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Dynamic adsorption of BR46 dye and raw textile effluent on Moroccan clay to solve the drought problem

A. Bennani Karim [1,2*], B. Mounir[1], M. Hachkar[1], M. Bakasse[3], Z Rais[4] and A. Yaacoubi[2].

[1] *The team of Analysis, Checks and Environment, high School of Technology, University Cadi Ayyad, Safi, Morocco.*

[2] *Environmental and Experimental Methodology team, Organic Applied Chemistry Laboratory, Faculty of the Sciences Semlalia, Marrakech, Morocco.*

[3] *Analysis of the Microphones Polluting Organic team, Faculty of Sciences, Chouaib Doukkali University, El jadida, Morocco.*

[4] *Industrial effluents team: characterization and treatment, electrochemistry laboratory, modeling and environment engineering LIEME-FSDM-FÈS*

** Corresponding author. E-mail address: asmaabennani@yahoo.fr*

Climate change, drought are expected to have severe consequences on the livelihoods of millions of people around the world, but its effects will not be evenly distributed [1]. Wastewater discharge from textile industry cause an environmental problem mainly in terms of COD and color. Treating dyeing effluent is a major economic and environmental issue to reduce the effects of drought and reuse water. The dynamic adsorption of the BR46 dye, the textile effluent color and organic load reduction by adsorption using dynamic regime, was evaluated by decantation and coagulation-flocculation pretreatments. The feasibility of each of the processes was studied separately.

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Introduction

Over half of the North African population now lives in cities, with the urban population expected to increase further over coming decades. Existing risks are likely to be amplified as the impacts of climate change are increasingly felt, together with demographic pressures and rapid urbanization. The human impact on the climate system is scientifically well-established.

According to the Intergovernmental Panel on Climate Change, (IPCC) [2] North Africa is the second most vulnerable area in the world to emerging climate- related risks.

Also, Drought has long been recognized as falling into the category of incremental but long-term and cumulative environmental changes, it is expected to become more frequent and severe, with increasing water demand due to population growth, limited and uncertain water supplies in the context of climate change characterized by increasing temperatures, and more extreme precipitation regimes [3, 4] and is also termed as a slow-onset or creeping event. Similar slow onset but rapid transition issues include: soil degradation and desertification processes, ecosystem changes and habitat fragmentation, nitrogen overloading, and coastal erosion, among others. Such creeping changes are often left unattended in their early stages. This contributes to the impact increase of the climate change affecting the agricultural production, water shortage which is reported by Intergovernmental Panel on Climate Change (IPCC) in its fourth assessment in many African countries [5]. Also, the floods and flash-floods in Morocco are mostly generated by torrential rainfalls [6- 7].

Several events causing human losses and economic damages have been reported in the recent years, in 1995 (Ourika valley), 2002 (Mohammadia, El Jadida, Taza, Tétouan, Settat, Berrechid) or 2009 (Rabat, Tanger, Nador, Casablanca, Khenifra, Tétouan, Agadir, Essaouira) and the vulnerability of the major Moroccan cities to extreme precipitation and floods increased in the last two decades [7]. With the different climate model projections available, it becomes possible to provide multimodel evaluations of the climate change impacts on extreme precipitation in Morocco. This alarming situation, in a country that already suffers from water insecurity, emphasizes the need for more efforts to implement climate change adaptation measures. So, Water Reuse and Recycling must be a very important process. The recycling or reuse of water for similar duties mainly depends on availability of suitable process technology for water purification. Due to wide fluctuations in industrial effluent quality, this becomes more challenging [8]. Adsorption process is one of the efficient methods to remove dyes from wastewater, especially if the adsorbent is inexpensive and readily available [9]. Coagulation–flocculation has always attracted considerable attention for yielding high removal efficiency in wastewater treatment; this process can be directly applied to wastewaters to remove organics together with suspended solids, without being affected by the toxicity in the wastewater. In addition, the main advantage of the conventional processes, like coagulation and flocculation, is the decolourization of the waste stream due to the removal of dye molecules from the effluents, and not due to a partial decomposition of dyes, which can lead to an even more potentially harmful and toxic aromatic compound [10]. The treatment by coagulation/CFMF was also applied for domestic wastewater [11], where the effects of alum, polyaluminium silicate sulfate (PASS) and lime as flocculants were studied. Harrelkass et al. [12], have proposed various combinations of physicochemical and membrane processes. Contact to cationic dyes as BR46 with skin cause irritation with redness and pain. Upon contact with eye will lead to permanent injury of human eyes and laboratory animals. [13]

