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Study of the adsorption of methylene blue by natural materials (olive stone, date pit and their mixture) in fixed bed column

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ABSTRACT/RESUME

Abstract:*The present study focuses on the recovery of two agro-food waste available in our country with significant quantities olive pomace and date pits for the removal of a synthetic dye which is methylene blue. Both materials were used in their native forms separated and mixed to improve their adsorptive capacity. A range of physico-chemical analysis was performed to characterize adsorbents used, among them: the FTIR spectroscopy and the scanning electron microscopy. The ability of adsorbents prepared to adsorbe methylene blue (MB) from the aqueous solution was investigated in a fixed bed column. The effects of several important parameters were studied, such as initial concentration of MB, flow rate and bed height. The corresponding breakthrough curves were calculated.*

I. Introduction

With the technological development and progress of various vital sectors, industrial activities are constantly increasing and producing effluents that are often contaminated with harmful and toxic substances. Among these harmful elements are dyes, which are the main constituents of industrial effluents from the textile, baking, dyeing, painting, plastic [1],pharmaceutical and cosmetic industries [2, 3].

The latter, loaded with dye, can present nuisances, and serious impacts, in the receiving environment, because they can affect thephotosynthesis activity in aquatic life[4], Due to the reduced penetration of light. And may also be dangerous, for some aquatic species, due to the presence of aromatic hydrocarbon, metals, and chlorides in their constitution, which are toxic. Therefore the removal of dyes from industrial effluents has become one of the main environmental concerns today not only to protect human health, but also for the protection of the natural environment.

Current methods used for their removal include physicochemical methods, such as flocculation, oxidation, ozonation, and reverse osmosis, and biological techniques. All these methods are different in terms of color removal, operation and financial cost. In recent years, researchers have focused on treatment processes using natural materials, especially waste from agricultural industries and activities suchas: tea waste [5],apricot stone [6] , peach stone[7],orange peel[8], because of their low cost[9].

And as olive pomace and dates pits, are agricultural waste products, available in our country rejected in significant quantities annually, into the environment. In the present work, we have opted for the valorization of these agro-alimentary by-products, and their use as adsorbents for the removal of the pollutant model that has been chosen methylene blue because of its wide presence in the charged effluents with dyes and its toxicological effect[10], the study was established in dynamic mode, the adsorbents are used in the separated native state and in mixture of the two materials to improve their adsorption capacities.

II. Materials and methods

II.1. Sorbent Preparation

The date pits were collected from the south of Algeria, and the olive stones were obtained from an olive oil production in the north region of Algeria. These two materials used are first washed several times under running water to remove adhering dust and impurities, then rinsed with distilled water. They are then exhausted with hexane to remove residual oil, and washed with distilled water several times and dried at 105 ° C, then they were crushed into small pieces. A sample based on the mixture of both materials was prepared.

The adsorbents used, and their composition in mass percentage are listed below:

Sample 1: 100% olive stone + 0% date pit (100% OS, 0% DP).

Sample 2: 100% date pit + 0% olive stone (100% DP, 0% OS).

Sample 3: 50% date pit + 50% olive stone (50% DP, 50% OS)

* **DP**: date pit in native state
* **OS:** olive stone in the native state

* The mixture of dates and olive stones was crushed with an electric grinder and sieved through a stack of sieves of different mesh size. The study focused on the size fraction between (80 μ and 630 μ). Then we kept them in desiccators until use. We worked with the samples in their native state.

II.2. The adsorbates

The dye used in this study is a cationic dye which is methylene blue, it is chosen because of its strong adsorption onto solids. The chemical structure of methylene blue is shown in the following figure

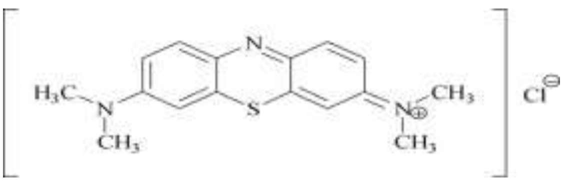

***Figure 1*:** Methylene Blue structure

The colored solutions are prepared by dissolving a mass of dye in distilled water at a concentration of 1000 mg / l. The MB solutions for biosorption experiments were prepared by diluting the colored solutions to the appropriate concentrations .

