Algerian Journal of Environmental Science and Technology
March edition. Vol.8. N°1. (2022)
ISSN : 2437-1114
www.aljest.org

Fixed-bed adsorption dynamics of methylene blue from aqueous solution using alginate-activated carbon composites adsorbents

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ARTICLE INFO

Article History :

Received ***: 04/03/2020***
Accepted ***: 30/11/2020***

***Key Words*:**

Composite adsorbents; Alginate; Activated carbon; Methylene blue; Fixed bed column.

ABSTRACT/RESUME

Abstract: *this study reports on the preparation of synthesis and use of new composite materials based on activated carbon (Ac) and biopolymer Alginate (Algn) for use in the treatment of wastewater loaded with organic pollutants such as blue methylene. Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy and Dispersive X-ray Spectroscopy (MEB-EDX) and zero charge point (pH_{ZPC}) first characterized the composite adsorbents. The performance of the synthesized adsorbent composites are tested their adsorption capacity of methylene blue on continuous mode in a column with fixed bed, the effect of the different parameters on the breakthrough curve was studied, such as initial dye concentration, bed height and flow rate. The results show that the maximum adsorption capacity of blue methylene increased as a function of the initial concentration and the flow rate, a maximum adsorption capacity of 51.75 mg g^{-1} obtain for an initial concentration of 300 mg $L^{-1}$and flow rate of 6 mL min^{-1}. The saturation time increased with the height of the bed, a minimum saturation time is 280 min, obtained with a flow rate of 6 mL min^{-1} and a bed height of 10 cm. The experimental results are well described by bed depth service time model (BDST), Thomas, Yoon-Nelson and Adams-Bohart models giving a correlation coefficient R^2 between 0.95 and 0.99.*

I. Introduction

Industrial developments almost always have an impact on the ecological environment and human society, including textile industries that generated wastewater containing synthetic dyes, with chromophoric groups that are very dangerous and harmful to the environment [1-4]. The presence of dyes in water bodies is unpleasant and causes diseases. The elimination of this pollution is a priority before rejecting them in the environment [5].

Conventional methods for wastewater treatment as filtration, coagulation, flocculation and precipitation tend to have high costs, are not very effective and leave residues. However, adsorption is the most used method, due to simplicity, low costs and the possibility of regenerated adsorbents [6, 7]. The adsorption process requires a very large surface area adsorbent, good thermal and chemical stability and easy separation of the adsorbent. Several materials were used in adsorption such as zeolites, organo-metallic materials and activated carbon [8].

Many studies have been conducted on adsorption and the factors that influence adsorption, using biopolymers such as Chitosan [9], chitosan/activated clay [10,11], nanocrystalline cellulose [12], composites of polyaniline, starch, polypyrrole [13] and hydrogels [14,15]. Moreover, new materials have been developed in which adsorbents were integrated into an alginate matrix,

further studying its performance in terms of pollutant removal [16-18].

Alginate is a biopolymer polysaccharide most studied for the removal of pollutants. Several biopolymers have been used for the preparation of composite adsorbents for the development of functional adsorbents to remove dyes including methylene blue. Activated carbon-alginate composite adsorbent are the most preferred over others because of their biodegradable behavior, non-toxic, less expensive, uses non-toxic chemicals and having a high adsorption capacity of pollutants [19]. Different studies have been published on the use of activated carbon for the removal of methylene blue [20-24]. The majority of this work is limited to batch processes in a single stirred vessel. The adsorption of pollutant in fixed bed column is widely used in industry [25]. The micro-column adsorption technique can boost fixed bed performance for large columns [26].

In this paper, we propose a new class of composite materials based on calcium alginate and activated carbon for the purpose of using them in the adsorption of methylene blue. These synthesized composites have been characterized by different methods of analysis to identify their chemical and morphological structure. Then, their adsorption properties of organic pollutants in a fixed bed column were evaluated using different models such as bed depth service time model (BDST), Thomas, Adams-Bohart and Yoon-Nelson.

II. Materials and methods

II.1. Synthesis of composite adsorbent (Algn-Ac)

A mass of 3 g of activated carbon powder from Merck (Germany) mixed with 100 mL of deionized water, stirred for half an hour; a homogeneous black solution is obtained. The solution is gradually poured to 100 mL of sodium alginate from LOBA Chemie Pvt with a concentration of (1%, w/v) under agitation for 2 hours. Using a peristaltic pump, this solution is rolled up drop by drop with a flow rate of 4 mL min^{-1} in a bath of 250 mL of calcium chloride from Sigma Aldrich (USA) with (2% w/w) concentration. Composite beads were formed instantly by the ionic gelation technique. After maturing for 30 min, the composite beads are washed and dried. Finally, we get composite adsorbents Alginate-Activated carbon (Algn-Ac) which used for adsorption of methylene blue (Merck).