Clays have been accepted as one of the appropriate low coast adsorbents for removal of dyes from wastewater [14]

Especially, in our previous work [13], it was found that the Moroccan clay of Safi has a potential to remove textile dye BR46.

In the present paper, we'll extend and complete our previous work to column study. It concerns on the first hand especially the study of the fixed-bed adsorption of the BR46 dye onto clay of Safi (Morocco). To optimize the performances of the filter, the height of the adsorbent bed, the flow rate and the initial concentration of dye will be taken as experimental variables. We are interested on the second hand in the treatment and discoloration of industrial waste from a textile industry by adsorption on the clay in the region of Safi (Morocco), which is a natural available adsorbent, to obtain clear water, reduce the organic load and to achieve the possibility of reuse and recycling. To do this, we tried two techniques economically feasible for the company:

- The adsorption technique in dynamic system using clay and sand adsorbent mixture (3% as clay percentage) on a bed of raw clay mixed with sand to prevent clogging after performing a settling test of industrial wastewater.
- The adsorption technique in dynamic system using clay and sand adsorbent mixture (3% as clay percentage) after carrying out a coagulation flocculation pre-treatment test.

Material and methods

1. Materiel

1.1. Adsorbates

The adsorbate used in this work are a basic dye named as ICI Basic Red 46 (MW = 357.5 g), which was purchased from SDI textile company (Safi, Morocco), and a wastewater sample collected from the discharges of sewers Textile Company at the release time of the final effluent in Casablanca on 12 February 2010. The physico- chemical characteristics of this effluent are shown in table 1

Tab. 1: 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) (nm)	527	----
DCO (mg O_2/L)	2600	500	Absorbance at the maximum wavelength λ_{max}	4,58	----
Chloride ions (mg/L)	113,6	200			

1.2. Adsorbent materiel

The adsorbent used in this work is a mixture of the Raw Safi Moroccan clay collected from a natural basin in the region of Safi (Morocco) on January 2007, crushed, sieved to 600 µm size fraction, and then dried at 105°C for 24h to be used for further experiments. The sand used in this study to mix with clay to avoid clogging is collected from lalla fatna beach (16 km from Safi city), washed, crushed, and sieved to 500 µm size fraction. The clay sand percentage is of 3%. The mineralogical identification is performed by XRD in Siemens D500 diffractometer using a 106 CuKα radiation (λ = 1.5406 Å) is produced under conditions of 40 kV and 20 mA, his predominant peaks are 9.99 Å, 7.16 Å, 4.25 Å, 3.03 Å and 2.9 Å which correspond to illite, kaolinite, quartz, calcite and dolomite [13].

2. Method

The behaviour of Moroccan clay in a fixed-bed column operation at room temperature was studied to determine the breakthrough point. Continuous flow adsorption studies were conducted into a glass column with inner diameter 2 mm and bed height 40 cm, filled with adsorbent clay and sand mixtures, which were prepared by mixing clay with quartz sand (3%wt of clay) in order to avoid clogging phenomenon, so, 6 g of clay is mixed with 200g of sand. This quantity of mixed adsorbent was packed between a glass beads layer of 5 mm size in order to provide a uniform flow of the solution through the column and filter paper at the end of the column in order to prevent the escape of the clay.
The operating parameters studied for the BR46 dye were the adsorbent mass (bed depth), volumetric flow rate and initial dye concentration. It was considered that the process reached the saturation state when the concentration of the effluent matched the initial dye concentration, or when this value became constant along time. All the experiments were carried out at room temperature (25 ± 1°C) and pH c.a. 6.5. The samples of the effluent were collected at regular intervals and analysed by UV-Vis spectroscopy. A spectrophotometer [GBC (Ajax, Ontorio) UV/visible 911] was used for the experiments. A linear correlation was established between the dye concentration and the absorbance at λmax= 532 nm, in the range Cdye = 1–20 mg/L with a correlation coefficient r^2 c.a. 1.For analysis of the solutions at higher concentrations, the appropriate dilutions were performed.