II.3. Instrumentation and characterization:

Characterization of a biosorbent is an important analysis to understand the behavior or mechanism of removal of methylene blue on the surface of the biosorbant forthat different analyzes were perforemed, among them scanning electron microscopyand the infrared transformed Fourier,

The scanning electron microscopy (SEM) technique was used to observe the physical surface morphology of adsorbents before adsorption of methylene blue from the images obtained.

FTIR analysis was performed to identify the chemical groups present in the biosorbents and complete the study of the functional groups. The FT-IR measurements were carried out using a Nicolet 560 FTIR Fourier Transform spectrometer coupled to a digital calculator allowing the spectra to be plotted between [4000 and 400 cm -1]. Characteristic bands of adsorbents were assigned according to the literature.

II.4. Study of adsorption in dynamic mode:

The biosorption performance of the adsorbent in a continuous system is an important factor in accessing biosorbent feasibility in real applications.

The adsorption studies on the materials used were carried out in a continuous reactor column, made by glass with an internal diameter of 20 mm and 250 mm height. The initial dye concentration, flow rate, and bed depth in the column were varied to obtain different retention times. The flow rate was regulated by a variable peristaltic pump which was used to percolate the methylene blue synthetic effluent by an upward flow through a bed of olive pomace, date pit and the mixture of the two materials.

The experiments were conducted until column saturation was observed. The kinetics of dye adsorption in a continuous flow reactor were also studied. Various concentrations (Ci= 50, 100 and 200 mg / l), heights (H = 3, 5 and 7 cm) and flow rate (Q = 5; 8.15 and 12 ml / min) were studied. Samples are collected at the outlet of the column at regular time intervals. Residual methylene blue concentrations were measured using a Visible UV spectrophotometer at 664 nm wavelength to establish the breakthrough curves.

The results of the adsorption of methylene blue in dynamic mode were represented by the breakthrough curves, which are expressed in terms of the final concentration (Ct) relative to the initial concentration (C0) as a function of time for a given condition,where Ct is the influent concentration, C0 is the effluent concentration.

The adsorption capacity of the adsorbent under certain operating conditions could be calculated from the breakthrough curve. The breakthrough point is the point where the concentration of the effluent (Ct) reaches about 0.1% of the initial concentration (C0). The corresponding time is the breakthrough time (tb). When the concentration of the effluent reaches 95% of the initial concentration, it is the saturation point and the time corresponds to the exhausting time (te) [11].

The total mass qtotal (mg) of adsorbates adsorbed on OS, DP and the mixture of both (50% DP + 50% OS) could be calculated using the following equation (1) [12].

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$$q_{total} = \frac{Q.A}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\, dt \qquad (1)$$

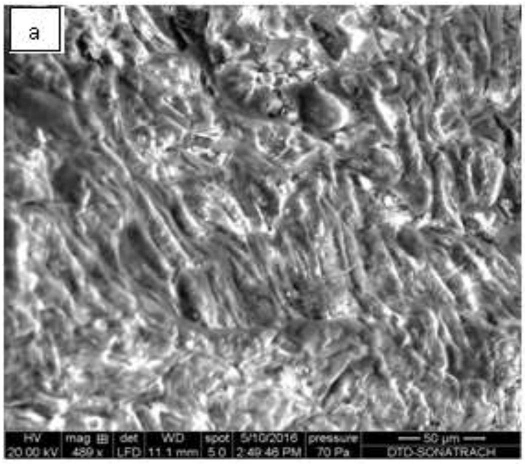
Where t total is the total flow time (min), Q is the flow rate (ml / min) and A is the area above the breakthrough curve, Cad (mg / L) is the adsorbed concentration. The total amount of adsorbates flow in the column is calculated by equation (2) [13].

$$m_{total} = \frac{C_0.Q.t_{total}}{1000} \qquad (2)$$

III. Results and discussion

III.1. Characterization

The olive stone and date pit and their mixtures used in this study were analyzed by the SEM to examine their morphology. The SEM image of the adsorbent before adsorption of methylene blue is illustrated in Fig. 2. It shows pores of different sizes and shapes, and also they have an irregular structure which can promote the biosorption of MB + ions on different parts. biosorbent. For the mixture the image also shows a very porous morphology, and an external surface full of cavities.