II.2. Composite adsorbent characterization

Synthesized composite adsorbent Algn-Ac was characterized by FT-IR using ATR platinum Diamond spectrometer in wavenumber ranges of 500-4000 cm^{-1}. Characterization SEM-EDX was analyzed bay Scanning Electron Microscopy MEB Quanta 250 FEI apparatus. The zero point of charge (pH_{zpc}) was determined by the *pH* drift method [27]. Methylene bleu outlet concentration was determined by measuring the absorbance at 665 nm with JENA UV-visible spectro-photometer.

II.3. Adsorption of Methylene Bleu

The adsorption of methylene blue was carried in continuous mode. A glass column of 1.7 cm in diameter and 20.0 cm in height. The solution flow ensured with a peristaltic pump. The processed samples are collected at the output of the measured time intervals. As long as the concentration of the output solution is below the upper limit, its purification takes place. The experiments were performed by examining the effect of bed height (5, 10 and 15 cm), the initial concentration of methylene blue solution (100, 200 and 300 mg L^{-1}) and the flow rate (4, 6- and 8 mL min^{-1}). In order to remove traces of methylene blue, the column was flashed with distilled water before each experiment. Adsorption in continuous mode in a fixed bed columns is expressed by the breakthrough curves, represented by the ratio between the concentrations of the dyes at their output and their initial concentrations as a function of time $\frac{C_t}{C_0} = \boldsymbol{f(t)}$, the latter are commonly used to determine the effect of different parameters influencing the adsorption column, such as the total amount adsorbed (q_{total}) (mg) in the column which calculated from equation. (1) [28].

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

When the equilibrium reached in the column, the maximum adsorption capacity of the dyes q_{eq} is calculated by equation. (2) [29].

$$q_{eq} = \frac{q_{total}}{m} \qquad \textbf{(2)}$$

As the total amount of dye adsorbed (q_{total}) per g of sorbent (m) at the end of total flow time, the adsorption column capacity at 50% breakthrough time was calculated from equation. (3) [30].

$$q_{eq}(50\%) = \frac{t_b.Q\,.C_0}{m} \qquad \textbf{(3)}$$

Where t_b the breakthrough time (min), Q is the flow rate (mL min^{-1}), C_0 is the feed concentration (mg L^{-1}) and m is the adsorbent mass (g).

III. Results and discussion

III.1. Composite adsorbent characterization

The functional groups of synthesis composite adsorbent were characterized bay FTIR Fig. 1. Characteristic peaks at 3244 cm^{-1} due to hydroxyl groups (OH^-) stretching. Peaks of vibration anti-symmetric and symmetric of the (COO^-) group at 1405 and 1590 cm^{-1}, band at 1025 cm^{-1} related to anti-symmetric stretching of (C-O-C) group. Other peaks were detected around 2913 cm^{-1} correspond to (C-H) aliphatic vibrations. Peak at 3720 cm^{-1} and 2323 cm^{-1} reveals the presence of amine (N-H), and

nitrile (C≡N) function. A weak band at 2046 cm^{-1} represents the elongation of alkyne function (C≡C), band at 815 cm^{-1} correspond to the deformation (=C-H) group. after methylene blue adsorption shows the appearance of three peaks at 1392 cm^{-1}, 799 cm^{-1} and 554 cm^{-1} attributed to (C-N) aromatic, (C-S) group of methylene blue and the (C=C) aromatic.

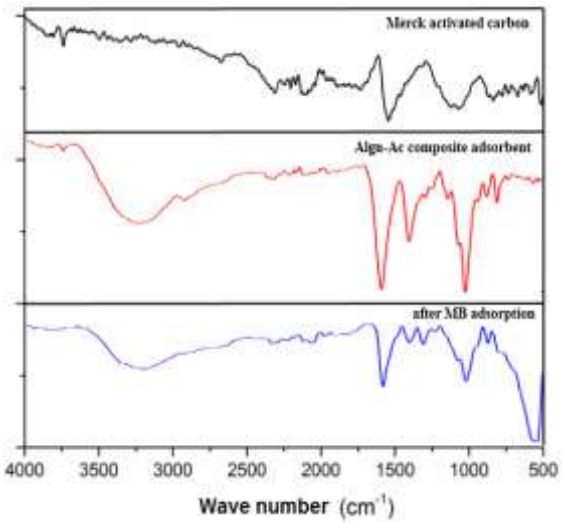

Figure 1. *FTIR spectrum of Merck activated carbon, Algn-Accomposite adsorbant and after MB adsorption*