Wastewater solution was pumped into column at a constant volume velocity of 4 mL/min (BV=bed volume) from the bottom of the column to the end using a peristaltic pump (Figure 1). The rate of discoloration (evaluated by measuring the absorbance for the wastewater effluent studies) was determined by difference between the initial concentration measurement (Abs_0,C_0) and his residual one (Abs_r, C_r). The amount of the residual organic load (DCO_{ad}) was determined by the difference between the original organic load (DCO_0) of the solute and the residual one (DCO_r). Organic load retention is represented by:

$$\% DCO = \frac{DCO_0 - DCO_r}{DCO_0} \times 100$$

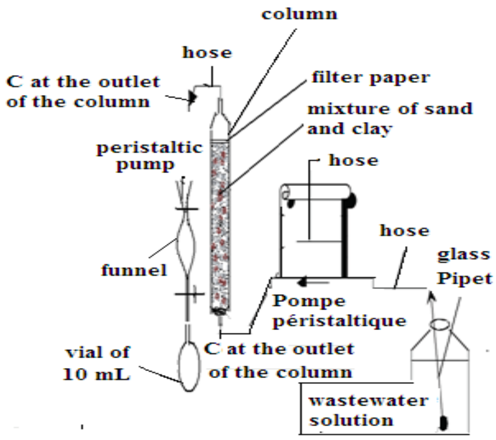


Fig. 1: Schematic diagram of laboratory based small column for fixed bed studies.

Results and discussion

<u>1. BR46 studies</u>

1. 1. General consideration on column data analysis

The breakthrough curves are a convenient tool to highlight the performances of fixed-bed column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of a sorption column [15]**.** The residual concentration (C_t) from the column that reaches about 3% of the influent concentration (C_0) is commonly designed as the breakthrough point. The point where the effluent concentration reaches 95% is usually called the ‘‘point of column exhaustion’’. The breakthrough curve is usually expressed by residual

concentration (C_t) or normalized concentration (C_t/C_0) as a function of time for a given bed depth.

The experimental amount of the BR46 dye adsorbed per unit mass of clay, qexp (mg/g), in the column was calculated using the relationship:

$$q_{\exp} = \frac{(C_0 - C_e)}{w} \qquad (1)$$

Where C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium dye concentration in the liquid phase, V (L) is the effluent volume of solution and w (g) is the amount of sorbent.

The effluent volume V (mL) can be calculated as: $V= F.t_{total}$

Where t_{total} and F are the total flow time (min) and the volumetric flow rate (mL/min)

The value of the total mass of BR46 dye absorbed, q_{total} (mg), can be calculated as:

q_{total} (mg) = $w.q_{exp}$

The amount of BR46 dye entering column, mtotal, is calculated from the following equation:

m_{total} (mg) = (C_0. V)

The removal percentage of BR46 dye can be obtained from equation: Y(%) = (q_t.100)/m_{total}

1.2. BR46 Column study

The study results of BR46 adsorption onto crude clay in a continuous system were presented in the form of breakthrough curves expressed by residual concentration (C_t) as a function of time. The effect of the following parameters was investigated, according to the procedure detailed in the experimental part: bed height, solution flow rate and initial dye concentration.