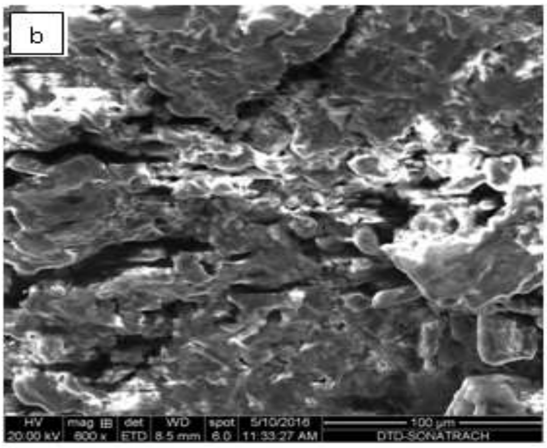


Figure2: *SEM image of: a) OS; b) DP; c) (50% OS+50% DP)*

FTIR spectroscopy analysis is mainly used to identify the functional groups present on the surface of the adsorbents. The FTIR spectra before MB biosorption are shown in Fig. 3.

The FTIR results revealed very similar spectra for olive pomace and date pit and their mixtures, which confirmed that the functional groups are similar. The FTIR analysis shows the presence of different oxygen groups, mainly: carbonyl, alcohol and phenol groups, ethers and esters. Therefore, the good sorption properties of olive pomace and date pit to MB + ions can be attributed to the presence of these functional groups.

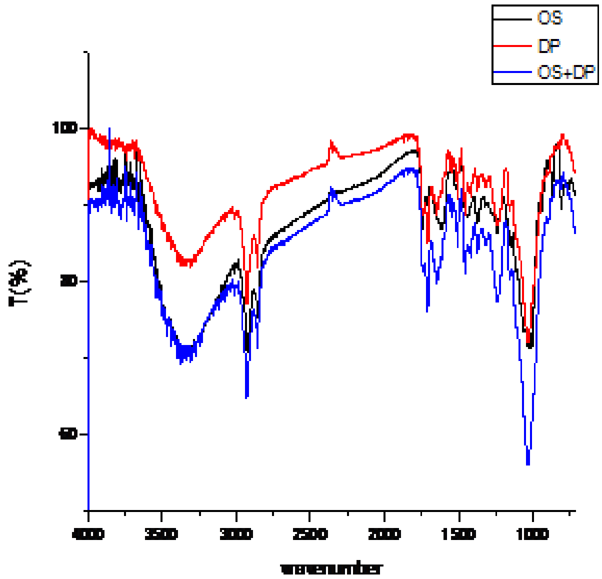


Figure 3: *The FTIR spectra of the adsorbents: DP, OS and the mixture (50% OS + 50% DP)*

The spectrum shows a broad band characteristic of the OH group linked to the OH stretching mode in alcohol and phenol appearing at 3333 cm-1 for OS and 3346 cm-1 for DP and the mixture, two absorption bands. stretching at 2920 and 2853 cm-1 for OS and 2933, 2866 cm-1 for DP and mixture, these bands are assigned to C-H stretching vibrations; and the characteristic C bands at 1720 cm-1 for OS, 1733 cm-1 for DP and the presence in the mixture of the two bands that appeared in the separate adsorbents OS and DP, these bands are characteristic of the C = O functional groups. The bands appearing at 1640, 1613 and 1543 cm-1 are attributed to the C = C vibrations in the aromatic rings. Bands at 1253 cm-1, 1240 cm-1 are related to C-O stretching in alcohols and phenols. The bands observed between 1013 cm-1 and 1040 cm-1 are attributed to the primary alcohol function. The bands observed between 866 cm-1 and 800 cm-1 are due to the off-plane deformation mode of C-H for the alkenes aromatic cycles.

