



Adsorption of cationic dyes onto Moroccan clay: Application for industrial wastewater treatment

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Abstract

The adsorption phenomena of Methylene Blue (MB), Basic Red 46 (BR46) and Green Malachite (GM) onto Moroccan clay were investigated in a column arrangement by using breakthrough technique. A continuous adsorption study in a fixed-bed column was carried out and the adsorbent bed height, the initial dye concentration and flow rate were taken as experimental variables. A Mixed sand-clay was used for the column experiments due to the fine particle size of clays. Data confirmed that the breakthrough curves were dependent on flow rate, initial dye concentration and bed depth. The higher adsorption capacity is reached at lower flow rate, higher bed height and higher initial dye concentration. Two kinetic models: Adams- Bohart and Clark were applied to experimental data to determine the characteristic parameters of the column that are useful for process design. The Clark model was found suitable for the description of the breakthrough curve when the residual concentration (C_t) is near than C_0 , while the Adams- Bohart model was only used to predict the initial part of the dynamic process. The optimal parameters obtained from the study of column dyes adsorption were used to evaluate the color and organic load reduction of a real textile effluent, by successive decantation (settling) and coagulation-flocculation. The feasibility of each of the two processes was studied separately and their operating parameters were optimized. Both processes allow the recovery of a great proportion of the initial effluent (75% and 92% respectively of organic load reduction). Consequently, dynamic adsorption coupled with the coagulation-flocculation allows obtaining crystal clear water onto the receiving environment, which is consistent with applicable standards for discharges of industrial liquid effluents. It can be also selected for the industrial unit.

Keywords: Adsorption, Moroccan clay, dyes adsorption, dynamic reactor, textile effluent

1. Introduction

Water is a scarce resource since only 0.03% of the world reserves are available for human activities. Population growth and industrial booms have given rise to an increasing need for water, while the offer has remained constant. Moreover, bad water management has contributed to definitively reduced supply. When dyeing textiles, water serves two purposes. Water vapor acts as heating agent for the bath while liquid water ensures the transmission of the color onto the fiber. Cotton is the most commonly used fiber world-wide and also the material whose preparation requires the greatest volume of water.

Several industries use dyes to accomplish different kinds of operation. The nature and amount of dyes vary from industry to industry, and from operation to operation. In effect, Dyeing 1 kg of cotton requires about 150 L of water, 0.6 kg of NaCl and 50 g of reactive dyes. Over 80,000 tons of reactive dyes are produced and consumed each year. This gives an idea of the total pollution generated by their use [1], their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes. These synthetic dyestuffs have been increasingly used in the textile, paper, rubber, plastics, cosmetics, pharmaceutical and food industries. Today there are more than 10,000 dyes available commercially, most of which are difficult to biodegrade due to their

complex aromatic molecular structure and synthetic origin [2, 3]. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharge into environmental water bodies. Even small quantities of dyes can color large water bodies, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. In addition, some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals, chlorides, etc., in their structure [4- 9]. After dyeing, a strongly colored dyeing bath highly loaded in organic compounds and highly concentrated in mineral salts is discharged in the municipal wastewater treatment plant. Several treatment technologies have been developed to decolorize dyeing wastewater. These treatment options include biological [10], physio-chemical [11], membrane filtration [12], ozonation [13] advanced oxidation [14] and integrated treatment processes [15]. However, these processes face certain technical and economical limitations such as cost and production of sludge [16]. Adsorption process is an innovative and economical alternative due to its performance and ease of operation [17]. Adsorption technology has attracted interest in this context as an effective and alternative treatment process and has many advantages over the existing conventional process. This process is not only economic and feasible but also produces high quality of water [18, 19].

Batch adsorption experiments are used easily in the laboratory for the treatment of small volume of effluents, but less convenient to use on industrial scale, where large volumes of wastewater are continuously generated. Batch adsorption provides certain preliminary information such as pH for maximum adsorption, maximum initial metal ion concentration, particle size for optimum adsorption of dye ions, and approximate time for adsorption of metal ion as well as the adsorption capacity of the adsorbent [18]. All these informations are useful for fixed-bed studies where the adsorbate is continuously in contact with a given quantity of fresh adsorbent, thus providing the required concentration gradients between adsorbent and adsorbate for adsorption. Fixed-bed operations are widely used in pollution control processes such as for the removal of ions by an ion-exchange bed or removal of toxic organic compounds by carbon adsorption [20]. Fixed-bed adsorption of pollutants involves percolation of wastewater through percolating material. During the flow of the wastewater through the percolator, the wastewater is purified by physicochemical processes [21]. The design and theory of fixed-bed adsorption systems focuses on establishing the shape of the breakthrough curve and its velocity through the bed. Breakthrough and bed volumes are usually employed in the evaluation of the performance of a fixed-bed column [22]. The performance of packed beds is described through the concept of the breakthrough curve.

The dynamic adsorption of dyes from aqueous solutions by clay has been studied by various authors [23, 24]. In this work, several column experiments were performed on clay of Safi mixed with sand with a percentage of 3% (to ensure its dispersion and avoid clogging phenomenon) to remove BR46, BM and GM dyes from aqueous solutions. To optimize the performance of the filter, the adsorbent bed height, the initial dye concentration and the flow rate will be taken as experimental variables. Models in the literature such as that of Adams- Bohart and Clark will be used to select the appropriate model to predict the adsorber performance in removing BR46, BM and GM under specific field conditions. Additional information on the efficiency of the clay adsorbent in the column mode has been gathered in order to ascertain the practical applicability of this adsorbent for real industrial wastewaters.

In this direction, we are interested in the treatment by adsorption of industrial waste from a textile industry by adsorption onto Moroccan clay from Safi (Morocco),

To do this, we tried two economically feasible techniques for the company:

- The adsorption technique in dynamic steady on a bed of raw clay mixed with sand to prevent clogging after performing a test of settling industrial discharge.
- The combined technique between the coagulation-flocculation and adsorption dynamic media of clay and sand.

2. Material and methods

2.1. Materiel

2.1.1 Adsorbates

2.1.1.1 The BR46, BM and GM Dyes

Some characteristics of the basic cationic dyes used as adsorbates are summarized in Table 1.

2.1.1.2. The textile wastewater

Wastewater samples are collected from the discharges of sewers Textile Company at the time of release of final effluent. The wastewater is mainly characterized by its color variation and high load of DCO. It was studied and characterized

within the first 24 hours. Each parameter was analyzed three times for reproducibility of results. Table 1 shows the average results for each analyzed parameter compared with Moroccan standards of wastewater discharge [25]. The results of these analyzes are presented in Table 2:

Table 1: Some characteristics of the basic cationic dyes used as adsorbates

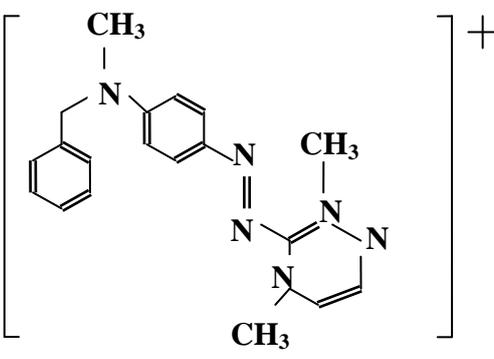
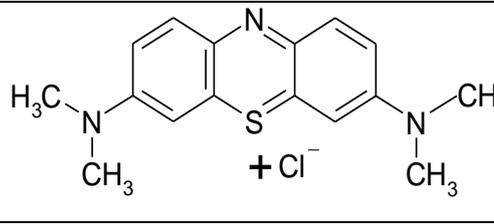
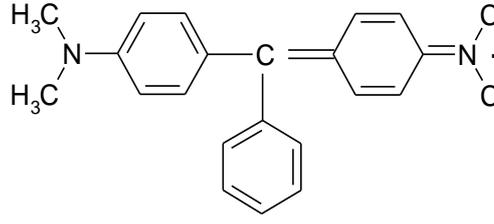
Adsorbat	Masse Molaire	Origine	λ_{\max}	Structure
BR46	357.5	SDI textile company (Safi, Morocco)	532	
BM	319.85	Superior School of Technologie	666	
GM	463.5	SDI textile company (Safi, Morocco)	618	

Table 2: Physico-chemical characteristics of the raw textile effluent

Parameters	Values	Standard	Parameters	Values	Standard
Temperature (°C)	35	30	Sulfates ions (SO ₄ ²⁻) (mg/L)	580	400
pH	5.1	6.5- 8.5	Phosphates ions (PO ₄ ³⁻) (mg/L)	160.6	
Conductivity (µs/cm)	1190	2700	Totale Phosphorus P _t (mg/L)	52.41	10
Turbidity (FTU)	230	----	Calcium title (°F)	13.4	----
Suspended solids (mg/L)	350	50	Peak wavelength (nm)	527	----
DCO (mg O ₂ /L)	2600	500	Absorbance at the maximum wavelength (λ_{\max})	0.3	----
Chloride ions (mg/L)	113.6	200			

2.1.2. Adsorbent materiel

The raw adsorbent Moroccan clay used in this work is collected from a natural basin in the region of Safi (Morocco), crushed and dried at 105 °C for 24h and used for further experiments. The chemical composition of this clay (wt. %) is: 53.11 % SiO₂, 16.95 % Al₂O₃, 5.94 % Fe₂O₃, 3.51 % CaO, 2.51 % MgO, 0.2 % SO₃, 4.64 % K₂O, 0.26% Na₂O, 0.09 % P₂O₅ [26].