**Effect of bed height (mass of the adsorbent)*

In order to evaluate the effect of bed height on the breakthrough curve, the initial adsorbate concentration and the flow rate were fixed at 160 mg/L and 4 mL/min respectively. In Fig.2 are presented the obtained breakthrough curves at bed heights of 15, 20 and 30 cm (2.25, 3 and 4.5 g of clay). Initially, the adsorption was very rapid. This may obviously be attributed to the fact that more amount of sorbent at a given bed heights provides more binding sites for the retention of dye molecules. 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. The bed depth increased, as well as the exhaustion time and consequently effluent volume (V_{eff}) increased. As shown also from Table 2, the removal efficiency of BR46 had an increasing trend in column with the increase in the mass of adsorbent. The slope of breakthrough curve decreased with increasing bed depth, which may result in a broadened mass transfer zone [15]. The curve associated to the longer bed (30 cm) tends to be more gradual, meaning the column is difficult to be completely exhausted [16].

On the other side, it's reported in the literature [17] that when the bed height was reduced, axial dispersion phenomena predominated in the mass transfer and reduced the diffusion of the solute, and therefore the solute had not enough time to diffuse into the whole of the adsorbent mass. Similar trends were obtained for adsorption of basic dye using activated carbon and low cost adsorbent [18].

These results indicate that the intermediate bed depth of 20 cm offer a good compromise for the breakthrough curve study. Therefore, the subsequent experiments were carried out with this bed depth.

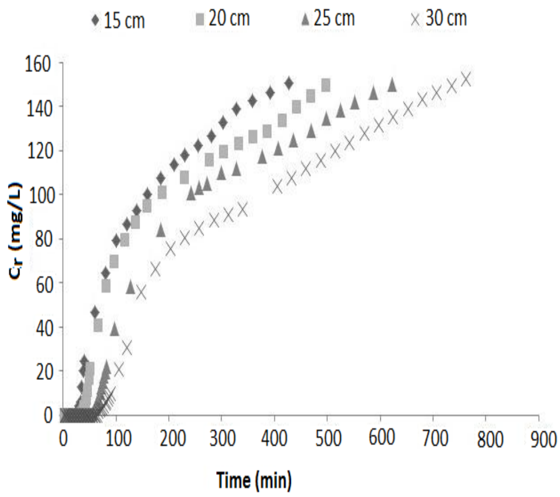


Fig.2 : Breakthrough curves for BR46 adsorption on Moroccan raw clay at different bed heights (initial dye concentration= 160 mg/L, Flow rate = 4 mL/min)

Tab. 2: Performances of fixed bed filter for BR46 removal according to the bed depth (C_0 = 160 mg/L, F = 4 mL/min)

Z (cm)	Ads. Amount (g)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{exp} (mg/g)	V (mL)	Y (%)
15	2.25	435	278.4	100.89	44.84	1740	36.2
20	3	560	358.4	135.99	45.33	2240	37.9
30	4.5	775	496	217.48	48.33	3100	43.8

**Effect of solution volumetric flow rate*

To find out the effect of flow rate on the breakthrough curves, adsorption experiments were carried out by varying the flow rate between 4 to 12 mL/min. In this process, the initial dye concentration and bed height were maintained at 260 mg/L and 20 cm respectively. The effect of flow rate on breakthrough performance at the above operating conditions is shown in Fig.3. From this figure, it was observed that the adsorption efficiency was lower at higher flow rate and the adsorbent gets saturated easily at higher flow rates. That can be explained by the fact that at higher flow rate, the external film mass resistance at the surface of the adsorbent tends to decrease and the residence time decreases. Hence the saturation time decreases, and in turn gives the lower removal efficiency [19]. As indicated in Fig. 3, the breakthrough curves became steeper as the flow rate increased. The lower removal of BR46 in column may be due, as a first approximation, to the shorter residence time of the solute in the column, which does not allow reaching the adsorption equilibrium. In other words, at low flow rate, the diffusion process, which probably controls the sorption, takes place. Hence, the adsorbent needs more time to bond the adsorbate efficiently. The optimum uptake capacity for flow rate of 4, 8 and 12 mL/min was found to be 47.34, 30.80 and 21.87 mg/g respectively (Table 3). The removal percentage of BR46 follows the same trend. As shown in Fig.2, the saturation occurred at 45, 103 and 410min when the flow rates were 4, 8 and 12 mL/min respectively. Hence, at lower flow rate, the BR46 ions had more time to contact with the adsorbent which resulted in higher removal of BR46 ions in the fixed bed column. Similar tendency has been found in other similar work [20].

