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POLLUTION

STUDY OF ADSORPTION OF METHYLENE BLUE ONTO COFFEE GROUND

Conflict of Interest

None declared.

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Abstract

In this work, we study the elimination of an organic dye to use intensively in textile industry (Methylene blue BM) by adsorption on the coffee ground. The adsorbent was characterized beforehand. The physical characterization (porosity and surface) was determined by electronic scan microscopy MEB revealed the presence of a mesopore area. The chemical characterization was carried out by the pH at the point of zero load (pHPZC), confirmed the character neutral of material. Several parameters are studied in order to optimize the ideal conditions for a good adsorption of the pollutant study; in particular, the kinetics of adsorption, mass of adsorbent, the effect of the pH of the solution examined the effect the stirring velocity, the effect of salts and the temperature. The results were adapted to the kinetic models and the isotherms of adsorption. The whole of the got results watch that the isotherms of adsorption of the systems adsorbing/adsorbed studied are described satisfactorily by the mathematical model of Freundlich. The pH of the solution as well as the presence of salts affects the output of discoloration. In addition, the thermodynamic study revealed that adsorption is spontaneous and endothermic.Therefore, one can conclude that this study showed that the coffee marc can be used like new natural adsorbent for the water treatment contaminated by the textile dyes.

Keywords: *adsorption, methylene blue, coffee ground*

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1 Introduction

Nowadays, the adsorbent material increasing demand for processes of environmental protection causes a complementary research in the manufacturing of the activated carbons starting from unclassical matters, in particular starting from the vegetation wastes. The raw materials being used as precursors are varied origins: lignocellulosic derivatives (wood, coconut hulls, almond hulls of hazelnuts and of walnut, apricot cores, apple pulp, cores of peaches thus that olive cores, date cores, the marc of the coffee, polymeric, as well as mineral coals. Quantities large of marc of the coffee are generated each year and constitute a significant source of agricultural waste. Such by-products corresponding to this loss are however likely to be of a considerable economic interest. It proves, thus, important to develop such waste. To work out adsorbent materials starting from agricultural waste makes it possible on the one hand to eliminate them and on the other hand to optimize the output and the manufacturing costs of the exploitations.

The use of the coffee ground in the water treatment polluted by the industrial wastes of textile such as the organic compounds (dyes) perhaps an interesting way of valorization of these materials. Many industries, and particularly those of the textile, reject into the rivers of the colored by-products. These organic compounds have a great influence on the level of the pH, and have a high toxicity; all these effects can involve serious ecological problems; these compounds are structurally very different the ones the others, from where a real difficulty to eliminate them by the classical methods of decontamination. Ozonization and oxidation by hypochlorite are the most effective methods of the colorless of water, but, they remain inadequate because of their high cost and the chlorinated residues which result from this. Many studies led to the clarification of processes of adsorption on adsorbent materials.

We proposed to make a study of adsorption of an organic dye used intensively in textile industry, the Methylene blue on a natural adsorbent which is the coffee ground which has a porous texture.

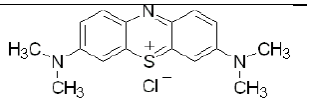
2 Experimental part

2.1 Equipment and methods

2.1.1 Studied dye

The studied dye is the methylene blue (BM) in cation matter. Its characteristics are presented in table 1

Table 1 – Caracteristic of the studied dye

dye	λ_{max}	molar mass g/mol	structure
« methylene bleu »	664 nm	373,9	

2.1.2 Adsorbent used

The coffee ground used is scented, soft and without bitterness. This waste abundantly is washed with distilled water then dried with drying oven (MELAG) with 110 °C during 24 hours It is then filtered (sieve AFNOR) to retain the fraction higher than 500 micron.