The EDX spectrum Fig. 2. Show a high percentage of oxygen and carbon 44.18% and 38.54% respectively from encapsulation of particles in alginate solution, which confirms in the FTIR analysis by an intense band of carbon and oxygen groups (OH, C-O-C and COO-). The calcium level is 16% due to impregnation in calcium chloride solution. While the sodium level does not exceed 1.29%.

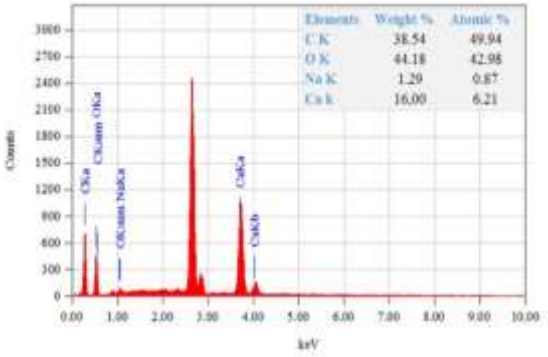

Figure 2. *EDX microanalyses of composite adsorbent Algn-Ac.*

Scanning electron micrographs indicate the external texture and morphology of the composite adsorbent Fig. 3. The image shows the spherical shape of the composite bead (Figure 3a, 3b), they have several cavities on the surface.due to the presence of the multitude of particles of activated carbon (Figure 3c, 3d and 3e). In general, the composite beads have a heterogeneous surface structure with calcium crystals (Ca^{2+}) on the surface of the composite beads due to the impregnation in the calcium chloride solution ((Figure 3e, 3f).

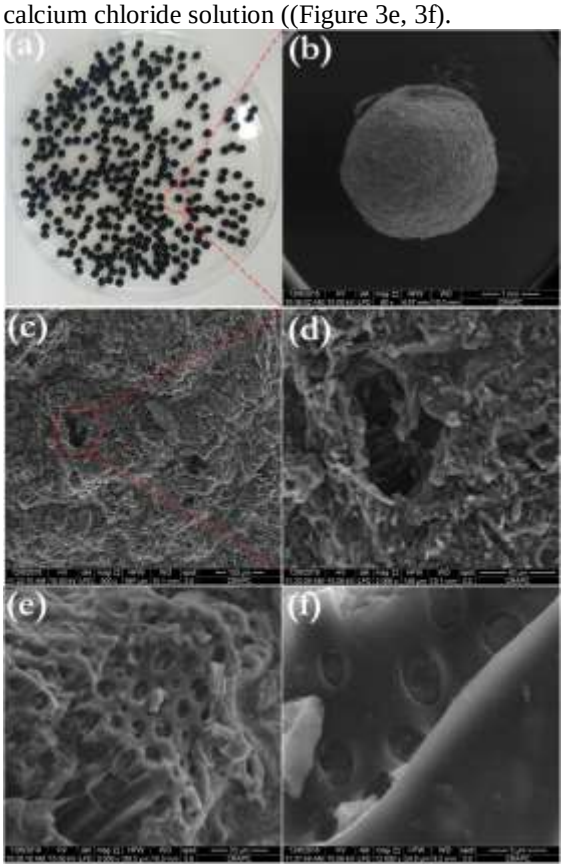

Figure 3. *Photograph (a) and SEM Image of composite adsorbent Algn-Ac (b), (c), (d), (e) and (f).*

Figure 4 show zero point of charge (pH_{pzc}) of Merck activated carbon and Algn-Ac composite adsorbent. Merck activated carbon is a neutral surface where the pH_{pzc} is 6.86, which increased to 8.69 and become weakly basic by encapsulation with sodium alginate due the effect of the alkaline media of the sodium alginate. For a *pH* greater than pH_{pzc} (pH > 8.69), the surface of the composite adsorbent is negatively charged, on the other hand, for *pH* less than pH_{zpc} (pH<8.69) the surface of the composite adsorbent is positively charged. MB is a cationic dye (positively charged) with *pH= 6.7 and* pKa=3.41, thus adsorptive removal is more favorable in acidic *pH* due to the phenomenon of electrostatic contact between the dye and (Algn-Ac) composite adsorbent