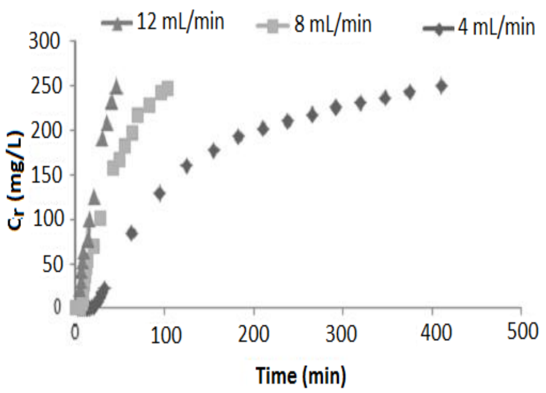


Fig. 3: Effect of various volumetric flow rates on the breakthrough curves of BR46 clay adsorption. (initial dye concentration= 260 mg/L, bed hight: 20 cm)

Tab. 3: Performances of fixed bed filter for BR 46 removal according to flow rate. (C_0= 260 mg/L, Z= 20 cm)

V (mL/min)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{exp} (mg/g)	V (mL)	Y (%)
4	410	426.4	142.02	47.34	1640	33.2
8	103	305.76	92.40	30.80	1176	30.21
12	45	245.7	65.61	21.87	945	26.7

**Effect of initial dye concentration*

Effect of initial dye concentration was carried out by varying the concentration of BR46 between160 to 260 mg/L. During these experiments, other parameters like bed height and flow rate were kept constant at 20 cm and 4 mL/min respectively. The sorption breakthrough curves obtained for initial dye concentrations of 160, 210 and 260 mg/L, are given in Fig.4. As expected, a decrease in the initial BR46 concentration gave an extended breakthrough curves indicating that a higher volume of the solution could be treated. The breakthrough time decreases with increase in inlet BR46 concentration as the binding sites became more quickly saturated and the dye loading rate increases. The net effect is an appreciable increase in adsorption capacity as presented in Table 4. As the effluent BR46 concentration increased from 160 to 260 mg/L, the exhaust time decreased from 775 to 552 min and the uptake of BR46 (q_{exp}) increase from 48.33 to 51.43 mg/g. Simultaneously, the removal percentage of BR46decreasesappreciably.At the highest BR46 concentration of 260 mg/L, the mixed adsorbent bed was exhausted in the shortest time (552 min) leading to the earliest breakthrough. The treated volume was the greatest at the lowest effluent concentration. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. This may also be attributed to the high influent BR46 concentration providing higher driving force for the transfer process to overcome the mass transfer resistance.

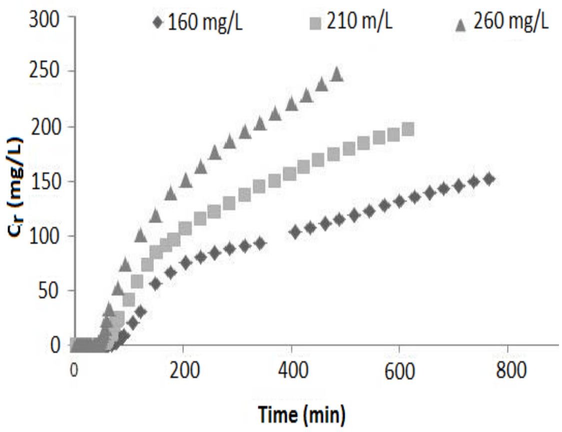


Fig.4 : Breakthrough curves for different initial concentrations of BR46 dye. (bed hight = 20 cm, flow rate = 4 mL/min)