2.1.3 Adsorption tests of the methylene blue on coffee ground of the coffee in system "batch"

Establishment of the calibration curve:

After having prepared the various solutions of reagents, the spectra of adsorption into UV-Visible of the methylene blue was obtained by a sweeping spectral by using a UV/visible spectrophotometer of the type SHIMADZU U V-1800.entre [400 and 800] of a solution of dye with 10 mg/l to determine the wavelength of maximum adsorption; what enabled us to obtain the following wavelength: λ_{max} = 664 nm.

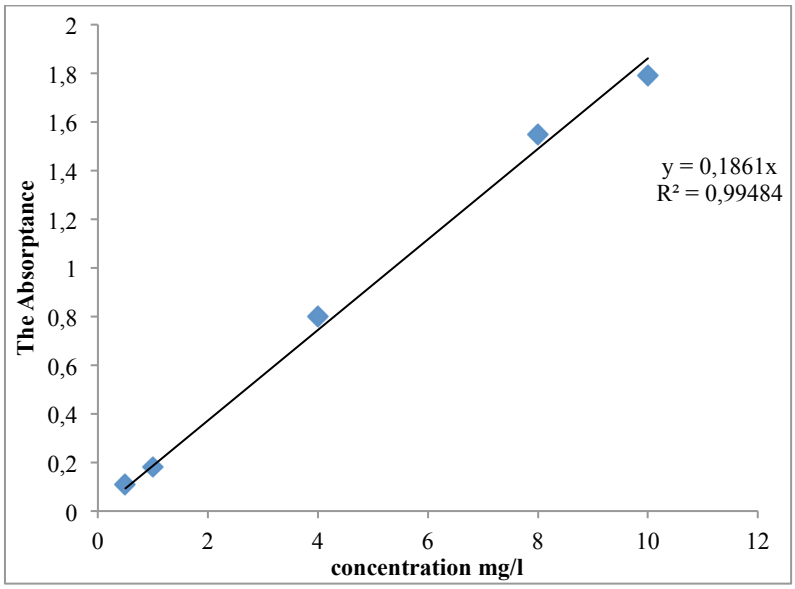


Fig. 1 – Calibration curve of the Methylene blue (BM)

2.2 Results and discussions

2.2.1 Physico-chemical properties of the coffee ground

The main features of the coffee ground used are presented on table 2:

Table 2 – Caracterisation of the marc of the coffee used

Water content (%)	0,8
Apparent density	0,51
Iodine index (mg/g)	462
Phenol index (mg/g)	38
pH with 20 °C	6,3

Properties acido-basic of the coffee ground

The measures of pH are taken with a pH-meter (JENWAY). A mass of 1 gr. of coffee ground is introduced into 150 ml distilled water, the mixture is homogenized using a regulated magnetic stirrer with 400 turn/times with room temperature. The graph obtained thus reveals stable kinetics in the neighbourhoods of pH= 6.3 our adsorbent is almost neutral.

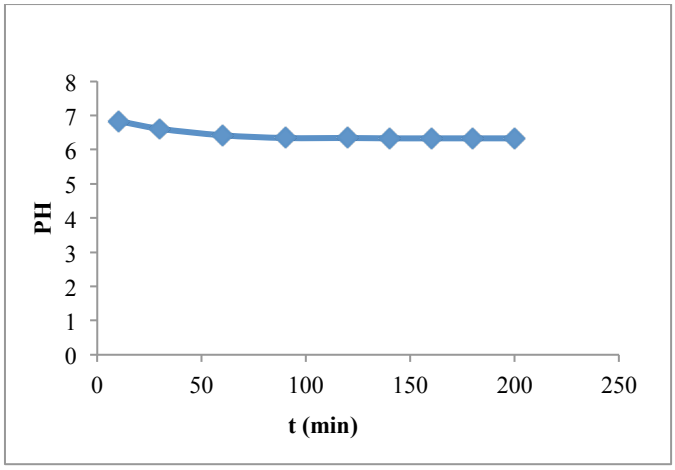


Fig. 2 – Evolution of the pH of coffee ground according to the time of contact

Technique of B.E.T

Specific area, the volume and the average diameter of the pores of our adsorbent (coffee ground) are determined by the technique of Brunauer, Emmett and Teller "BET" by using nitrogen to 7 K, the sample is subjected as a preliminary to a desorption with reduced pressure (< 10^{-4}Torr),at temperature of degasification of 150°C during 12 hours. The device used is of type "Quantachrome Instruments". The classification of the pores currently adopted by the International union of chemistry pure and applied (U.I.C.P.A) is founded on their sizes, three categories of pores were defined [2].