III.2. Dynamic adsorption

III.2.1. Effect of bed height

The breakthrough curves at different bed heights were shown in Figures 04 (a,b,c) and column parameters in Table 1.By increasing the bed height, the breakthrough curves shiffted to the higher times. Increasing the bed height from 3 to 7 cm caused an increase in breakthrough time from (35 to 155 min), and (40 to 165 min), and bed exhaustion time from (240 to 445 min) and (280 to 425 min), for olive stone (100% OS, 0% DP) and date pit (100% DP, 0% OS) respectively, and for the mixture of the two adsorbents (50% DP, 50% OS) results are improved by comparing them with the separate adsorbents, for the breakthrough time from (85 to 310 min) and the bed exhaustion time from (310 to 695 min).

At higher bed height, more biosorbent became available, more sorption site increased for fixation of dye molecules that result in increase of contact time and then increased breakthrough time and saturation.

The results obtained in Table n°1 shown that an increase of 50% of date pit in the mixture of the adsorbents (50% DP, 50% OS) represented an improvement in the amount of the adsorbed dye and have an increase of 24,77%, it was obtained by 17,21 and 21,47 mg for (100% OS, 0% DP) and (50% DP, 50% OS) respectively when the bed height was 3 cm.

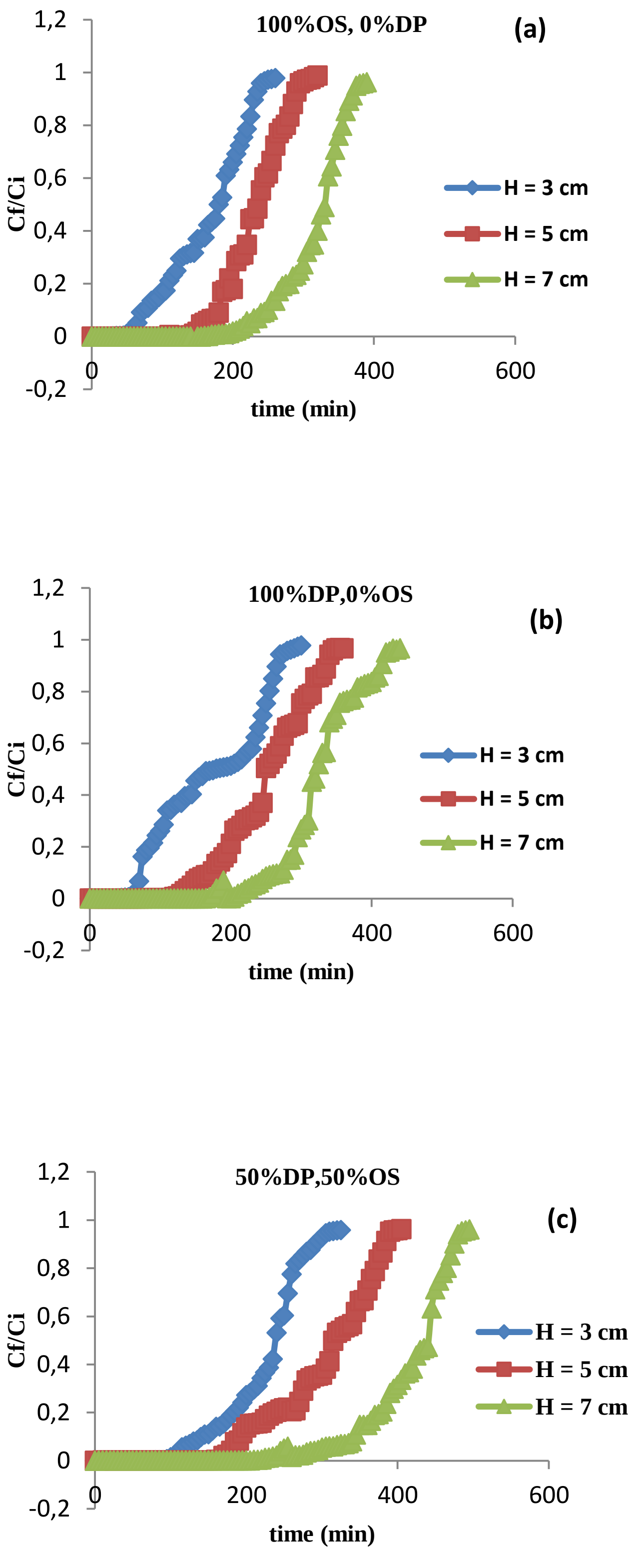


Figure 4: *Breakthrough curves for adsorption of MB by olive stone **(a)** ; date pit **(b)** ; mixture of date pit and olive stone **(c)** for different bed height values (pH = 5.6 Q = 8.15 ml / min Ci = 100 mg /l)*