Tab. 4: Performances of fixed bed filter for BR46 removal according to the initial dye concentration (F= 4mL/min, Z = 20 cm)

C_0 (mg/L)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{exp} (mg/g)	V (mL)	Y (%)
160	775	496	217.48	48.33	3100	43.8
210	632	531.3	223.50	49.69	2530	42.0
260	552	574.6	231.43	51.43	2210	40.2

2. Wastewater studies

**Column adsorption treatment of industrial waste pretreated by decantation*

The wastewater characteristics show in table 1 lead us to make a decantation and coagulation flocculation pre-treatment before adsorption treatment. The optimal decantation time corresponding to the maximum organic load, turbidity and absorbance reduction was found by taking Samples after every 15 minutes of settling to measure turbidity, COD and absorbance. All values of theses parameters remained constant after one hour of settling. The results are summarized in Figure 5. It shows that the settling of one hour has reduced the pollution organic load, turbidity and color by 48, 40 and 51% respectively.

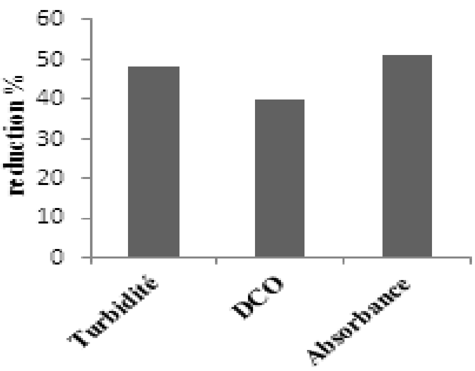


Fig.5: Variation of decantation reduction percentage as function of DCO, turbidity and absorbance.

** Adsorption treatment of decanted wastewater by the Clay of Safi*

Wastewater dynamics adsorption was made after the effluent pretreatment settling. The discoloration and organic load reduction studies are shown in Table 5. (T °: 25 ° ± 2 °, column height: 40 cm, clay mass: 6 g, sand mass: 200 g, λ_{max} = 527 nm)

Tab.5: Organic load and absorbance evolution of the treated effluent, pretreated with decantation (DCO_0 = 1600 mg O_2/L)

Treated Volume	DCO (mg O_2/L) (DCO_0 = 800 mg/L)	Absorbance
10	387,6	1,174
20	498,35	1,342
60	590,64	1,355
70	756,76	1,367
130	830,59	1,5
330	1052	1,639
440	1255,17	1,65
1000	1380	1,8
2000	1500	2,15

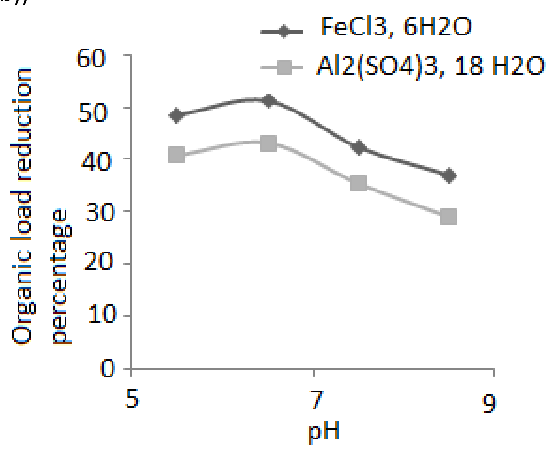
Dynamic adsorption for the effluent pretreated by decantation process reduced significantly its organic load and color. The industrial waste adsorption studies were made after conducting the effluent settling. The results show that 2L is the necessary volume for a total adsorbent saturation to reach the initial organic load. We note as well that the vast reduction of the organic load is obtained for the first volumes (10 mL, 20 mL and 60 mL: 387,6 mg/L ; 498,35 mg/L ; 590,64 mg/L); the quality of this treated effluent is in compliance with industrial discharges (near than 500 mg/L) [21]. We note also that the rapid saturation of the