The results of measurement of the specific surface of coffee ground are gathered in table 3.

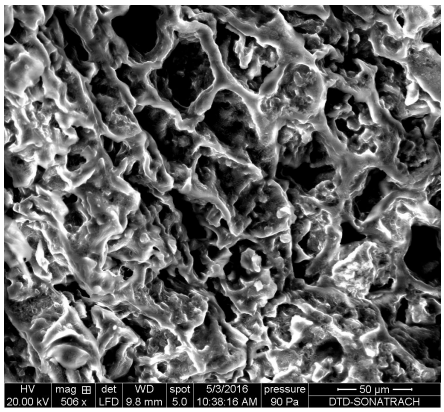
Table 3 – Determination of the specific surface of coffee ground by the method of (B.E.T)

Specific surface ($m^2.g^{-1}$)	**Average diameter (nm)**	**Average volume of the pores ($ml.g^{-1}$)**
0,58 **(0,5-2 $m^2.g^{-1}$)**	62 **(>50 nm)**	0,53 **(0, 2-0,8 $cm^3.g^{-1}$)**

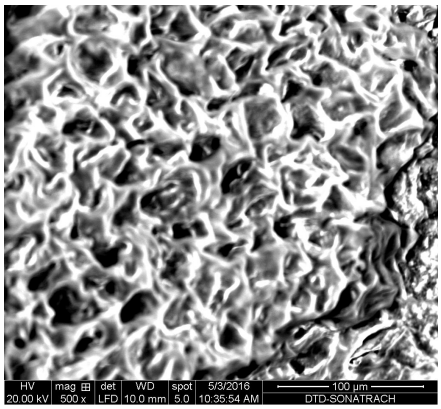
These results enable us to conclude that our adsorbent (coffee ground) comprises primarily macropores.

Porosity:

The determination of the porosity of our coffee ground was carried out via the electron microscope with sweeping (MEB) of brand (QUANTA 650) to see the form of the pores and their respective diameters. The photographs (1 and 2) show the various states of porosity as well as the presence of cavities. It of form and diameter is varied primarily made up of macroporous, which is confirmed further by the type of isotherm obtained (type C).



P1X500 (50 µm)



P2X500 (100 µm)

Fig. 5 – Photographs with the M.E.B of the coffee ground

Analysis by x-ray fluorescence

The analyses of x-ray fluorescence were carried out on a spectrometer of x-ray fluorescence of brand PAMALYTICAL-AXIOS. The sample reduced out of powder is subjected to a source of secondary X-radiation of fluorescence characteristic of its chemical composition.

The percentage of the elements obtained by x-ray fluorescence are consigned in table 4.

Table 4: Results of the analysis by x-ray fluorescence of the coffee ground

Elements	Pourcentage (%)	Elements	Pourcentage (%)
SiO_2	0,73	MnO	0,03
Al_2O_3	0,1	P_2O_5	0,1
Fe_2O_3	0,00	K_2O	0,01
CaO	1,11	Na_2O	0,00
TiO_2	0,01	MgO	0,01
BaO	2,59	SrO	0,003
		(CO_2)	95,3
		Total	99,993

Table 4 shows that the adsorbent is rich in biogenic salts. Among these elements quantified in the form of oxides we can quote: BaO, CAD, SiO_2, Al_2O_3, P_2O_5. The rest of the composition of the adsorbent represents the minor elements.

Elementary analysis

The MEB, assisted of an electronic microsounder (EDAX), as enabled us qualitatively to appreciate, the majority elementary chemical composition of activated carbon. It should be noted as this probe detects only the elements whose content is higher than approximately 0.5%. The elements present in the coffee ground and their percentages are presented in table 5 and figure 6.