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Table n ° 1: Parameters of the column obtained at different bed hight

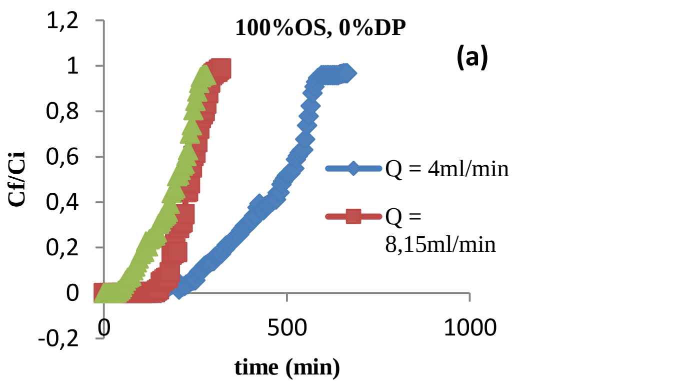
	Parameters of the column obtained at different bed hight					
type of adsorbant	**height(cm)**	**t_b(min)**	**t_e(min)**	**m_0(mg)**	**m_{total}(mg)**	**m_{ads}(mg)**
100% OS, 0% DP	3	35	240	178,387	195,6	17,212
	5	105	350	256,725	285,25	28,525
	7	155	445	311,737	346,375	34,637
100% DP, 0% OS	3	40	280	207,662	228,2	20,538
	5	125	360	324	360	36
	7	165	425	382,5	425	42,5
50% DP, 50% OS	3	85	310	231,174	252,65	21,475
	5	230	570	418,095	464,55	46,455
	7	310	695	509,78	566,42	56,642

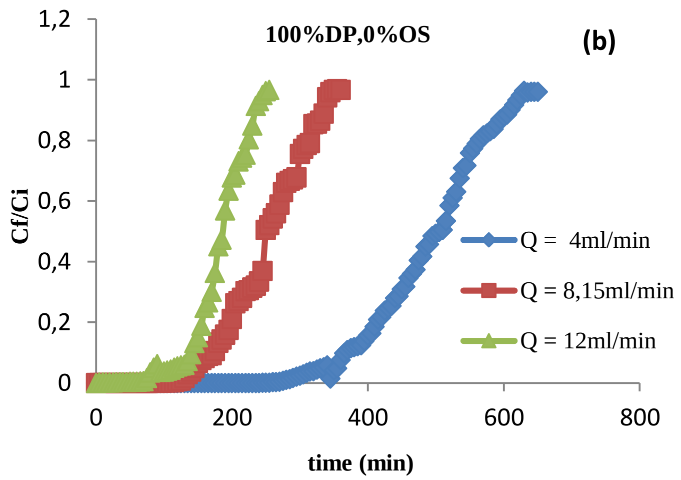
III.2.2 Flow rate effect

Flow rate is one of the important characteristics for the continuous treatment of dye effluents. Experiments were conducted to investigate the effect of flow rate on methylene blue dye removal by setting the initial concentration at 100 mg / l, bed height at 5 cm and varying the flow rate from (4 to 12 ml / min). The results of the breakthrough curves were shown in Figures 5 (a,b,c) and the parameters of the column in Table 2.

Increasing flow rates decreased the residence time of the colored solution in the column, which reduced the contact time leading to an early breakthrough. At higher flow rates, all dye molecules didn't have enough time to penetrate and diffuse throughout the adsorbent particles.

The result obtained in the table showed that an increase of 50% of date pit in the mixture of the adsorbents (50% DP, 50% OS) represented an improvement in the amount of the adsorbed dye and have an increase of 47,83%, it was obtained by 27,6 and 40,8 mg for (100% OS, 0% DP) and (50% DP, 50% OS) respectively when the flow rate was 12 ml/min.