The mineralogical identification is performed by XRD in Siemens D500 diffractometer using a 106 CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) is produced under conditions of 40 kV and 20 mA. The predominant peaks are 9.99 Å, 7.16 Å, 4.25 Å,

3.03 Å and 2.9 Å which correspond respectively to illite, kaolinite, quartz, calcite and dolomite [26]. The clay CEC was determined by mixing (between 0.3 and 0.5 g) of dried clay for 24 hours at 240 ° C with 25 mL of the Cu solution (EDA) 2 (0.05 M). The mixture was stirred for 30 minutes at least to ensure a complete adsorption of the complex on the clay. Separating the mixture (solution-clay) is carried out by centrifugation. The number of moles of Cu (EDA) 2 remaining (non-adsorbed by the clay) is determined by colorimetry by analyzing the copper released after destruction of the complex in acid medium and after exchange in the clay [27]. The found CEC clay of Safi is: 23.5 meq/100g.

2.2. Methods

For the dyes experiments, the continuous flow adsorption studies were conducted in a glass column made of Pyrex glass tube of 2 cm inner diameter and 30 cm height which was filled with mixed adsorbent: clay and sand mixtures. The adsorbent-sand clay mixtures were prepared by mixing adsorbent clay with quartz sand in order to avoid clogging phenomenon (sand : previously washed repeatedly to remove excess salt , sieved to a particle size between 0,5 and 1 mm , clay : crushed and sieved to a particle size of about 600 microns).

A known quantity of mixed adsorbent was packed between a layer of 5 mm size glass beads in order to provide a uniform flow of the solution through the column, a filter paper is placed in the end of the column in order to prevent the escape of the clay. A clay quantity of 2.25; 3; 3.75 and 4.5 g was mixed with 75, 100, 125 and 150 g of sand to provide bed depths of approximately 15 cm, 20 cm, 25 and 30 cm, respectively. So, clay sand percentage of 3% (optimal percentage to avoid clogging. In effect, several experiments have been carried out at different percentage, 3% is found optimal). A blank test on the sand only has been achieved; the results showed that his dyes adsorption is negligible.

BR46, BM and GM cationic dyes solutions at known concentrations (160, 210 and 260 mg/L) and pH of 6.5 was pumped upward through the column at the optimal flow rate obtained using a peristaltic pump until the dye concentration at the outlet of the column becomes almost equal to that of the input (Fig. 1). The BR46, BM and GM dyes solutions at the outlet of the column were collected respectively at regular time intervals and the concentration was measured using a spectrophotometer [GBC (ajax, ontario) UV/visible 911] at 532, 666 and 618 nm respectively. The solutions concentration passing through the columns was monitored continually by collecting manually the samples in volumetric flasks. All the experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$). The breakthrough curves were constructed as C_t vs. time. Flow was in turn fixed (after testing at 4; 8 and 12 mL / min); 4 mL / min was optimal for all experiments of this work. Adsorption of the dye onto the clay was carried out at room temperature.

The reproducibility during mass loss measurements was ensured by repeating the experiments three times under identical conditions and average values are reported. Standard deviations during experiments were found to be within $\pm 5.0\%$. The sand used in this study was sieved to a particle size between 0.5 and 1mm, and repeatedly washed to remove excess salt. The clay used in the adsorption column tests was ground, sieved to a particle size of about 600 microns. The relative size of the clay sand near than 1 thus obtained, allows obtaining uniform dispersion of clay particles.

For the wastewater experiments, in order to ensure a better reduction of color and organic load, continuous flow adsorption studies were conducted in a glass column made of Pyrex glass tube of 2 cm inner diameter and 40 cm height which was filled with mixed adsorbent: clay and sand mixtures (3% wt of clay, so 6g of clay and 200 g of sand). Discoloration was evaluated by measuring the absorbance. The rate of discoloration was determined by difference between the initial measurement (Abs_0 , C_0) of the initial concentration of the solute and the residual concentration (Abs_r , C_r). Monitoring the staining was carried out by UV-Visible after determination of the wavelength corresponding to the maximum absorption (400 nm and 800 nm) in the effluent studied. The dosage of the organic load was determined according to AFNOR T 90-101 [28]. The amount of organic load restraint at a given time (DCO_{ad}) was determined by the difference between the original measure (DCO_0) of the solute concentration and the residual at this time (DCO_r). Retention of the organic load is represented by:

$$\%DCO = \frac{DCO_0 - DCO_r}{DCO_0} \times 100 \quad (1)$$

The dye concentration of the filtrate was measured by visible spectrophotometry [GBC (Ajax, Ontario) UV / VIS 911] at the wavelength corresponding to the maximum absorbance of the sample.

2.3. Effects of operating variables

2.3.1. Effect of bed height for the adsorption of BR46, BM and GM dyes

The Moroccan clay used as adsorbent of different weights (2.25g; 3g; 3.75g and 4.5 g) was placed in separate glass columns as discussed in Section 2.2. The bed heights differ from one column to another (15, 20, 25 and 30 cm respectively). 160 mg/L working standard at pH 5.5 ± 0.2 was percolated through each of the column using 4 mL/min as flow rate and the effluent from each column was collected at an interval of 2.5 min and kept for dye analysis.

2.3.2. Effects of BR46, BM and GM dyes concentration

Different concentrations of 160, 210 and 260 mg/L were used subsequently. Kinetic experiments were carried out by percolating the working standards through the clay adsorbent bed. 4.5 g of the clay (so, a bed height of 30 cm) adsorbent was placed in separate glass columns as described above (Section 2.2). The different working concentrations of dyes were

percolated through the different columns. The effluent from the column were collected at intervals of 2.5 min and kept for dye ion analysis using 4 mL/min as flow rate.

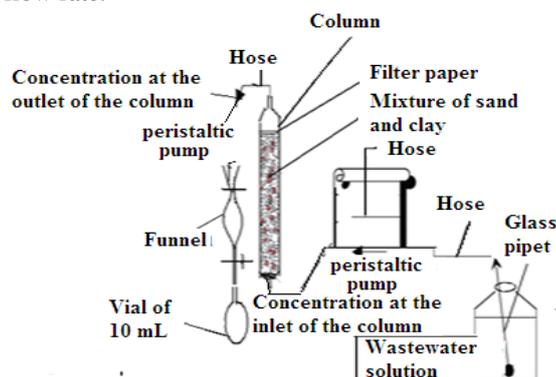


Figure 1: Schematic diagram of laboratory based small column for fixed bed studies.

2.3.3. Effect of flow rate for the adsorption of BR46, BM and GM dyes

The Moroccan clay adsorbent of different flow rate (4, 8.5 and 12 mL/min) was placed in separate glass columns as discussed in section 2.2. 260 mg/L, 210 mg/L and 160 mg/L for the BR46, BM and GM respectively working standard at pH 5.5 ± 0.2 was percolated through each of the column and the effluent was collected at one interval of 2.5 min and kept for dye analysis.

2.4 Settling wastewater experiments

To begin the study of the effect of settling, it was necessary to find the optimal settling time corresponding to the maximum reduction of the pollution organic load in the effluent studied. Samples were taken after every 15 minutes of settling to measure turbidity, DCO and absorbance for 150 minutes in total. After one hour of decanting, all values of the different parameters remained constant.