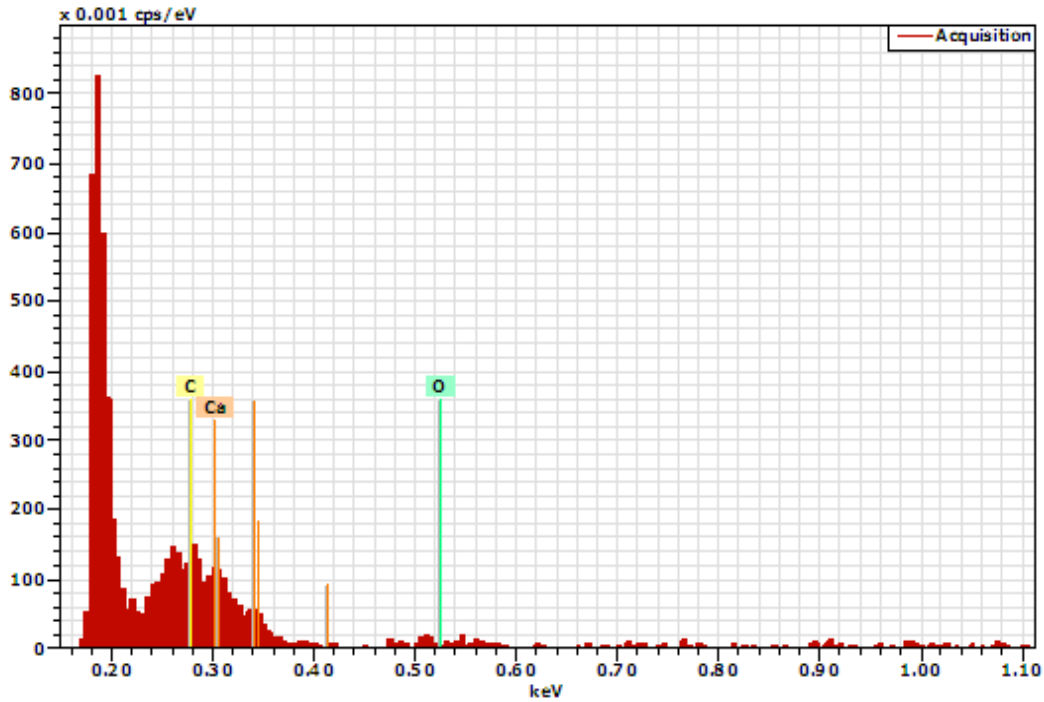


Fig. 6 – Majority peaks of the elements present in coffee ground

Table 5 – Elementary analysis of coffee ground

Element	Percentage (%)
C	76,41
Ca	6,78
O	16,82
Total	100

It should be noted that this probe detects only the elements whose content is higher than approximately 0.5% and which the hydrogen content could not be given by this technique.

As one could expect it, the coffee ground is made up mainly of carbon (peak majority 76,4%), but also of much of oxygen certainly coming from the many oxygenated functions of surface.

Structural analysis by spectroscopy IRTF

The structural analysis by infra-red spectroscopy transformed furrier were carried out using a spectrometer with transform of furrier of the type (Nicolet 560 FTIR) coupled to a digital calculator allowing the layout of the spectra between [4000 and 400 cm-1]. The spectrum of analysis by will infrared of coffee ground is represented on Figure 7. The most intense bands are deferred in Table 6. The broad absorption band ranging between 3400-3200 cm-1 corresponds to the vibrations of elongation of the hydrogen of the group hydroxyls O-H and adsorbed water. The spectra of IRTF show absorption bands ranging between 2930 and 2850cm-1 resulting mainly from the vibrations of elongation of C-H of the aliphatic molecules.

The spectra also shows a band to 1450 cm-1 due to the vibrations of elongation of connections C=C, the bands ranging between 1000 and 1350cm-1 is assigned vibrations of the connections CO [3].