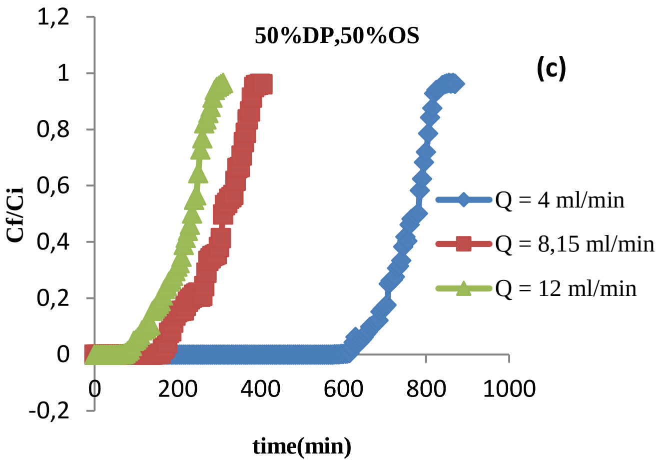


Figure 5:*Breakthrough curves for adsorption of MB by olive stone* ***(a)*** *; date pit* ***(b)*** *; mixture of date pit and olive stone* ***(c)*** *for different flow rates (pH = 5.6 H = 5 cm Ci = 100 mg / l)*

Table n ° 2: Parameters of the column obtained at different flow rates

	Parameters of column obtained at different flow rates					
type of adsorbant	**flow rates (ml/min)**	**t_b(min)**	**t_e(min)**	**m_0(mg)**	**m_{total}(mg)**	**m_{ads}(mg)**
100% OS, 0% DP	**4**	**155**	**590**	**265,5**	**295**	**29,5**
	8,15	**105**	**350**	**256,725**	**285,25**	**28,525**
	12	**25**	**230**	**248,4**	**276**	**27,6**
100% DP, 0%OS	**4**	**255**	**630**	**340,2**	**378**	**37,8**
	8,15	**125**	**360**	**324**	**360**	**36**
	12	**30**	**240**	**331,2**	**360**	**28,8**
50%DP, 50%OS	**4**	**585**	**990**	**445,5**	**495**	**49,5**
	8,15	**230**	**570**	**418,095**	**464,55**	**46,455**
	12	**100**	**340**	**367,2**	**408**	**40,8**

III.2.3. Effect of initial dye concentration

The effect of the initial concentration was studied by setting the bed height to 5 cm, flow rate to 8.15ml / min, and varying the initial concentration from (50 to 200 mg / l). The results of the breakthrough curves were shown in Figures 6 (a,b,c)and the parameters of the column in Table 3. It is observed from the figure that the low concentrations of colored solution delayed the breakthrough and required longer time for saturation, this is due to the low concentration gradient which caused slower transport due to the decrease of the diffusion coefficient, on the other hand, an increase in the initial concentration accelerated the breakthrough and reduced the saturation time.The results indicated that increasing the initial concentration improved the efficiency of column biosorption. The maximum removal of the dyeswa obtained at 200 mg / l.

The results presented in the table show that for the different concentrations (50, 100, 200 mg / l), the maximum capacities of the bed were respectively (13.35, 28.53 and 47.27 mg / g) for the sample (100% OS, 0% DP) and (19.32, 36, 53,79) for (100% DP, 0% OS).