2.4.1. Coagulation, flocculation wastewater experiments

The coagulation-flocculation tests were carried out by the use of coagulants include: aluminum sulphate $Al_2(SO_4)_3 \cdot 18 H_2O$, ferric chloride $FeCl_3 \cdot 6H_2O$, 2% by weight, at a dose ranging from 100 to 300 g/m³, and flocculant: acrylamide copolymer to 0.4 mg / L. The choice of coagulant and flocculant was based on their effectiveness in the treatment of effluents containing dyes [29- 33]. The treatment was carried out in a bench unit "Jar Test" consisting six beakers volume of 700 mL, filled with 250 mL of effluent. The effect of coagulant dose and pH on the organic load and color reduction was also studied. The solutions were stirred mechanically at room temperature (20 ± 2)° C. Coagulation was performed at a speed of 170 rpm for 2 minutes and flocculation at a speed of 30 rpm for 30 minutes (until the flock appearance). Then the effluent was decanted for 60 min in the same flocculation reactors [17]. The experiments were done three times; the final result of each studied parameter is the average of three values.

This treatment involves three steps:

- Determination of optimum coagulation-flocculation pH of the treated effluent. For this purpose, coagulation flocculation tests were conducted at four pH values (5.5; 6.5; 7.5 and 8.5), at constant mass of coagulant and flocculants. The pH was adjusted using hydrochloric acid or sodium hydroxide solutions (0.1 M).
- The identification of the optimal dose of each coagulant for the effluent treatment at its optimum pH by varying concentrations of the six beakers of Jar-test.
- The dynamic adsorption treatment for coagulated and flocculated effluent at pH and the optimum dose of coagulant.

3. Results and discussions

3.1. BR46, BM and GM dyes studies in dynamic system

The results of BR46, BM and GM dyes adsorption on the mixed sand and clay using a continuous system were presented in the form of breakthrough curves which showed the loading behaviors of dyes to be adsorbed from the solution expressed in terms of residual concentration as a function of time (C_r vs. t).

C_0 and C_r : Initial and Residual dye concentration (mg / L); q_v : Flow rate (mL/min)

3.1.1. Effect of flow rate for the BR46 and BM dyes

To examine the effect of flow rate on the dynamic adsorption process, the flow rate was varied from 4 to 12.5 mL/min at a bed height of 20 cm and 160 mg/L, 210 mg/L and 260 mg/L as initial dyes concentrations for GM, BM and BR46 respectively. The effect of flow rate on breakthrough performance at the above operating conditions is shown in Fig.2.and Table 3.

As shown in Fig. 2, as the flow rate was increased, the breakthrough curve became steeper. At a lower flow rate, the time is more sufficient for diffusion of BR46, BM and GM into the inner pores of the clay through intra-particle diffusion. As a result, more dyes ions could be captured by the adsorption sites inside the adsorbent at the lower flow rate. However, as shown in Table 3, early breakthrough and exhaustion occurred at a higher flow rate. With the increase of flow rate from 4 to 12.5 mL/min, the removal efficiency was decreased from 33.2% to 26.7%, 35.1% to 27.1% and from 44% to 33.33% for the BR46, BM and GM dyes respectively. This may be explained by the fact that the breakthrough curve became steeper as the flow rate increased. It can be due to the fact that at a high rate of influent, the dyes ions did not have enough time for the contact with clay adsorbent, which resulted in a lower removal of BR46, BM and GM dyes in column. In other words, at low flow rate, the diffusion process which controls the sorption becomes slow, and hence, the adsorbent needs more time to bond the adsorbate efficiently [33]. The optimum uptake capacity for flow rate of 4, 8.5 and 12 mL/min was found to be 47.34; 30.80 and 21.87 mg/g respectively (Table 3). As shown in Fig.2, when the flow rates were 4; 8.5 and 12 mL/min respectively, the saturation occurred at 410, 103 and 45 min for BR46, 332.5; 129.41 and 59.16 min for BM and 575; 156.47 and 65.83 min for the GM dye. Hence, at lower flow rate, the dyes ions had more time to contact with the adsorbent, which resulted in higher removal of BR46, BM and GM dyes ions in the fixed bed column. The flow rate of 4 mL/min is thus used for further experiments. These results are in agreement with those reported in previous studies [33- 34].

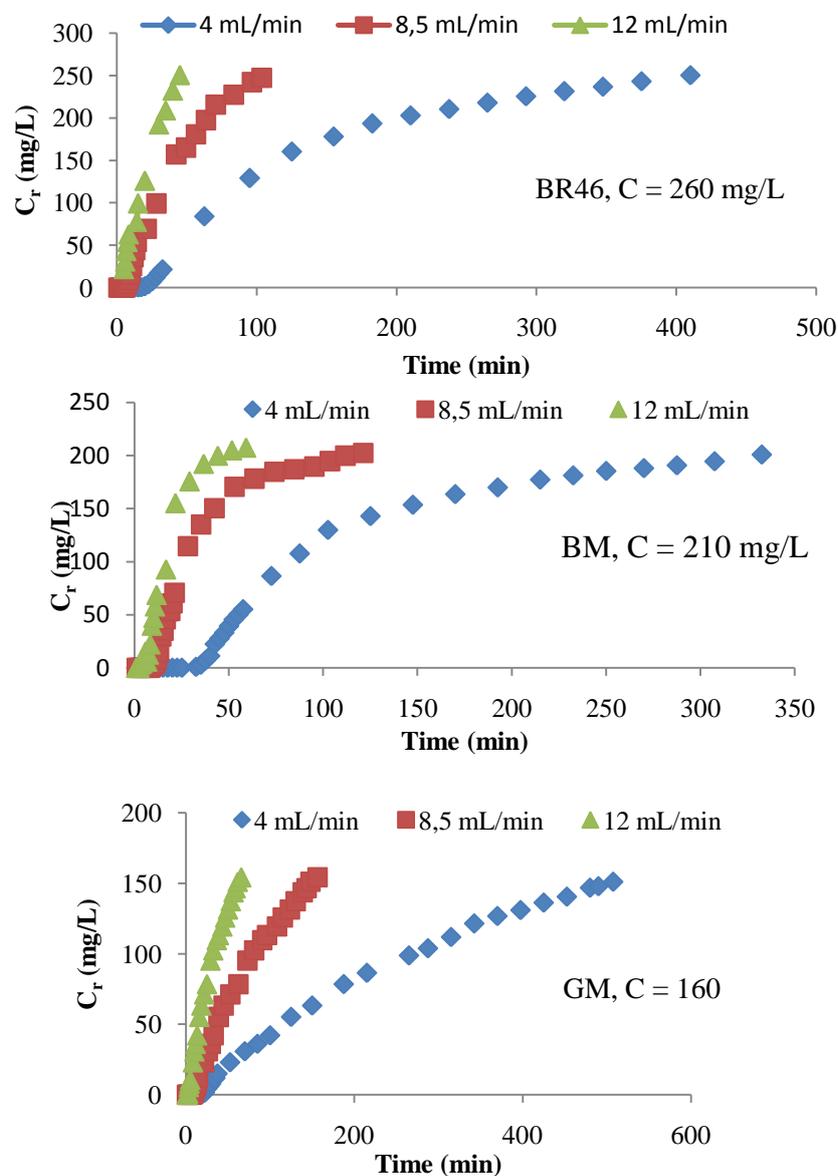


Figure 2: Breakthrough curves for BR46, MB adsorption onto clay at different flow rates, bed height = 20 cm, temperature = $28 \pm 1^\circ\text{C}$.

3.1.2. Effect of initial BR46, BM and GM dyes concentration

The effect of initial BR46, BM and GM dyes concentration on the dynamic adsorption process is shown in Fig. 3. It was clearly observed that the exhaustion time decreased with increase of initial dyes concentration. As expected, a decrease in the initial dyes concentration gave an extended breakthrough curve indicating that a higher volume of the solution could be treated. The breakthrough time decreased with increase in inlet BR46, BM and GM concentration as the binding sites became more quickly saturated and the dyes loading rate increases [35]. The net effect is an appreciable increase in adsorption capacity as presented in Table 3. As the influent GM, BM and BR46 concentrations increased from 160 to 260 mg/L, the exhaust time decreased from 780 to 575 min, 580 to 420 min and 775 to 552 min respectively. At the highest dyes concentration of 260 mg/L, the mixed adsorbent bed was exhausted in the shortest time leading to the earliest breakthrough and the treated volume was the greatest at the lowest influent concentration. These results demonstrated that higher initial influent concentrations led to higher driving force for mass transfer, lower concentration gradient caused a slower transport due to a decrease in the diffusion coefficient or mass transfer coefficient. Or in other words, the diffusion process is concentration dependent the larger is the initial dye concentration; the steeper is the slope of breakthrough curve and smaller is the breakthrough time. Hence the adsorbent achieved saturation more quickly, which resulted in a decrease of exhaust time and adsorption zone length [36- 37]. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time [35].