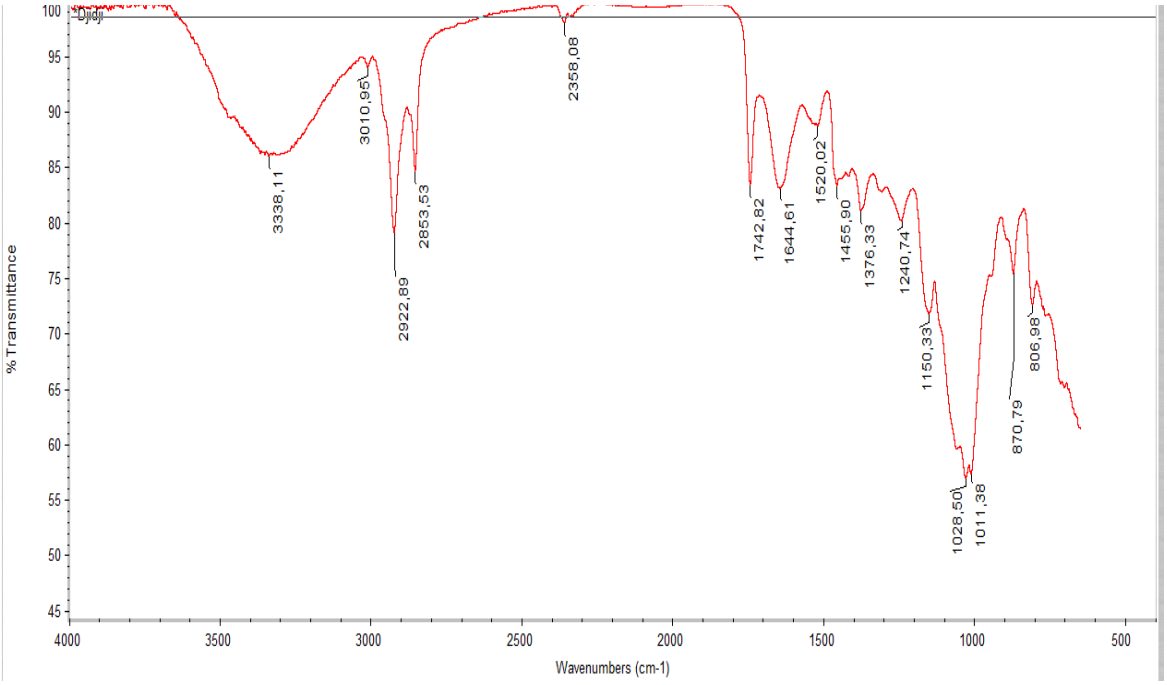


Fig. 7 – Spectrum IR of coffee ground

Table 6 – Result of the infra-red analysis of the coffee ground

Bands of vibration (cm^{-1})	Attribution
2922,89	C-H
1520,02	C-C/ C=O/ N-H
1455,9	C-H (CH_3)
1028,5	C-OH
806,9	=C-H
3338,11	O-H bound
1455,9	C=C aromatic
1376,33	OH deformation in the plan
1240,74	CO

2.2.2 Tests of adsorption

The kinetics of adsorption (effect of the time of contact)

0.25 gr. of the coffee ground are put in contact with 100 ml of the colored solution. The mixture is agitated during 4 hours with room temperature and with a stirring velocity equal to 400 turns per minute. The taking away is collected with predetermined time intervals (10 min). The quantity (qt) of adsorbed dye is given by the following relation:

$$Q_t = (C_0 - C_r).V/m$$

Q_t : quantity of dye adsorbed per gram of adsorbent (mg/gr).

C_0 : initial concentration of the dye (mg/l).

C_r : residual concentration at time t (mg/l).