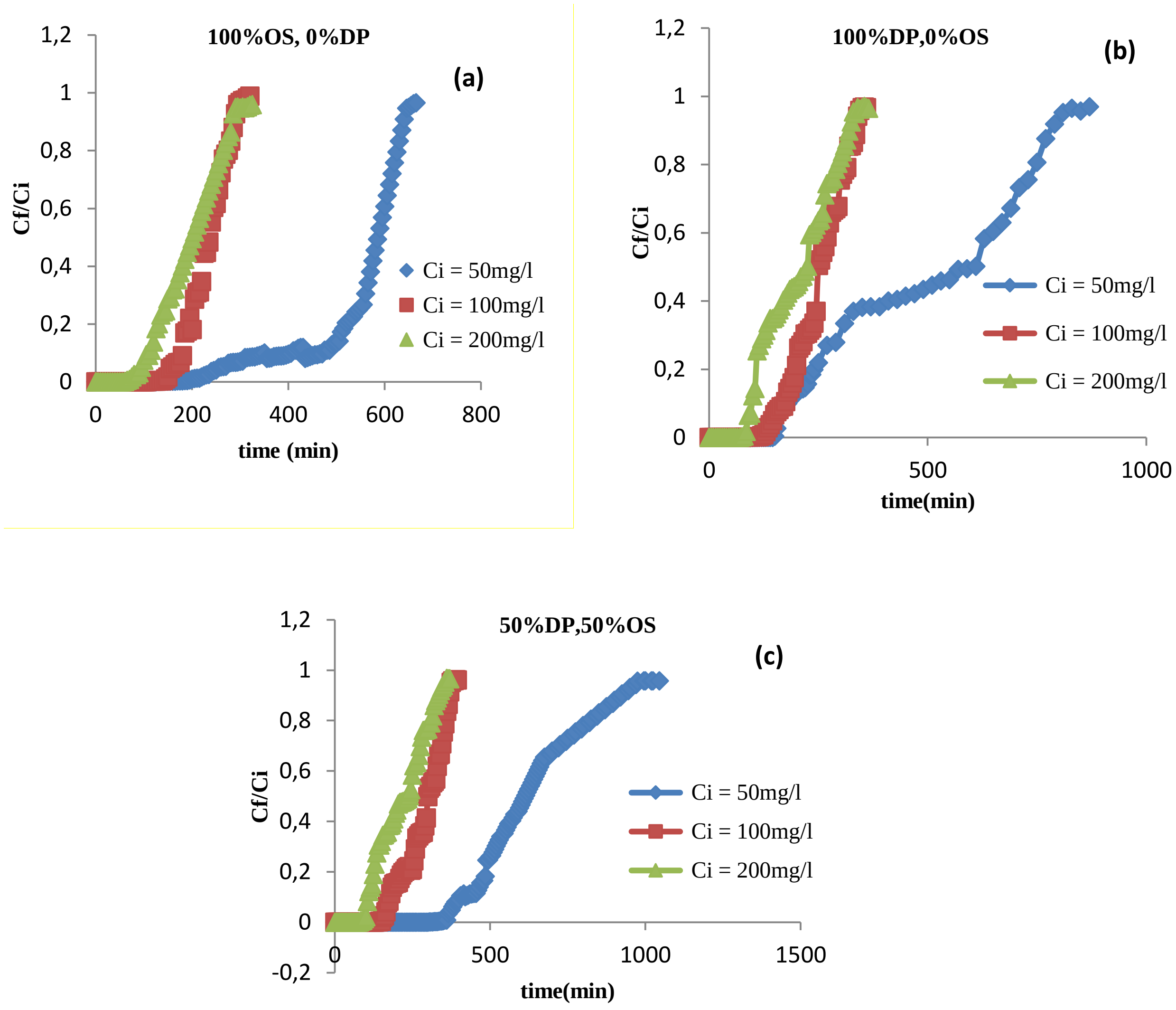


***Figure 6:** Breakthrough curves for adsorption of MB by olive stone **(a)** ; date pit **(b)** ; mixture of date pit and olive stone **(c)** for different concentration values (pH = 5.6 H = 5 cm Q = 8.15 ml / min)*

IV. Conclusion

The aim of this work was to study the dynamic removal of the cationic dye methylene blue from aqueous solutions by adsorption on olive stone and date pit and their mixture in a fixed bed column. .
This study demonstrated that the adsorbent materials studied can be used as low-cost adsorbents for the removal of methylene blue from aqueous solutions.
The column study showed that:
• Breakthrough time and bed exhaustion time increase with increasing bed height due to the availability of sorption sites.
• When the flow rate was lower, breakthrough and exhaustion time were longer , this relationship could be explained by the fact that the contact time was longer and therefore the interaction between the dye and the adsorbent is greater.
• Increasing the concentration causes an increase in the amount of adsorbed dye and reduces breakthrough time and saturation.
The study of fixed bed removal of Methylene Blue showed that biosorption is favored for the lower flow rate (4 mL / min), greater height and at the lower initial BM concentration. An improvement in the amount adsorbed by the mixture of the two materials used compared to the separate fraction.

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