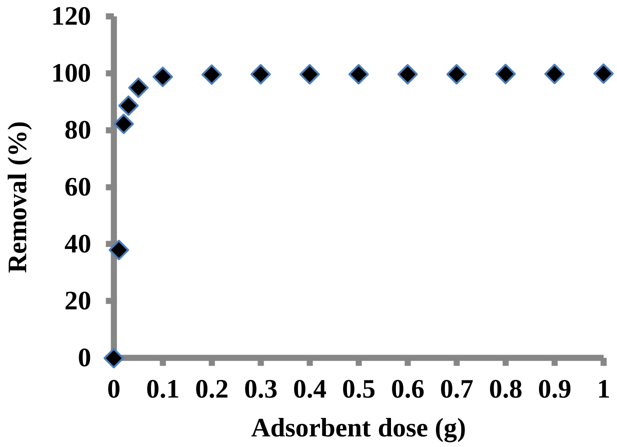


Fig.2: Effect of adsorbent dose on Methylene Blue adsorption (V=50mL, t=2H, pH=10)

The **Fig.2**revealed that the adsorption removal yield increase with the increasing of the adsorbent dose until the optimal value of adsorbent dose of 100 mg, after this value there was any significant change of the MB elimination.This can be explicated by the increases of the surface area and thus the number of available adsorption sites**. Mahammedi and Belkacem (2015)[7]**were obtained a maximum MB removal using4 g/L using natural clay.

3.3.Effect of contact time and kinetic study:
The plot of removal yield versus time is shown in **Fig. 3**.In this plot, it is apparent that MB removal by the adsorption increased rapidly in the initial stage (20 min) and became slower in the later stages until the attainment of equilibrium.

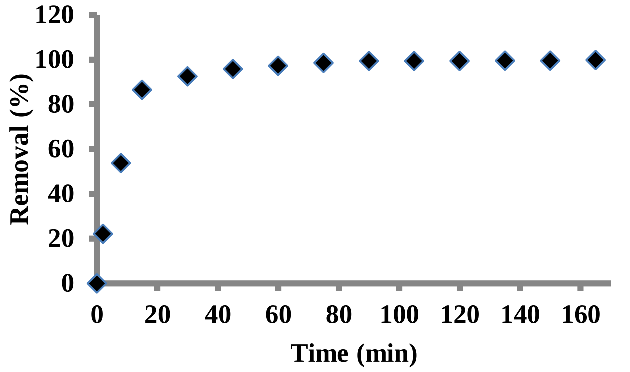
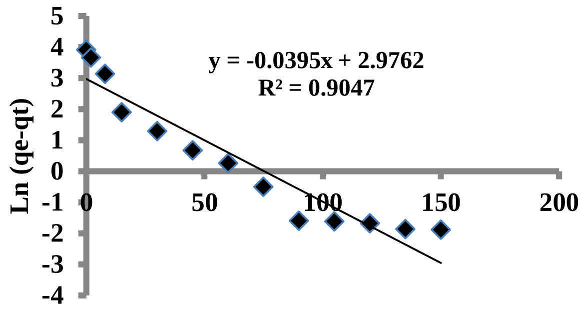


Fig.3: Effect of contact time on Methylene Blue adsorption (V=500mL, pH=10, m=1g)

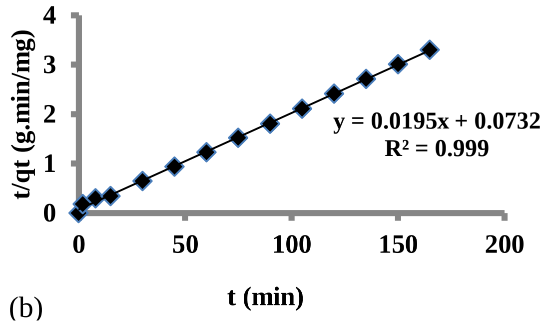
As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the dye molecules are transported from the exterior to the interior sites of the adsorbent particles. Equilibrium time for the adsorption of MB found by **Amuda et al.,(2014)[8]**was found to be 60 min to reachonly an adsorption yield of 90% using Steam-Activated Carbon Produced from Lantana camara Stem.