V : volume of the solution (L).

m : mass of the adsorbent (gr.).

$$\% \text{ of colorless} = [(C_0 - C_r)/C_0].100$$

The kinetic study of the elimination of dye by adsorbent material (coffee ground) shows an increase in percentage of colorless at with the increase in the time of contact. Indeed, after 100 minutes of contact the methylene blue output of colorless of the solution du reaches almost the 100% for the concentration of 5mg/l by dye. The results are presented in figure 8.

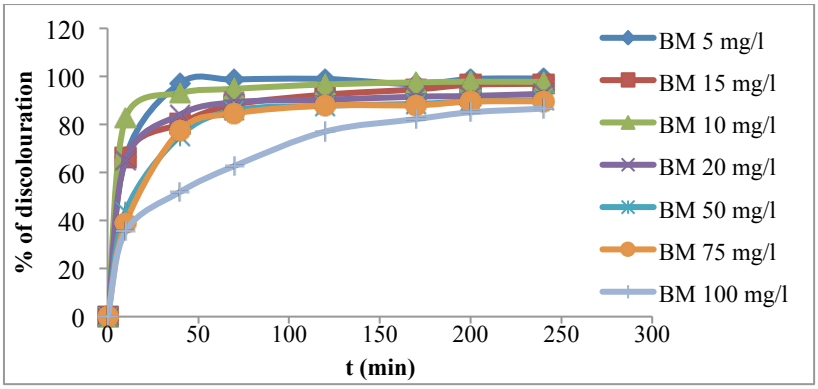


Fig. 8 –Effect of the time of contact on the percentage of colorless of the Methylene blue by the coffee ground (time of contact= 4:00; m =0,25 G; pH=6,4; Agitation = 400 tr/min; V =100 ml, T = 19 ±2°C)

Influence of the pH on discolouration

One adjusts the initial pH of the solutions colored by using solutions of NaOH (0,1N) and HCl (0,1N) for different the studied values of pH (2, 4, 6, 8 and 10) Figure 9, watch that with acid pH lower than 4, the adsorption of the MB on the coffee ground is with its minimum whereas has pH higher than 4 adsorption is maximum with a percentage of colorless of 90% and remains constant until the limit of the study with pH 10.

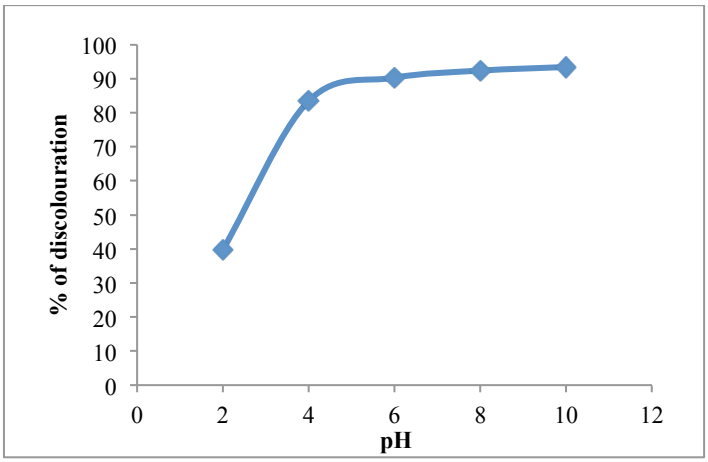


Fig. 9 – Effect of the pH on % of colorless of the Methylene blue by the coffee ground (time of contact= 4:00; m =0,25 G; C= 20mg/l; Agitation = 400 tr/min; V=100 ml, T =19 ±2°C).

For MB (pH free=6,4), the capacity of adsorption obtained of 40% with PH< 4 instead of 90% beyond this pH can be explained, by the fact why with pH< 4, the load of surface of coffee ground becomes positive in the presence of surplus of H+ ions in solution which return competing with the MB which is coloring cation. The adsorption of the BM is thus affected.