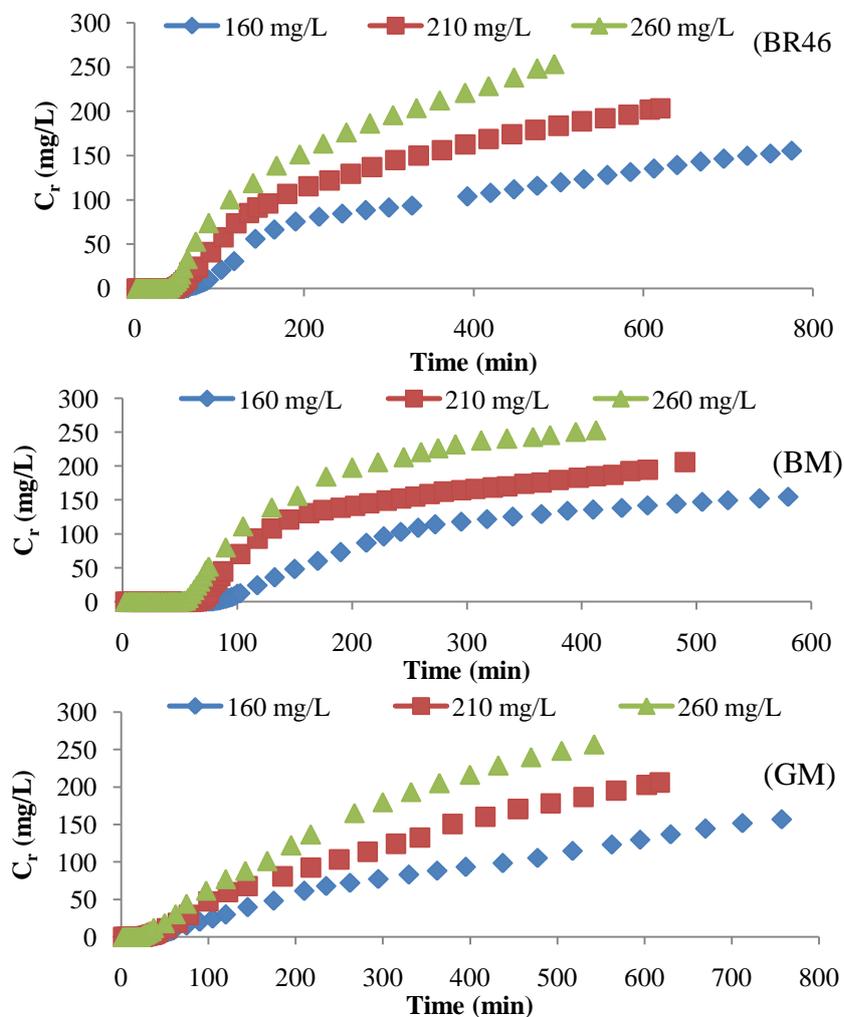


Figure3: Break through curve for different feed concentration of BR46, BM and GM dyes at constant bed height of 30 cm and hydraulic loading rate of 4 mL/ (min).

As shown in Table 3, the equilibrium column capacity (q_e) increase by increasing the GM, BM and BR46 dyes concentrations (from 160 to 260 mg/L) from 53.78 to 58.54 mg/g, 35.46 to 38.98 mg/g, 48.33 to 51.43 mg/g respectively. It can be due to the fact that the adsorbent requires much more time to reach the adsorption

equilibrium at lower initial dyes concentrations. A high influent concentration saturates the adsorbent bed more quickly, and the breakthrough is reached before all the active sites of the adsorbent are occupied by the dyes ions. The removal percent of the GM, BM and BR46 for the tested influent concentrations of 160, 210 and 260 mg/L are going from 48.4% to 44%; 42.9% to 39.1%, 43.8% to 40.2% respectively. This indicates that an increase in the concentration could modify the adsorption rate through the bed, which may be explained by the fact that the greater concentration gradient cause a faster transport due to an increase for the diffusion coefficient or mass transfer coefficient [36-38], which can be attributed also to the fact that the high influent dyes concentration can provide higher driving force for the transfer process to overcome the mass transfer resistance [36- 37]. Similar trends were obtained for adsorption of basic dye and lead II using activated carbon [35], removal of methyl orange dye from water onto raw and acid activated montmorillonite in fixed beds [39].

3.1.3. Effect of bed height

To investigate the effect of bed height, 2.25, 3; 3.75 and 4.5 g of clay was mixed with 75, 100, 125 and 150 g of sand to provide bed depths of approximately 15 cm, 20 cm, 25 and 30 cm, respectively. The effect of different bed heights on breakthrough curves of BR46, BM and GM dyes adsorption are given in Fig. 4 and Table3.

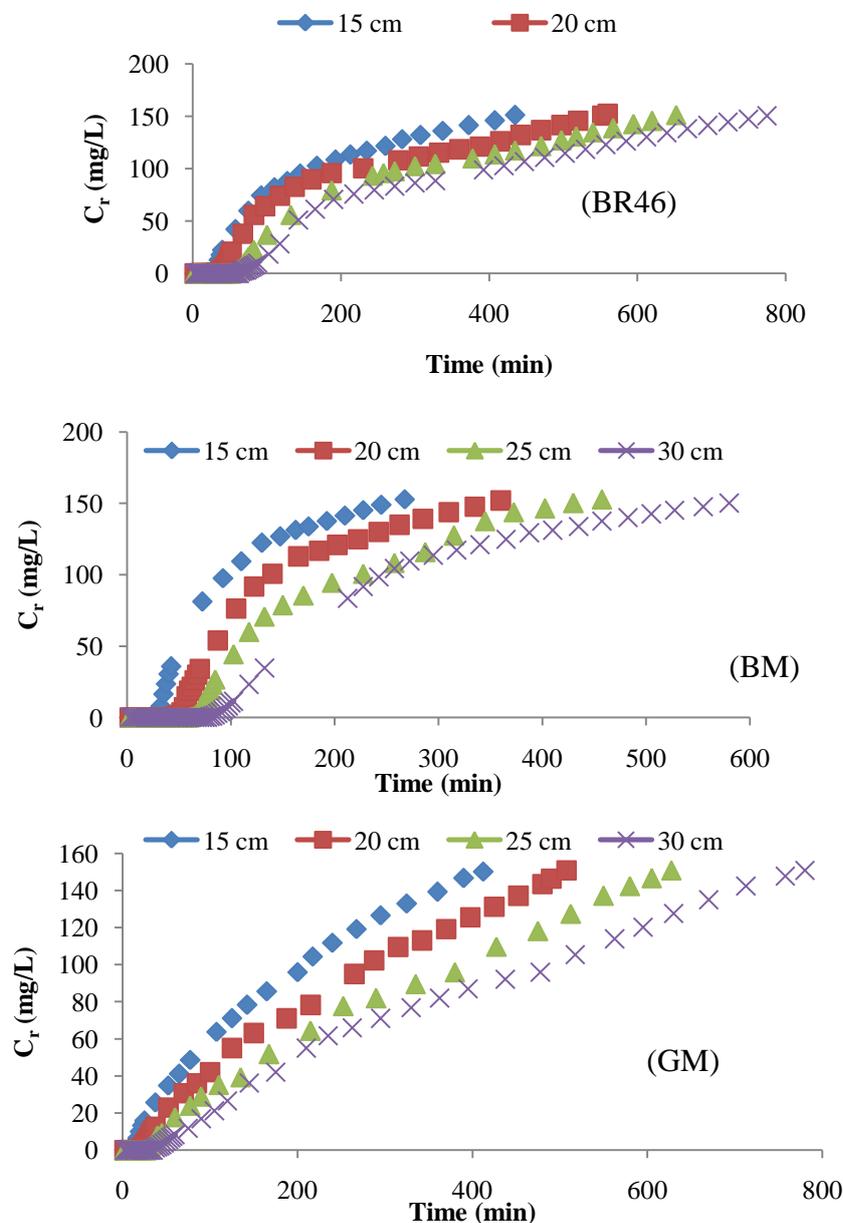


Figure 4: Breakthrough curves for BR46, BM and GM adsorption on Moroccan raw clay at different bed heights ($C_0 = 160 \text{ mg/l}$, $q_v = 4 \text{ mL/min}$, $T = 25 \pm 1^\circ\text{C}$).