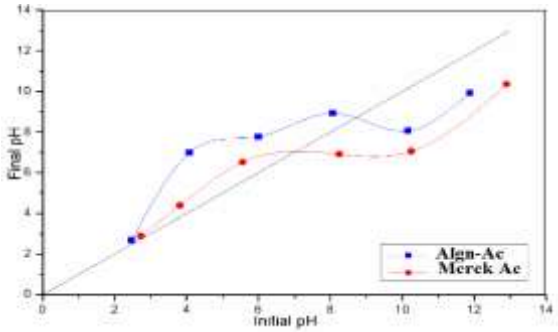

Figure 4. *pH drift plot of Algn-Ac composite adsorbent and Merck activated carbon (AC)..*

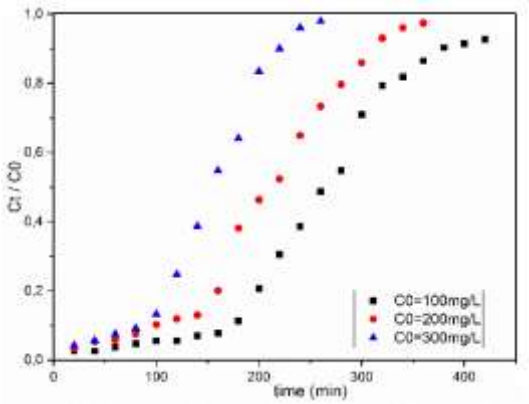

Figure 5. *Inlet concentration effect on breakthrough curves. (Flow rate Q =6 mL min^{-1}, bed height Z = 10 cm, room temperature)*

For all the concentrations studied, the break curves are spread with practically identical slopes. The high concentrations accelerate the break-through and require a lower saturation time Table 1, this is due to the presence of a strong concentration gradient, between the solution and the dye surface and against cons we see a strong driving force that allows a displacement very fast from Methylene Blue to Algn-Ac composite beads

Table 1. *Effect of inlet MB concentration on the saturation time (t_s), and the equilibrium uptake (q_{eq}) at 50% of C_t/C_0 for adsorption of MB.*

C_0 (mg L^{-1})	Q (mL min^{-1})	Z (cm)	t_s (min)	q_{eq}(50%) (mg g^{-1})
100	6	10	420	5.17
200	6	10	380	7.06
300	6	10	280	8.77

Feed flow rate effect

Flow is one of the important features for the continuous treatment of dye effluents. The plots of reduced concentrations as a function of time are shown in Figure 6. We note from Fig. 6. that the breakthrough curve is steeper at high flow, the increase of this parameter limits the diffusion of the solute, the dyes does not have enough time to diffuse in all of the composite beads. The low flow rates are characterized by long residence times this increases the contact time between the BM dye and the Composite Beads, causing an increase in the volume of the purified solution, late breakthrough of the column and against the speed of movement of the front of the adsorption decreases Table 2**.**

Table 2. *Effect of flow rate (Q) on equilibrium uptake (q_{eq})50% and saturation time (t_s) for methylene blue adsorption.*

Q (mL min^{-1})	C_0 (mg L^{-1})	Z (cm)	t_s (min)	q_{eq}(50%) (mg g^{-1})
4	100	10	480	5.63
6	100	10	420	7.06
8	100	10	400	10.33

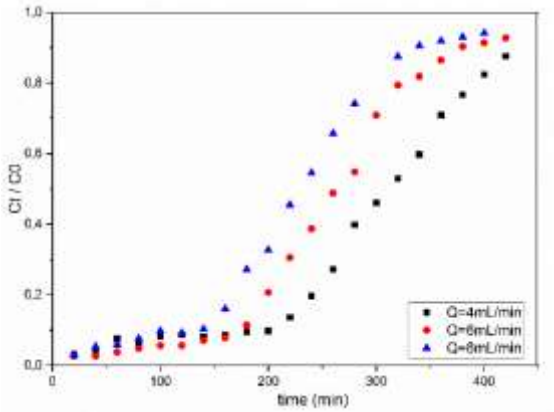

Figure 6. *Feed flow rate effect on breakthrough curves (C_0=100 mgL^{-1}, Z = 10 cm, room temperature)*

Bed height effect

Figure 7 shows the breakthrough curves obtained for BM adsorption. On the Algn-Ac composite bead for different bed heights of 5, 10 and 15 cm at a constant rate of 6 mL min^{-1} and 100 mg L^{-1} concentration of BM.