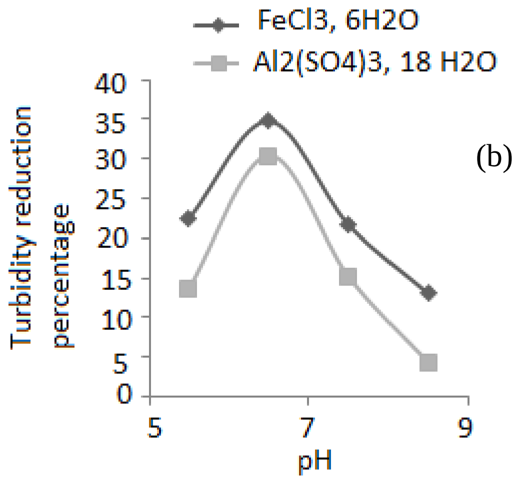
material can be explained by adsorption on the surface due to the fact that the clay is predominantly kaolinitic with a very small interlayer space [13].

**Column adsorption treatment of industrial waste pretreated by coagulation flocculation*

Dynamic adsorption for the effluent pretreated decantation process reduced significantly its nic load and color. Yet, despite this, it remains slightly colored. The use of other pretreatment method is desirable. The coagulation-flocculat method seems generally effective for the remo of suspended solids and colloidal particles. constant dose of coagulant (100 mg / L) and flocculant (0.4 mg / L), we studied the optimum pH from 5.5; 6,5; 7,5 and 8,5 pH values. The optimum coagulant dose from 100, 200 and 300 mg/L for the ferric chloride and aluminum sulphate, on the evolution of COD and turbidity is studied at the optimal pH found. Results found after many experiments show that pH = 6,5, coagulant dose of 200 mg/L, are optimal for a best removal of turbidity, coloration and organic load; Ferric chloride is more effective compared to aluminum sulfate treatment (Figure 6 (a, b); Figure 7 (a, b))

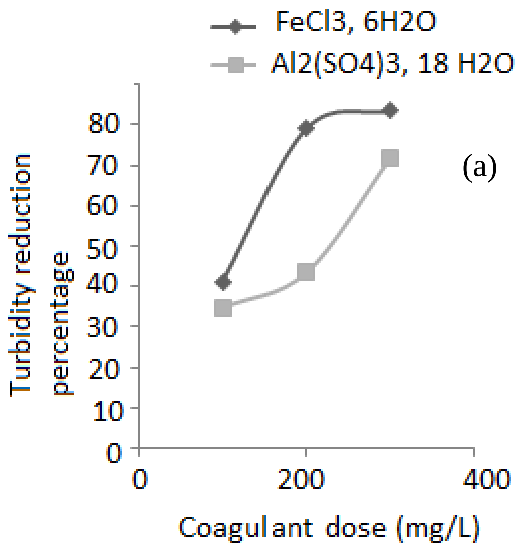
(a)





(b)

Fig. 6. a. b. Organic load, turbidity reduction evolution as a function of pH., (T °: 25 ° ± 2 °, speed coagulation: 170 tr / min, agitation time: 2 min, speed flocculation: 30 trs / min with agitation time: 30 min, the coagulant dose: 100 mg / L, the flocculant dose: 0.4 mg / L).



(a)

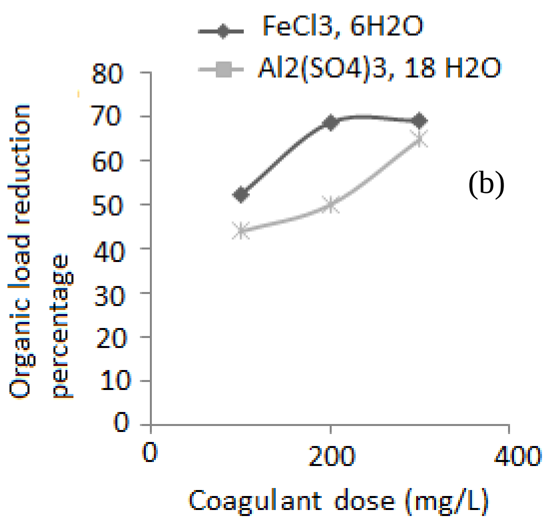


Fig. 7. b. a. organic load, turbidity reduction evolution as a function of coagulant dose. (T °: 25 ° ± 2 °, coagulation speed: 170 rev / min with agitation time: 2 min, flocculation speed: 30 trs / min with agitation time: 30 min, optimum pH: 6.5)