Influence of the mass of adsorbent on colorless

The masses of the coffee ground used are: 0.05 – 0.1 – 0.2 – 0.5 – 1 gr. As we can note it according to figure 10, the percentage of colorless of the methylene blue increasis with the increase in the mass of the adsorbent used to stabilize itself with great values of this last. Indeed, the increase in the amount of the adsorbent makes grow the number of the sites available for the fixing of the dyes (increase in the free area of the adsorbent), which supports consequently the phenomenon of colorless [4].

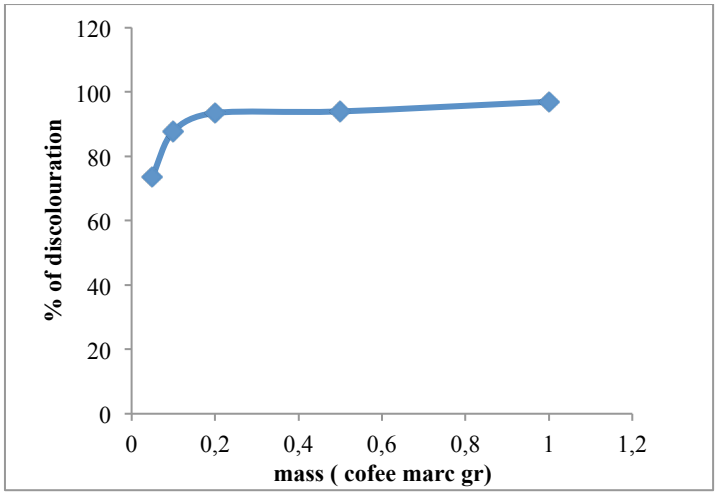


Fig. 10 – Effect of the mass of adsorbent (coffee grou) on % of colorless of the Methylene blue (time of contact= 100 min; pH = 6.4; C= 20mg/l; Agitation = 400 tr/min; V =100 ml, T 19= ±2°C)

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Influence stirring velocity

The experiment is carried out in system batch, we mix 0.25 gr. of adsorbent with solutions of dyes (100ml), while varying the stirring velocity from 300 to 800 tr/min (300, 500,600,700, and 800). The results represented on figures 11, watch that the increase stirring velocity to 600 turns/times, makes increase the rate of colorless (93.8%). Beyond 600 tr/min the percentage of colorless decreasis. We consider that it there is a stirring velocity optimal (600 turns/times), sufficient to support the contact between the particles of coffee ground and the molecules of dyes.

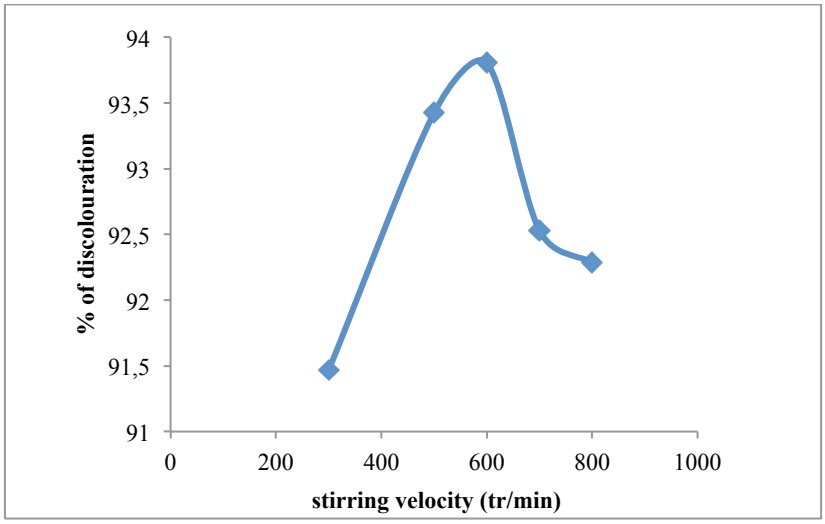

Fig. 11 – Effect of the temperature on % of discoloration of the Methylene blue (time of contact= 100MIN; pH = 6.4; C= 20mg/l; V =100 ml, mass of the coffee ground=0,25gr; T=20 ±2°C

Influence of temperature

The influence of the temperature is studied with solutions of concentrations equal to 20 mg/l, plunged in a bath MEMMERT to keep the constant studied temperature. We study following adsorption at the temperatures: 10, 20, 30, 40, 50, and 60°C. Figure 12 fact of appearing two distinct parts:of 10°C until the 40°C, one notes that the rate of colorless remains almost constant by 40°C with 60°C, the percentage of colorless decreases in a remarkable way what leaves suppose that the fixing of the methylene blue on the coffee ground is carried out endothermicly.