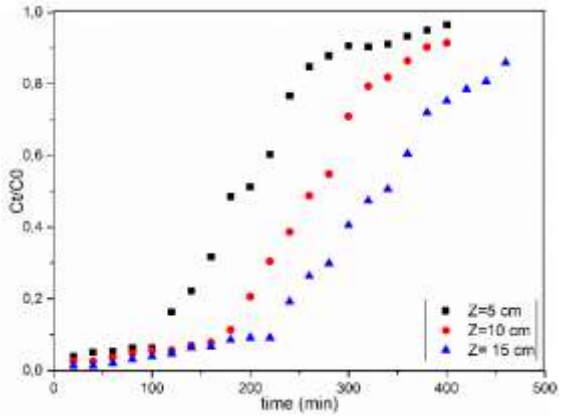

Figure 7. *Bed height effect on breakthrough curves. C_0=100mg L^{-1}, Q = 6 mL min^{-1}, room temperature).*

At high bed height, breakthrough occurs slowly, because of the longest path to travel by the solute

for the highest bed height, the amount of adsorbed MB is greater. We also note that the increase of the height of the bed from 5 to 15 cm seem to have a great influence on the piercing and saturation times Table 3. The saturation time increased from 300 to 480 min

Table 3. *Effect of Bed height on the saturation time (t_s) for adsorption of methylene blue.*

Z (cm)	Q (mL min^{-1})	C_0 (mg mL^{-1})	t_s (min)
5	6	100	300
10	6	100	380
15	6	100	480

III.3. Breakthrough data modeling

Bed Depth Service Time (BDST)

The BDST model offers a simple approach and the most rapid prediction of fixed bed column adsorption performance based on a surface chemical reaction between the adsorbent and the adsorbate. The BDST model gives a linear relationship between pause time and bed height [31-33]. The equation can be expressed as follows: equation. (3).

$$ln\left(\frac{C_0}{C_b}-1\right)=ln\left(exp\left(\frac{KZN_0}{\vartheta}\right)-1\right)-KC_0\,t \qquad \textbf{(3)}$$

A linear relationship between bed-depth and service time may be given by equation. (4).

$$t=\frac{N_0}{\vartheta C_0}Z-\frac{1}{K_aC_0}ln\left(\frac{C_0}{C_b}-1\right) \qquad \textbf{(4)}$$

C_0 is the solute initial concentration (mg L^{-1}), C_b is the concentration of solute at breakthrough (mg L^{-1}), Z the column bed depth (cm), ϑ the linear velocity (cm min^{-1}), N_0 the adsorption capacity per unit volume of fixed bed (mg mL^{-1}) representing the column saturation concentration, K_a is the adsorption rate constant (L mg^{-1} min^{-1}) and t the column service time (min).

Figure.8 shows plots of t vs Z will give a straight line with slope = $\frac{N_0}{\vartheta C_0}Z$ and an intercept = $\frac{1}{K_aC_0}ln\left(\frac{C_0}{C_b}-1\right)$ which N_0 and K are respectively obtained.

The service time increases pseudo-exponentially with increasing bed depth, indicating that a larger bed height would have a longer life time, thus requiring a longer time for replacement of the composite beads. We obtain a straight line with a very good regression coefficient: (R^2> 0.98) which shows that the results obtained are well representative of the experimental data Table 4

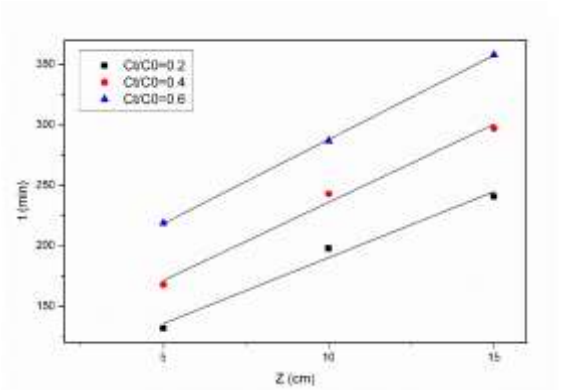

Figure 8. *Bed depth service time as a function of bed height for MB adsorption (C_o =100 mg L^{-1}, Q = 6 mL min^{-1} and Z = 10 cm)*

Table 4. *Calculated BDST model constants for methylene blue adsorption, (Co =100 mg L^{-1}, Q = 6 mL min^{-1} and Z = 10 cm)*