3.3.1. Kinetic study:
The plot of $t/q_t$and Ln (q_e-q_t) versus time t, were shown in the **Fig.4**



(a)

Fig.4: (a) Pseudo first order,



(b)

Fig.4: (b) Pseudo second order plot of papaya seed biosorbent

From the results we observed that the adsorption of Methylene Blue was better fitted with the pseudo second order with a R^2=0.99 (**Table.1**).

Table.1: Adsorption kinetic parameters of Methylene Blue

Pseudo-second order			Pseudo first order	
Qe (mg/g)	K_2 (g /mg .min)	R^2	K_1 (min^{-1})	R^2
51.28	0.133	0.99	0.039	0.90

These results indicate that the kinetic model of the adsorption is based on the assumption that the rate-limiting step is a chemical adsorption involving valance force through sharing or exchange of electrons between adsorbent and adsorbate.Similar result was also obtained by **Han et al., (2017)** using Molybdenum Disulfide Nanostructure **[9].**

3.3.2. Adsorption isotherm study:

The adsorption capacity of the adsorbent, interaction between the solute-solution and the nature of adsorbed accumulation materials on the surface of the adsorbent can be explained using isotherm models. The **Fig. 5** shows the plot of Langmuir and Freundlich isotherm models.

Results shown in **Fig.5**revealed that the biosorption of MB on papaya seed adsorbent is the monolayer type since the correlation coefficient (R^2) calculated from Langmuir isotherm is below 0.99, which indicate lessapplicability for Langmuir isotherm.

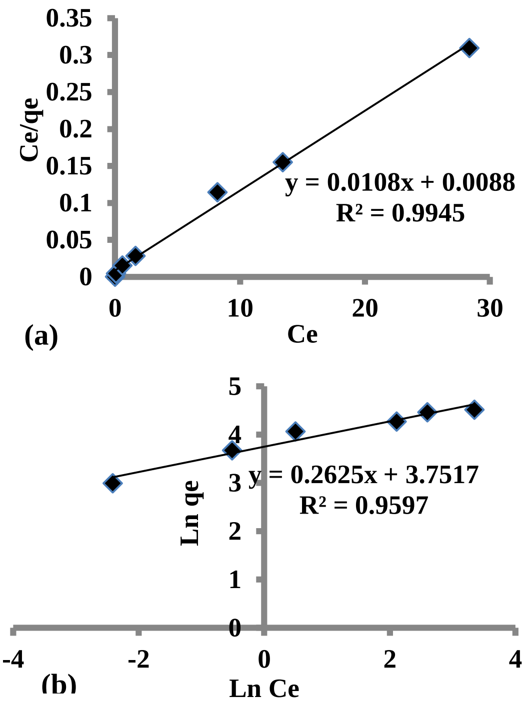


Fig.5 Adsorption isotherm of MB on papaya seed (a) Langmuir model, (b) Freundlich model

These results are in accordance with the result obtained in our Patent number PCT/MA2016/000003 for the removal of MB by combination of adsorption process into clay material and flocculation by polyelectrolyte extracted from cactus cladode.

IV. CONCLUSION

Papaya seed were selected as a suitable agriculture product thanks its abundance in Morroco and its disposal in the environment without any treatment. Several parameters were studied to deduce their effect on Methylene Blue adsorption. The adsorption of Methylene Blue increase with the increasing of time, temperature and adsorbent dose. The results show that the optimal condition of treatment of pH =10, adsorbent dose of 200mg in 100mL and very low contact time of 20 min are sufficient to eliminate 98.8% of Methylene Blue. The adsorption isotherm was well reproduced with Langmuir model and show that the adsorption is the monolayer type, the kinetic study shows that the adsorption follows the pseudo second order model.

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