The curves show that initially, the adsorption is very rapid probably associated with the availability of reaction sites able to capture dyes ions around or inside the cells. In the next stage of the process due to the gradual occupancy of these sites, the uptake becomes less effective. The column is capable of accumulating adsorbate even after breakthrough occurs although at a progressively lower efficiency. As seen in Fig.4, increasing bed height for BR46, BM and GM dyes increases the breakthrough time (From 435 to 775 min, 267.5 to 280 min and 264 to 499 min respectively) and the effluent volume (From 1740 to 3100; 1070 to 2320 and 1650 to 3120 mL respectively). This might be due to the more contact time caused by a long bed height [37]. It can be also explained by the fact that the increase in clay doses could provide more adsorption sites [40], causing a higher volume of dyes solution treated and higher percentage of BR46, BM and GM removal. So, the t_{total} is prolonged as the bed height was increased (Table 3). The slope of breakthrough curve decreased with increasing bed depth, which resulted in a broadened mass transfer zone [21; 36], but the curve of the longer bed (30 cm) tends to be more gradual, meaning the column is difficult to be completely exhausted [41]. In addition, the adsorption efficiency in dynamic process would be affected by the contact time. It was found that the axial dispersion mechanism predominated in the adsorbate transfer at a lower bed height, and the time for the diffusion of dyes ions was limited [42]. Therefore, the contact time for the dyes ions adsorption was enhanced, and the equilibrium column capacity for the BR46, BM and GM improved from 44.84 to 48.33; 27.34 to 35.46 and 48.38 to 53.78 mg/g respectively.

Table 3: Parameters in fixed-bed column for BR46, BM and GM adsorption dyes by Moroccan clay.

C_0 (mg/L)	v (mL/min)	Z (cm)	t_{total} (min)	m_{total} (mg)	Q_{total} (mg)	Q_{exp} (mg/g)	V_{eff} (mL)	Y (%)	
160	4	15	435	278.4	100.89	44.84	1740	36.2	BR46
160	4	20	560	358.4	135.99	45.33	2240	37.9	
160	4	30	775	496	217.48	48.33	3100	43.8	
160	4	30	775	496	217.48	48.33	3100	43.8	
210	4	30	632.5	531.3	223.5	49.69	2530	42	
260	4	30	552.5	574.6	231.43	51.43	2210	40.2	
260	4	20	410	426.4	142.02	47.34	1640	33.2	
260	8,5	20	103.5	305.76	92.4	30.80	1176	30.21	
260	12	20	45	245.7	65.61	21.87	945	26.7	
160	4	15	267.5	171.2	61.51	27.34	1070	35.9	
160	4	20	360	230.4	89.25	29.75	1440	38.7	
160	4	30	580	371.2	159.57	35.46	2320	42.9	
210	4	30	495	415.8	167.2	37.17	1980	40.2	
210	4	20	332.5	279.3	98.04	32.68	1330	35.1	
210	8,5	20	129.41	231	66.84	22.28	1100	28.9	
210	12	20	59.16	170	46.23	15.41	810	27.1	
260	4	30	420	436.8	170.91	38.98	1680	39.1	GM
160	4	15	412.5	264	108.85	48.38	1650	41.2	
160	4	20	507.5	324.8	150.48	50.16	2030	46.3	
160	4	30	780	499.2	242.01	53.78	3120	48.4	
210	4	30	665	558.6	253.93	56.43	2660	45.4	
260	4	30	575	598	263.43	58.54	2300	44	
160	8,5	20	156.47	212.8	83.68	27.87	1330	39.32	
160	12	20	65.83	126.4	50.04	16.68	790	33.33	

The amount of the dyes adsorbed per unit mass of activated weed, q (mg/g) in the column was calculated using the relationship:

$$Q_{exp} = Q_t / m = \frac{\sum_{i=1}^n V_{(t_i - t_{i-1})} [1 - (C_i / C_0)] C_0}{m} \quad (2)$$

Where ' Q_t ' (mg) is the total amount of dye ion adsorbed in the clay column, ' i ' is the number of sampling points, ' m ' (g) is the mass of activated weed packed in the column, ' v ' (mL/min) is the flow rate of the input, ' t_i ' is the i_{th} time point and $(C/C_0)_i$ is the ratio of output concentration over the initial input concentration.

The effluent volume, V_{eff} (mL), can be calculated from the following equation [36-38]:

$$V_{\text{eff}} \text{ (mL)} = q_v * t_{\text{total}} \text{ (3)}$$

Where q_v is the volumetric flow rate (mL/min), t_{total} is the total flow time (min).

The value of the total mass of the dye adsorbed, q_{total} (mg), can be calculated from the area under the breakthrough curve (Eq. (4))

$$q_{\text{total}} \text{ (mg)} = q_{\text{exp}} * m \text{ (4)}$$

Where q_{exp} is the experimental adsorption capacity, m (g) is the amount of the adsorbent.

The total mass of the dye added to the column is calculated by

$$m_{\text{total}} \text{ (mg)} = C_0 * V_{\text{eff}} / 1000 \text{ (5)}$$

Where: C_0 (mg/L) is the initial dye concentration, V_{eff} is the total volume of the treated effluent.

The percentage removal of the dye is calculated by:

$$Y(\%) = q_{\text{total}} * 100 / m_{\text{total}} \text{ (6)}$$

Where q_{total} is the dye total mass of adsorbed dye, m_{total} is the total mass of dye introduced into the column.

3.2. Column adsorption models

3.2.1. The Adams- Bohart model

The Adams- Bohart model assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species. The Adams- Bohart model is used for the description of the initial part of the breakthrough curve, expressed as [43]

$$\ln \frac{C}{C_0} = KC_0 t - KN_0 \frac{Z}{u} \text{ (7)}$$

C_0 is the pollutant concentration in the inlet of the adsorber column (mg /L); K is the rate constant (L /mg .min); N_0 is the maximum adsorption capacity (mg /L), Z is the height of the adsorbent bed (cm), C is the residual concentration (mg/L) and u is the velocity (cm/ min).

From this equation, values describing the characteristic operational parameters of the column can be determined from the plot of $\ln C/C_0$ against t using the nonlinear regressive method.

Wearing $\ln(C/C_0) = f(t)$, the linear part of the curve is used to determine the maximum adsorption capacity. The following figure (fig. 5) is a representation of $\ln(C/C_0) = f(t)$ for the BM dye at different bed height and concentration of 160mg/ L. the $\ln(C/C_0) = f(t)$ for the BR46 and the GM are not shown.

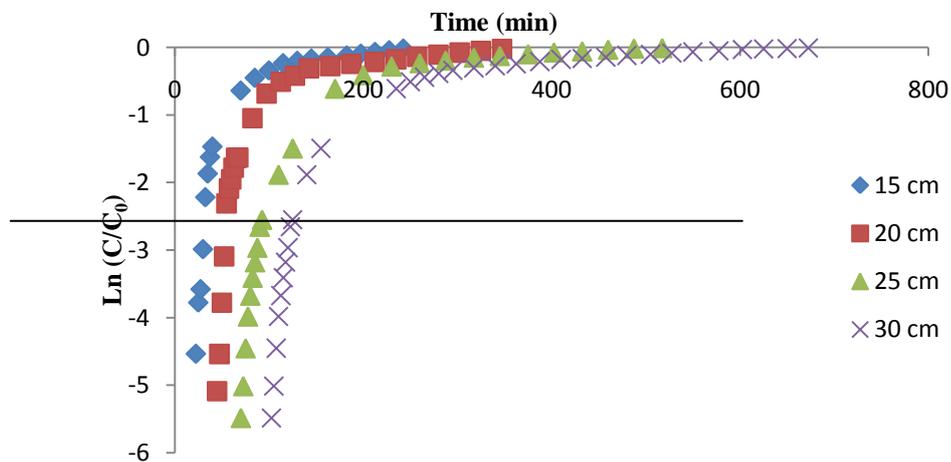


Figure 5: Representation of $\ln(C/C_0) = f(t)$ at different heights of the adsorbent bed ($q_v : 4 \text{ mL/min}$, $C_0 = 160 \text{ mg/L}$ T : $25^{\circ} \pm 2^{\circ} \text{C}$) for the BM dye.

The adsorption capacities of BR46, MB and GM dyes calculated from the Adams- Bohart model at different adsorption capacity and bed height are presented in Table 4. Based on the values of the correlation coefficient R (close to 1), we can notice, that the model describes correctly the adsorption phenomenon. Furthermore, it can be noted from table 4 that the adsorption capacity increases by increasing the adsorbent bed height and initial dye concentration. This may be due to the increase in the number of sites available by increasing the adsorbent mass, and the increase of the dye molecules

diffusion from the solution to the surface of the adsorbent by increasing the initial dye concentration. It was indicated also that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column [44, 45]. The Adams–Bohart model provides a simple and comprehensive approach to conduct and evaluate sorption-column test. However, its validity is limited to the range of conditions used [45].