C_t/C_0	K_a (x10^4) (L mg^{-1} min^{-1})	N_0 (x 10^{-2}) (mg L^{-1})	R^2
0.2	1.704	28.830	0.985
0.4	0.378	34.120	0.991
0.6	0.272	36.760	0.999

Thomas model

Thomas model is a mathematical model proposed for studying continuous adsorption, based on the Langmuir isotherm, and assumes that the dye diffuses through a liquid film around the surface of the composite beads. This model is widely used to determine the adsorption capacity and the adsorption rate constant when designing the adsorption columns [34,35], which is given by equation. (5). [36].

$$\frac{C_t}{C_0}=\frac{1}{1+exp^{K_{Th}\left(\frac{q_e\ m}{Q}-C_0t\right)}} \qquad \textbf{(5)}$$

Where C_t and C_0 are the concentrations of MB (mg L^{-1}), K_{Th} is the rate constant (L mg^{-1} min^{-1}), Q is the flow rate (L min^{-1}), q_e is the total adsorption capacity (mg g^{-1}), and m is the mass (g) of the adsorbent. The values of the characteristic parameters of this model were determined by the curve of $\frac{C_t}{C_0}$ as a function of time (t) Figure 9.

Table 5. Shows that the correlation coefficient (R^2) greater than 0.95, indicates that the model of Thomas Well good fit of experimental results. According to the results of this model, the total adsorption capacity (q_e) increases when the concentration of dye increases due to the driving force of adsorption which is the difference in concentration of dye in the solution and on the

composite adsorbent [37], this force increases with the increase of the concentration. The increase in BM flow rate from 4 mL min^{-1} to 6 mL min^{-1} causes an increase in the constant kth of 14.6 10^5 mg^{-1} min^{-1} to 16.8 10^5 mg^{-1} min^{-1}. On the other hand, the increase of bed causes a decrease of the capacity of bed (q_e).

Table 5. *Thomas model parameter of MB adsorption on Algn-Ac composite bead.*

C_0 (mg L^{-1})	Z (cm)	Q (mL min^{-1})	Parameter		
			K_{Th} (x10^4) (L mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
100	10	6	15.90	23.61	0.968
100	10	8	16.50	17.05	0.979
200	10	6	10.25	47.03	0.963
100	10	4	14.50	10.92	0.957
300	10	6	9.06	51.75	0.970
100	5	6	16.80	22.62	0.951
100	10	6	14.30	38.30	0.991
Adams–Bohart model					

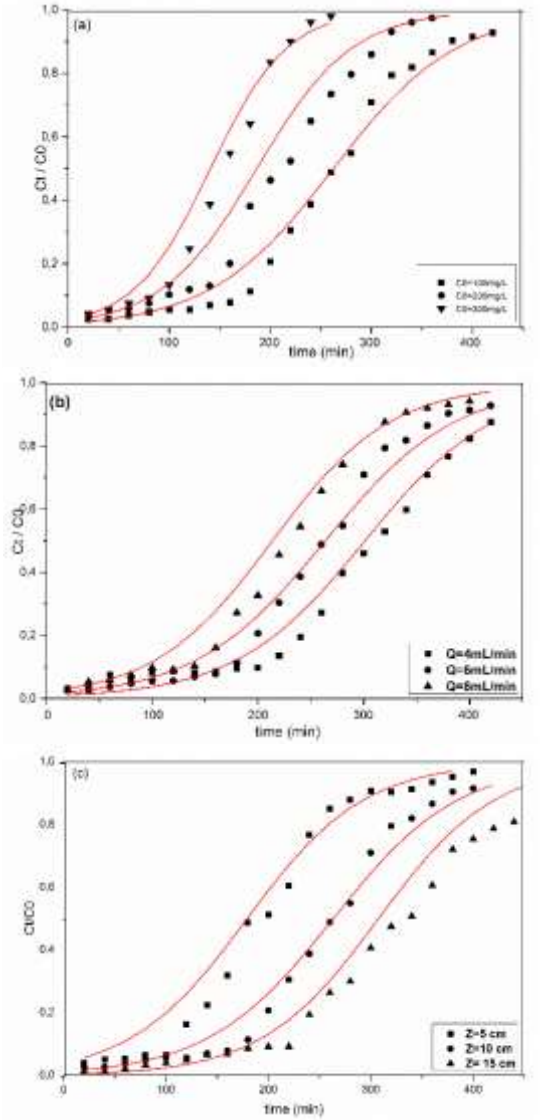

Figure 9. *Non-linear plot of Thomas model for adsorption of MB on Algn-Ac composite bead at (a) different Initial concentration, (b) different flow rates and (c) different bed height.*