The adsorption tests of the pretreated effluent by ferric chloride (200 mg / L, pH = 6.5) in dynamic system has been made by operating at room temperature. The results are summarized in the Table 6:

Tab. 6: Organic load evolution of the treated effluent, pretreated with coagulation flocculation

Treated Volume	DCO (mgO_2/L) DCO_0 = 800 mg O_2/L)
10	201,2
20	311,54
50	420,34
80	490,5
120	560,6
220	630,4
420	655,5
1000	700
1720	727

Table 6 represents the adsorption results expressed by the organic load reduction of the effluent, pretreated by coagulation flocculation, in dynamic regime and the optimum operating conditions. The results shown are 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 that obtained for the adsorption of the clarified effluent.

Dynamic adsorption treatment of the pretreated effluent by coagulation-flocculation at the optimum pH and ferric chloride dose is an effective remediation technique because it allowed an organic load reduction from 2600 mgO_2/L (initial DCO of the wastewater) to 201 mgO_2 / L, a value lower than the standard industrial waste which is 500 mgO_2 / L [21], so, an organic load elimination of 92% from the initial effluent.

Proposed process

We propose in our work an industrial process of waters recycling according to decantation, coagulations pretreatments before the dynamic adsorption.

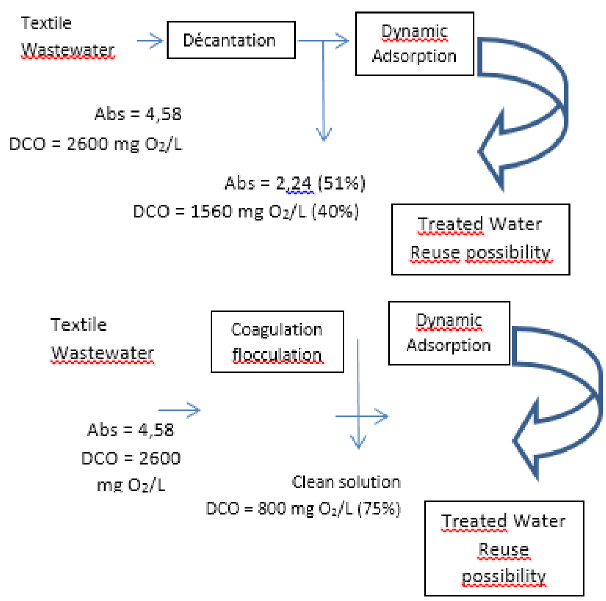


Fig. 8: An industrial process of waters recycling

Conclusion

Drought, water shortage are recognized as a slow-onset or creeping event, most countries regions and communities, currently manage these phenomena risk through reactive, crisis-driven approaches. In a pro-active approach, early warning systems are important as they are central to integrated risk assessment, communication and decision support system of the water shortage information systems. Fixed-bed column study was conducted to find out the effectiveness of natural adsorbent, Moroccan clay of Safi for BR46

adsorption. The investigations suggested that the adsorbent is efficient for BR46 removal from water. The adsorption of BR46 in a fixed-bed of mixed clay and sand was strongly dependent on the initial BR46 concentration, flow rate and the bed height.

Dynamic adsorption treatment reactor of the pretreated effluent by coagulation-flocculation at the optimum pH and ferric chloride dose is effective remediation technique because it allows the reduction of the organic load of 2600 mgO_2 / L mgO_2 to 201 / L, a value lower than the standard industrial waste which is 500 mgO_2 / L [21], which is an elimination of the organic COD assessed by 92% in relation to the initial effluent. This allows us to reuse this treated water in the spaces irrigation and thus to contribute to fight against the climate change impacts.

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