Table 4: Parameters for the Adams- Bohart BR46, BM and GM dyes

C₀ (mg/L)	q_v (mL/min)	Z (cm)	K (L/mg.min)	N₀ (mg/L)	R²	
160	4	15	0.0013	618.15	0.99	BR46
160	4	20	0.001	657.32	0.95	
160	4	25	0.0009	688.85	0.95	
160	4	30	0.0004	753.34	0.94	
210	4	15	0.001	662.10	0.98	
210	4	20	0.0008	696.97	0.98	
210	4	25	0.0007	747.61	0.97	
210	4	30	0.0006	788.69	0.96	
260	4	15	0.0008	688.85	0.98	
260	4	20	0.0007	709.39	0.96	
260	4	25	0.00058	790.12	0.97	
260	4	30	0.00057	803.02	0.95	
160	4	15	0.0012	608.12	0.97	BM
160	4	20	0.0012	622.92	0.98	
160	4	25	0.0012	708.43	0.97	
160	4	30	0.00097	775.79	0.97	
210	4	15	0.001	629.14	0.98	
210	4	20	0.001	679.77	0.95	
210	4	25	0.0009	742.35	0.95	
210	4	30	0.001	804.93	0.97	
260	4	15	0.0009	631.52	0.95	
260	4	20	0.0008	710.82	0.94	
260	4	25	0.0008	785.82	0.94	
260	4	30	0.0007	839.33	0.95	
160	4	15	0.0011	469.58	0.99	VM
160	4	20	0.0011	501.59	0.96	
160	4	25	0.0007	528.82	0.94	
160	4	30	0.0005	592.35	0.95	
210	4	15	0.0008	534.55	0.98	
210	4	20	0.0008	580.89	0.96	
210	4	25	0.0006	593.31	0.98	
210	4	30	0.0006	643.47	0.97	
260	4	15	0.0007	570.38	0.98	
260	4	20	0.0006	602.38	0.96	
260	4	25	0.0005	625.79	0.97	
260	4	30	0.0004	685.03	0.98	

3-2-2 Model Clark linearized

This model is considered to be a particularly attractive approach to describe dynamic adsorption. It has a sound theoretical basis of a mass-transfer concept in combination with the Freundlich adsorption isotherms and has a precise analytical solution enabling determination of dynamic adsorption rate constants [42]. In previous equilibrium studies, it was found that the Freundlich model was valid for the description of BR46, BM and GM adsorption onto clay [26, 46, 47], which allows the use of the Freundlich constants (Table 5) to calculate the Clark model parameters. The model is given by the following equation [48, 49]:

$$C = \left[\frac{C_0^{n-1}}{1 + Ae^{-rt}} \right]^{1/n-1} \quad (8)$$

where n is the Freundlich's isotherm heterogeneity parameter, A and r are known as the Clark constants. These are given by the equation 9:

$$\ln\left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right] = \ln A - rt \quad (9)$$

where C_0 is the adsorption rate coefficient, C: is the concentration at the time t.

$$\ln\left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right] \quad (10)$$

The evolution of the $\ln\left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right]$ versus time at $Z = 30$ cm, $q_v = 4$ mL/min, $C_0 = 160$ mg/L is shown in the figure 6.

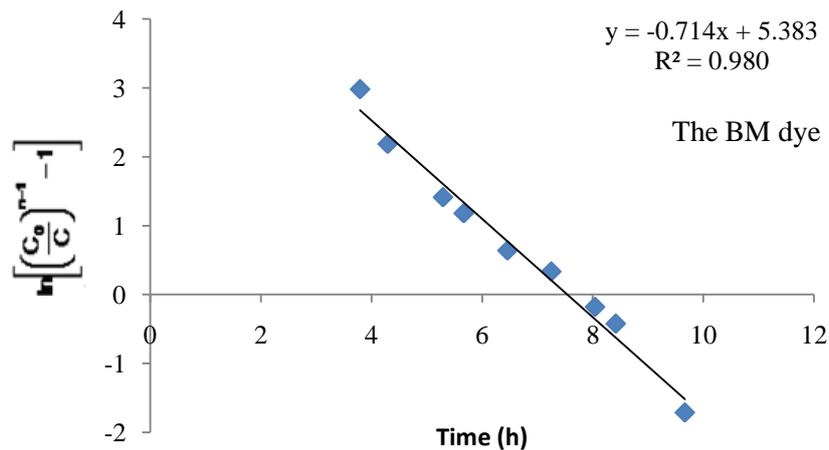


Figure 6: A and r parameters for the Clark model ($C_0=160$ mg/L, $q_v=4$ mL/min, $Z=30$ cm), (Figures corresponding to the determination of A and r parameters for the Clark model and the BM dye, figures corresponding to the BR46 and GM dyes are not shown)

The calculated values for the BR46, BM and GM dyes are summarized in Table 5:

Table 5: Parameters A and r model for Clark BR46, BM and GM dyes

		A	r_0 (h^{-1})	n	R^2
$C_0 = 160$ mg/L	BR46	39.74	0.405	4.04	0.98
	BM	217.78	0.714	6.94	0.98
	GM	97.02	0.472	3.68	0.96
$C_0 = 210$ mg/L	BR46	38.23	0.496	4.04	0.99
	BM	92.89	0.596	6.94	0.98
	GM	97.12	0.569	3.68	0.99
$C_0 = 260$ mg/L	BR46	39.30	0.617	4.04	0.97
	BM	133.31	0.984	6.94	0.97
	GM	127.48	0.708	3.68	0.98

After adjustment of the parameters A, n and r, Clark curves $C=f(t)$ can be traced by means of the equation (8):

$$C = \left[\frac{C_0^{n-1}}{1 + A e^{-rt}} \right]^{1/n-1} \quad (8)$$

As described above, we used the Freundlich's isotherm heterogeneity parameters obtained from equilibrium data previously reported in our earlier studies [26, 46, 47]. According to the model fit parameters shown in Table 5 and the fig. 7 which shows the experimental and theoretical curves for the BR46, BM and GM dyes ($q_v=4$ mL /min, $Z= 30$ cm, $C_i= 160,210$ and 260 mg/L), we can conclude that the Clark model appears to be suitable for description of the BR46, BM and GM dyes adsorption at the ratios of C_i/C_0 higher than about 0.08 and when the residual concentration (C_i) is near than C_0 ;