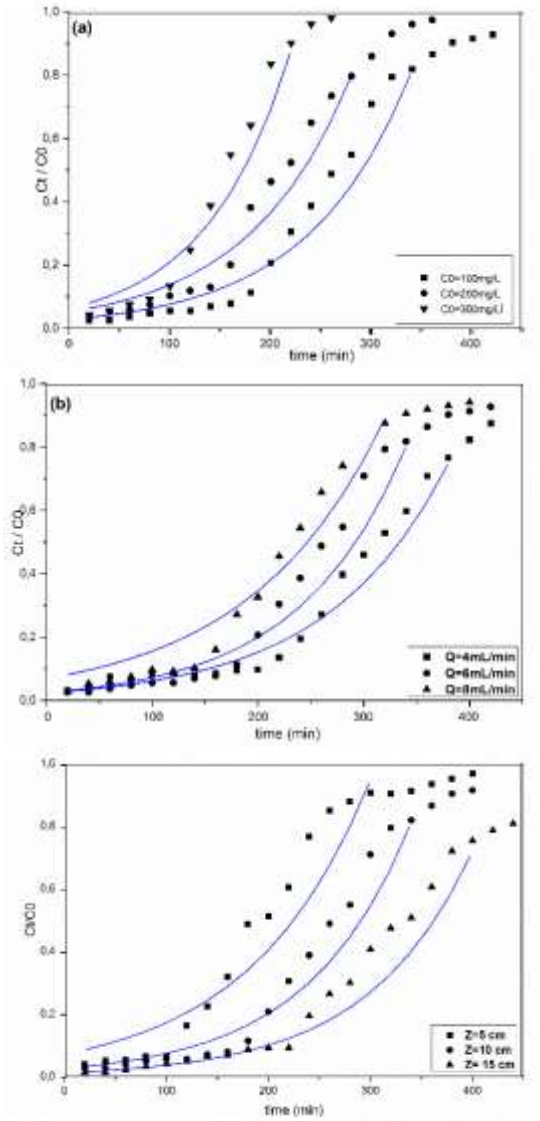

Figure 10. *Non-linear plot of Adams–Bohart model for adsorption of MB on Algn-Ac composite bead at (a) different Initial concentration, (b) different flow rates and (c) different bed height*

Algerian Journal of Environmental Science and Technology
March edition. Vol.8. Nº1. (2022)
ISSN : 2437-1114
www.aljest.org

This model expressed by equation. (6).

$$\left(\frac{C_t}{C_0}\right) = exp^{K_{AB}C_0 t - \frac{K_{AB}N_0 Z}{\vartheta}} \quad \textbf{(6)}$$

Where K_{AB} is rate kinetic constant of Adams-Bohart model (L mg^{-1} min^{-1}), ϑ is the linear velocity (cm min^{-1}) and C_0 and C_t (mg L^{-1}) are the influent and effluent methylene blue concentrations. The values of K_{AB}, N_0 and correlation coefficients (R^2) are presented in the Table 6. The

Table 6. *Adams–Bohart model parameter of MB adsorption on Algn-Ac composite bead*

C_0 (mg L^{-1})	Z (cm)	Q (mL min^{-1})	Parameter		
			K_{AB} (x10^5) (L mg^{-1} min^{-1})	N_0 (mg g^{-1})	R^2
100	10	6	8.20	73.83	0.896
100	10	8	4.70	118.37	0.829
200	10	6	0.33	146.02	0.854
100	10	4	8.10	76.19	0.956
100	5	6	7.70	192.99	0.803
100	15	6	9.60	77.59	0.952

parameters characteristic of the column determined from a plot of (C_t/C_0) on time (t) Figure. 10. The increase in flow and concentration considerably increases the adsorption capacity N_0 and decreases the K_{AB} constantsconstants, increasing the concentration from 100 to 200 mg L^{-1} improved the maximum adsorption capacity by 60% and lowered the kinetic constant from 8.2 10^{-5} to 0.33 10^{-5}**.** The correlation coefficient R^2<0.97 indicates that the Adam-Bohart model did not correspond very well to the experimental data.

Yoon-Nelson model

The Yoon – Nelson model is a simple theoretical model, suitable for the one-component system, it is applied to predict the time required and rate constant for 50% adsorbate breakthrough. This model requires less experimental data for construction [35]. The model parameter obtained with equation. (7).

$$\frac{C_t}{C_0} = \frac{1}{1+exp^{K_{YN}(\tau - t)}} \quad \textbf{(7)}$$

Where K_{YN} (min^{-1}) is the rate constant and τ (min) is the time required for 50% adsorbate breakthrough Fig. 11. The results obtained are shown in the Table 8.