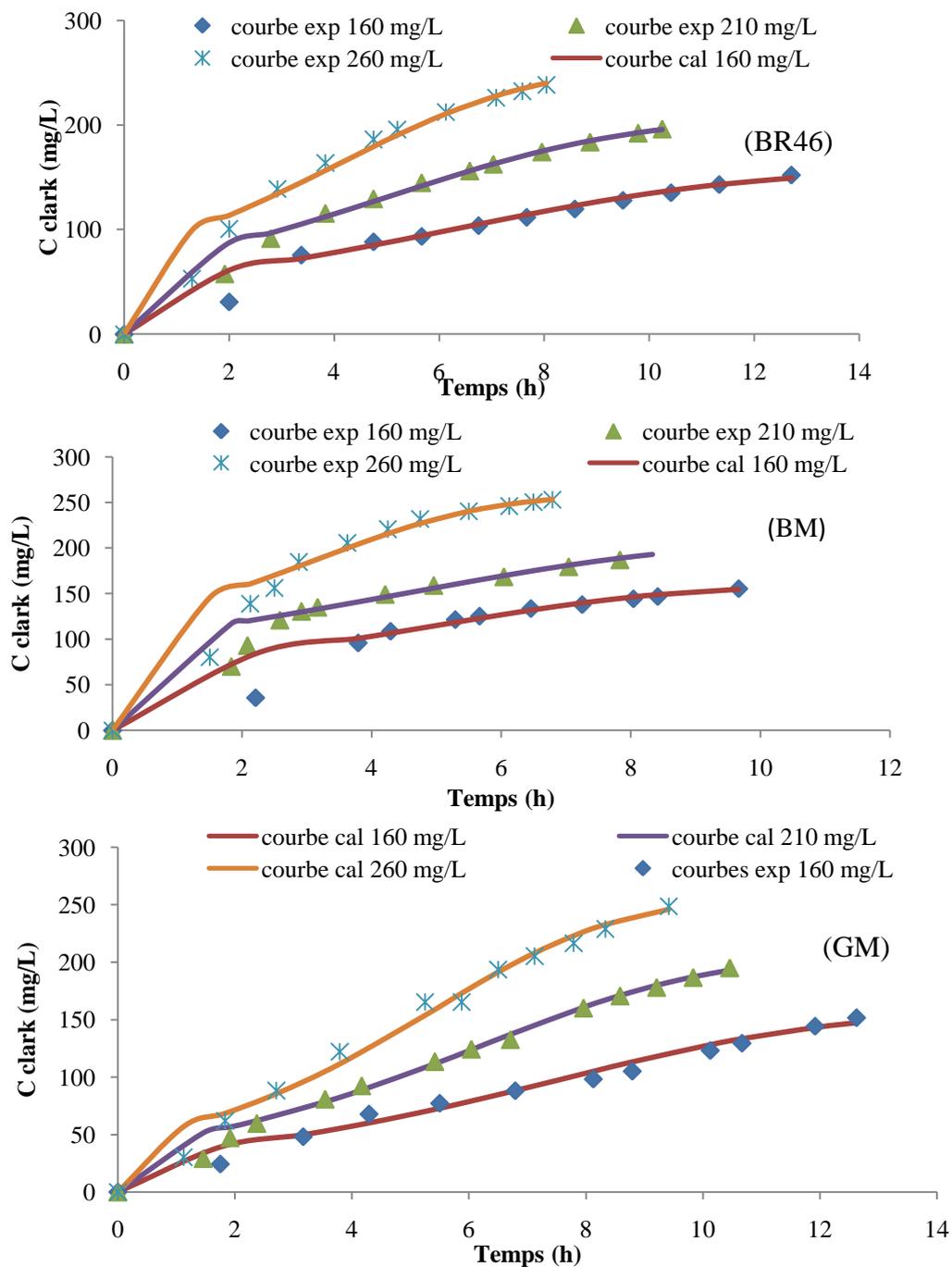


Figure 7: Experimental and calculated curves using the Clark model ($q_v = 4 \text{ mL / min}$, $Z = 30 \text{ cm}$, $T^\circ: 25^\circ \pm 2^\circ$)

In the present study, we used this model for the full range of the studied dyes concentration. The estimated values of Clark constants A and r determined using Eq. (9) are listed in Table 5. Results show that the constants were significantly influenced by the initial dye concentration. This behavior indicates that the kinetics of BR46, BM and GM dyes dynamics adsorption onto clay is dominated by external mass transfer [50].

The good superposition of the experimental curves and those calculated from the Clark model at the ratios of C_t/C_0 higher than about 0.08, means that the assumptions of Clark, which will be mentioned below in this concentration range [51], are true:

- The rate of adsorption is governed by the transfer of the outer film grain
- The absent adsorption reversibility and the upper non limitation of storage capacity allows to the equilibrium isotherm to be Freundlich type.
- The flow of fluid is of the piston type.

3.3. Wastewater studies

3.3.1. Column adsorption treatment of industrial waste pretreated by decantation

3.3.1.1. Decantation treatment

The “decantation pond” is the area used to deposit low density sludge separated from the liquid [25]. Experiment shows that the settling of one hour has reduced the pollution organic load, turbidity and color by 48, 40 and 51% respectively (Figure not shown).

3.3.1.2. Decanted wastewater Adsorption treatment by the Moroccan Clay of Safi

Testing mode industrial wastewater, dynamics adsorption was made after conducting a settling (decantation) of the effluent (percentage organic load reduction of 40%, so a DCO value of 1600 mg O₂/L). The organic load reduction study by dynamic adsorption on clay showed that 2 L is the necessary amount for a total discoloration and 85% as a percentage of organic load reduction (Figs 8 and 9). Indeed, the curve representing the reduction rate of the color decreases logarithmically with the volume of treated effluent until the total column saturation, while the curve of the organic load decreases according to a polynomial function of equation with a correlation coefficient near than 1. We note as well that the greater organic load reduction is obtained for the first volumes (10, 20 and 30 mL), the quality of these treated effluent is in compliance with industrial discharges. The rapid saturation of the material can be explained by adsorption to the surface due to the fact that the clay adsorbent is predominantly kaolinitic with a percentage of 29% [26], so a very small interlayer space. Thus, the organic load expressed in DCO obtained from the first sample collected was 387.5 mgO₂ / L. It meets the discharge of industrial effluents [25].

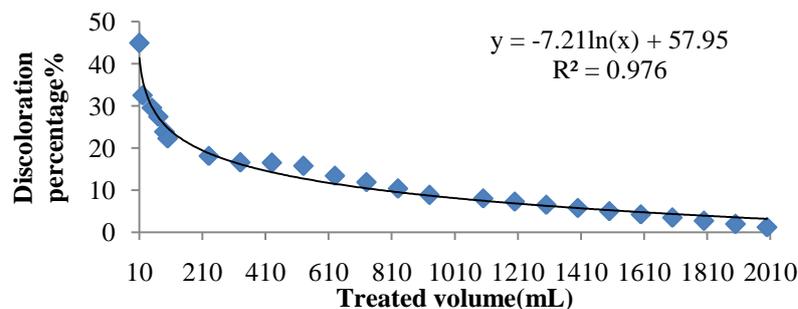


Figure 8: Discoloration percentage of the textile effluent decanted as function of the treated volume by adsorption reactor dynamic onto Moroccan clay. (T °: 25 ° ± 2 °, column height: 40 cm, clay mass: 6 g, sand mass: 200 g, λ_{max} = 527 nm)

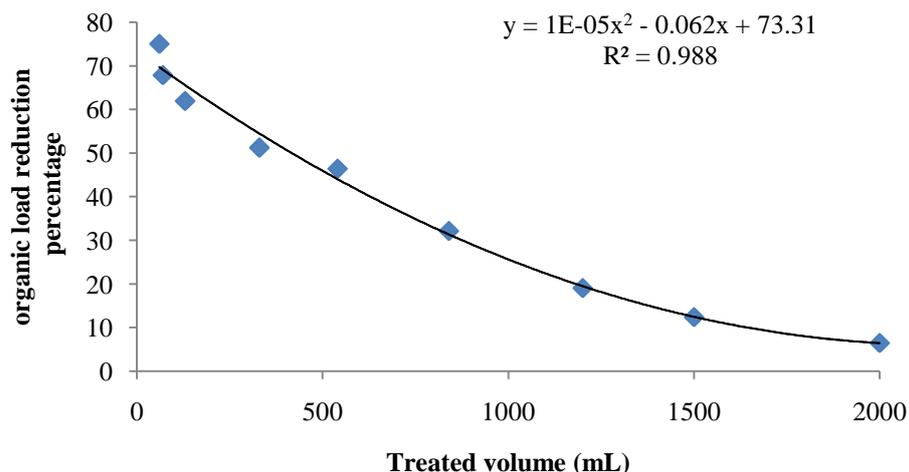


Figure 9: Reduction of organic load as function of the treated volume by adsorption onto Moroccan clay (T °: 25 ° ± 2 °, column height: 40 cm, clay mass: 6 g, mass of sand: 200 g)

The decantation used to separate suspended matter in a liquid of low density coupled with dynamic adsorption process seemed suited to the treatment of our effluent, However, despite these significant reductions of organic load and absorbance for this effluent, it remains slightly colored (discoloration percentage : 45%). With the hope

of improving the efficiency of discolorating effluent, the provision of other pretreatment method is desirable. The method of coagulation-flocculation seems generally effective for the removal of suspended solids and colloidal particles [1, 52; 53; 54]. Coagulation requires the pH optimization to determine which one provides the best flock formation. [55-57]. It depends on the nature of the coagulant and pollution considered [54; 57 and 58]. These returns are also improved by optimizing the coagulant dose.

3.3.2. Column adsorption treatment of industrial waste pretreated by coagulation-flocculation

3.3.2.1. Optimization of coagulation pH

At constant dose of coagulant (100 mg / L) and flocculant (0.4 mg / L), we studied the pH effect in the optimal range of coagulants used (pH of: 5.5; 6.5; 7.5 and 8.5 for the FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ on the evolution of DCO and turbidity [57]. Curves representing the evolution of the organic load DCO and turbidity as a function of pH are shown in Figs 10 and 11:

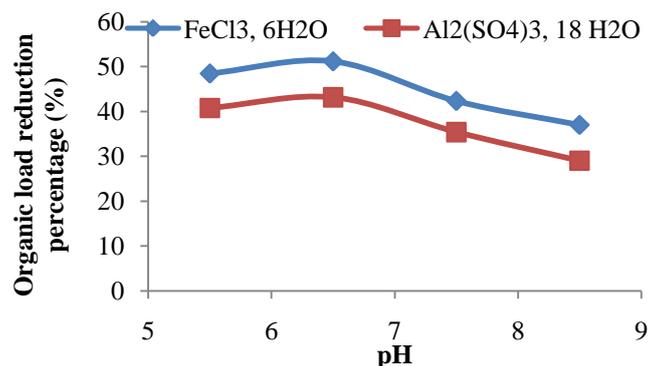


Figure 10: Variation of the organic load percentage as function of pH for the FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$. ($T^\circ: 25^\circ \pm 2^\circ$, speed coagulation: 170 tpm, agitation time: 2 min, speed flocculation: 30 tpm with agitation time: 30 min, the coagulant dose: 100 mg / L, the flocculant dose: 0.4 mg / L).

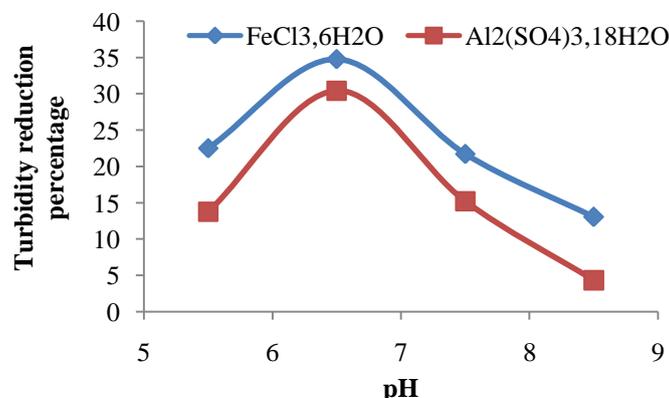


Figure 11: Variation of the turbidity as a function of pH for the FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ ($T^\circ: 25^\circ \pm 2^\circ$, coagulation speed: 170 trs / min with agitation time: 2 min, flocculation speed: 30 trs / min with agitation time: 30 min, coagulant dose: 100 mg / L, flocculant dose: 0.4 mg / L)

We note from Figures 10 and 11 that the maximum reduction of the organic load and turbidity was recorded at pH 6.5. We note also that the FeCl_3 treatment is more effective because it allowed a further reduction of the organic load and turbidity of 8% and 5% respectively compared to $\text{Al}_2(\text{SO}_4)_3$ treatment.

3.3.2.2. Optimization of coagulant dose

To find the optimal coagulant amount for best removal efficiency of the wastewater studied, we have varied the coagulant concentration in different beakers of Jar-test to follow the turbidity and the organic load evolution as function of different amount of coagulant added. To do this, we have maintained the pH at its optimal value (6.5), the same operating conditions of the other parameters such as: agitation time, the flocculant dose and the temperature constant. The results of these tests are summarized in Table 6.

Table 6: Variation of the organic load (DCO) and turbidity percentage as function of FeCl₃ and Al₂(SO₄)₃ coagulant dose (T °: 25 ° ± 2 °, coagulation speed: 170 rev / min with agitation time: 2 min, flocculation speed: 30 rpm with agitation time : 30 min, optimum pH: 6.5)

Coagulant dose	FeCl ₃		Al ₂ (SO ₄) ₃	
	DCO percentage removal	Turbidity percentage removal	DCO percentage removal	Turbidity percentage removal
100	52.3	41.3	43.93	34.78
200	68.77	79.13	50	43.47
300	69.24	86.95	64.99	76.08

The results deduced from this table show that:

- *The turbidity percentage removal increase as the concentration of Al₂(SO₄)₃ and FeCl₃ increases.
- *The organic load (DCO) percentage removal increases with the increase of the dose of the coagulant until a residual value of 200 mg / L, which remains constant even if the coagulant is added. Thus, the optimum coagulant dose is 200 mg / L.
- *The FeCl₃ treatment is more effective compared to aluminum sulfate treatment because it allowed a further removal of the organic load and turbidity of approximately 18% and 35% respectively compared to Al₂(SO₄)₃.

3.3.2.3. Dynamic adsorption reactors treatment

In this section, we were not able to exploit the absorbance of the samples collected at different volumes because they are almost transparent (the signals obtained are very low). The coagulation flocculation treatment allows to reduce the organic load to 800 mg O₂/L, so a reduction percentage of 70%. The adsorption tests of the treated effluent by optimal FeCl₃ coagulant dose (200 mg / L, pH = 6.5) coagulation-flocculation were carried out in dynamic system at room temperature. The results are shown in Fig.12.

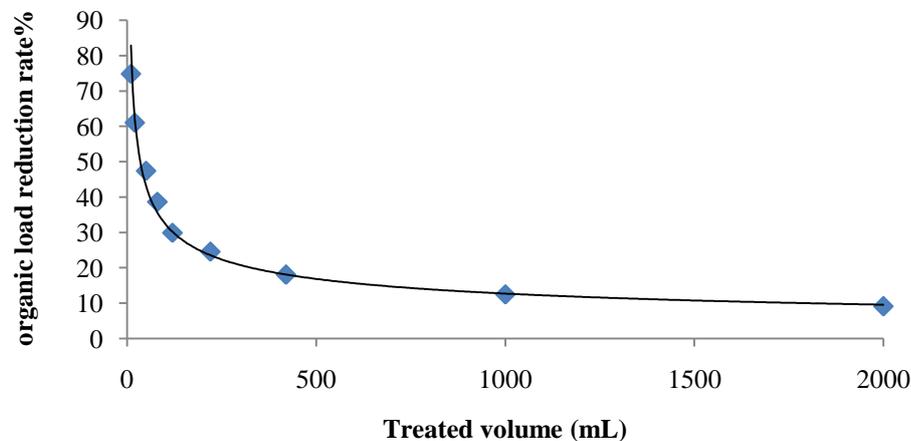


Figure 12: Reduction of DCO rejection coagulated flocculated by volume treated (T °: 25 ° ± 2 °, column height: 40 cm, clay mass: 6 g, sand mass: 200 g)

The Fig 12 show the organic load reduction obtained by coagulation flocculation pretreatment and adsorption in dynamic system at the optimum operating conditions. The results are nearly similar to those obtained by settling pretreatment and adsorption dynamics. However, this method recorded a total discoloration of the treated effluent and a better organic load reduction compared to the results obtained for the adsorption of the effluent pretreated by settling method.

The treatment by dynamic adsorption reactor of the pretreated effluent by coagulation-flocculation at the optimum pH and FeCl₃ dose is an effective discoloration and organic load dejection technique because it allows an organic load reduction from 2600 to 201 mgO₂ /L, which is lower than the standard industrial waste (500 mgO₂/L) [25]. The elimination of the organic DCO is assessed to 92% in relation to the initial effluent.

Conclusion

Fixed bed column study was conducted to find out the effectiveness of natural adsorbent, Moroccan clay of Safi for cationic BR46, BM, GM dyes and the textile effluent dynamic adsorption using mixed sand and clay reactor. Investigation suggested that the adsorbent is efficient for the cationic dyes adsorbates removal from water. In effect, the adsorption of dyes in the fixed bed of mixed sand and clay was strongly dependent on the initial dyes concentration, flow rate and the bed height. It is found that the breakthrough time decreases with the increase in the initial dye concentration and flow rate, but it increase with increasing bed height. The experimental results show that increasing flow rate in fixed bed adsorption resulted in steeper breakthrough curves, with shorter breakthrough times. For increasing dye concentration, steeper breakthrough curve was obtained and breakthrough was reached earlier. With a smaller bed height, the dye concentration at the outlet of the column becomes near to that of the input in earlier and short time and more rapidly than that for a higher bed height.

Different dynamic adsorption models (continuous flow), were applied to find the maximum adsorption capacities of clay (Adams- Bohart and Clark models). We notice that the curve modelling using Bohart and Adams, describes the experience in the field of low concentrations, however, for the Clark model, a good representation of curves in the domain of large concentrations is obtained.

The textile effluent treatment shows that:

1. The textile effluent studied is slightly acidic and carries a high pollutant load;
2. The effluent decantation has reduced the pollution organic load, turbidity and color in the order of 48, 40 and 51% respectively;
3. The optimum settling pretreatment conditions for the textile effluent treatment are defined as one hour;
4. The FeCl_3 is more efficient than $\text{Al}_2(\text{SO}_4)_3$
5. The optimum pH and dose of coagulant for the coagulation flocculation pretreatment are 6.5 and 200 mg / L, respectively.
6. The adsorption treatment of the decanted effluent in the dynamic mode, in the optimal conditions showed a reduction of the organic load and color at 75% and 45% respectively;

The combined treatment of coagulation flocculation and adsorption in the optimum conditions (pH and coagulant dose) has eliminated completely the color and reduce the organic load until a percentage of 92%.

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