The results of this model show that; the 50% breakthrough increases with increase and height of bed, and decreases with increasing concentration and the flow rate. In bed height of 15 cm and a flow rate of 6 mL min^{-1} were at 335.20 min against the rate constant K_{YN} increases with increasing concentration, flow, and decreases with increasing Bed height.

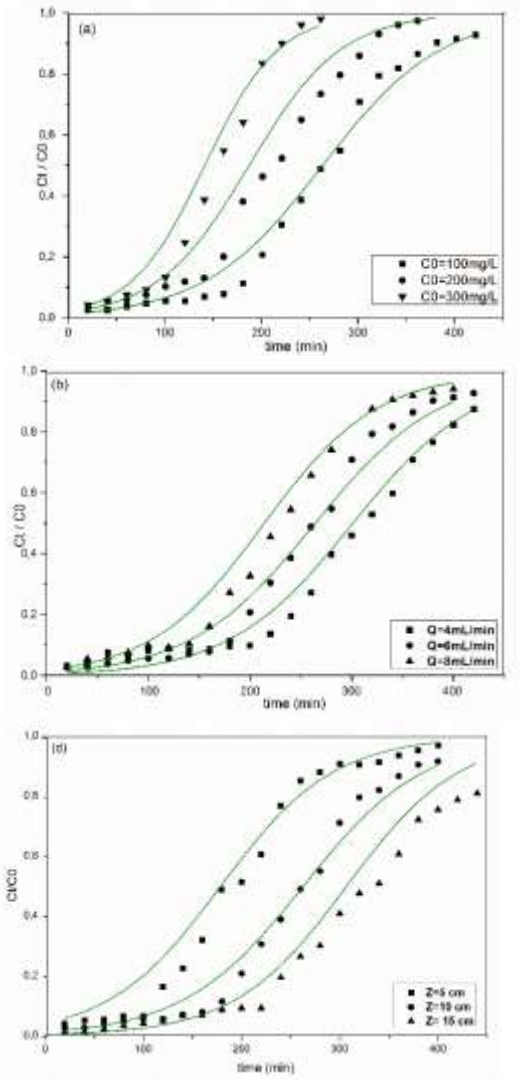

Figure 11. *Non-linear plot of Yoon – Nelson model for adsorption of MB on Algn-Ac composite bead at (a) different Initial concentration, (b) different flow rates and (c) different bed height.*

Table 8. *Yoon – Nelson model parameter of MB adsorption on Algn-Ac composite bead.*

C_0 (mg L^{-1})	Z (cm)	Q (mL min^{-1})	Parameter		
			K_{YN} (x10^2) (min^{-1})	τ (min)	R^2
100	10	6	1.57	274.50	0.968
200	10	6	2.05	203.80	0.983
300	10	6	2.72	149.51	0.970
100	10	4	1.52	304.13	0.969
100	10	8	1.65	234.49	0.979
100	5	6	1.62	209.20	0.944
100	15	6	1.43	335.20	0.991

IV. Conclusion

A study of the effect of the various parameters flow rate, bed height, and initial concentration on the adsorption of methylene blue in continuous mode on composite beads synthesized by Merck activated carbon and sodium alginate in a system singular (a single dye). FTIR spectroscopic analysis showed a change in the functional groups between Merck activated carbon and composite bead by the appearance of new bands. The adsorption has been evaluated by the maximum adsorption capacity of BM increases with the increase of the concentration, a value of 51.750 mg g^{-1} was obtained at a concentration of 300 mg L^{-1}. However, increasing concentration and flow rate tends to accelerate saturation of the column. The kinetic models Thomas, Adam's-Bohart and Yoon-Nelson are applied to describe the adsorption mechanism and to provide more detailed information about the optimal parameters of the column. Analysis of model parameters demonstrated that the Thomas model with a good correlation $R^2 \geq 0.95$ is the most appropriate to describe the adsorption of MB on Algn-Ac composite bead.

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Please cite this Article as:
Boucherdoud A., Kherroub D.E., Bestani B., Benderdouche N., Douinat O.,Fixed-bed adsorption dynamics of methylene blue from aqueous solution using alginate-activated carbon composites adsorbents, ***Algerian J. Env. Sc. Technology***, ***8*:1 (2022) 2329-2337**