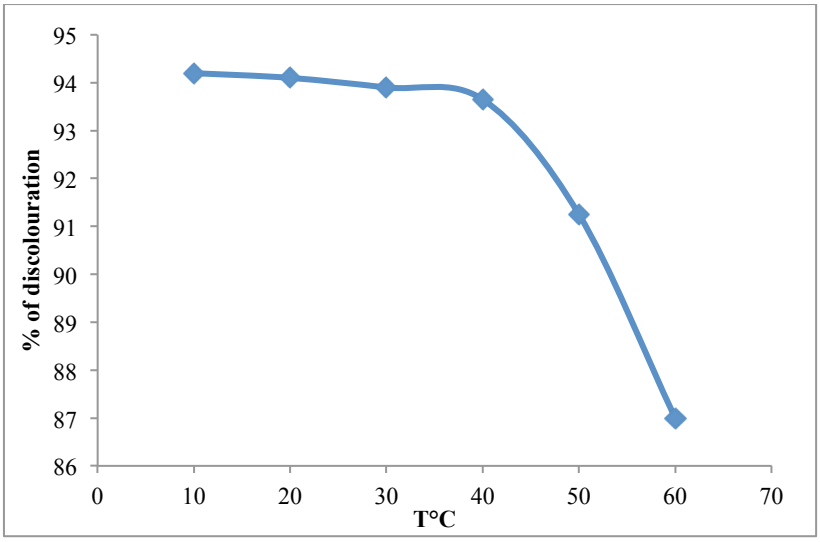

Fig. 12 – Effect of the temperature on % of colorless of the Methylene blue (time of contact= 100 min; pH= 6.4; C= 20mg/l; V =100 ml, mass of coffee ground=0,25gr; speed of agitation= 400 tr/min)

We can confirm this result by the notion of the enthalpy (ΔH).The value of the enthalpy of adsorption can be calculated according to the following expression:

$$\text{Ln } Q_{ads}(T1)=\ln C- \Delta H/RT_1 \quad , \quad \text{Ln } Q_{ads}(T2)=\ln C- \Delta H/RT_2$$

$$\Delta H=R\ln [Q_{ads}(T2) / Q_{ads}(T1)]/(1/T_1-1/T_2)$$

Temperature (°C)	10-40	40-60
Enthalpy (J/mol)	+107,046>0	-62,227<0
Nature of adsorption	endothermic	exothermic

With the increase in the temperature, results the rise in the mobility of dye in solution and the reduction of the attraction forces where of diffusion of dye on the surface of marc of the coffee. The capacities of adsorption of the methylene blue will be slowed down consequently.

Influence of salts

It is known that the waste water of textile contains, with variable concentrations, ions organic and inorganic, mainly of the cations and anions such as nitrates, chlorides, sulfates, carbonates and the carbonate hydrogen. Thus with an aim of better understanding the influence of these ions on the process of retention of the methylene blue by marc of the coffee, of the experiments were carried out while adding to each solution with 20 mg/L of dye and time t=0, a salt such as NaCl with (0,1M) and (1M). Pilot solutions were also agitated in presence and absence of the support (marc of the coffee).

Figure 13 shows that, the NaCl addition, clearly increasis the rate of colorless of the cation dye (methylene blue). And this adsorption will be still better when the content salt increases (NaCl 1M). In absence of the adsorbent (coffee marc), salt contributes slightly to the process of colorless. This phenomenon can be explained by the fact why salts support the bringing together-association of the particles by the formation of new sites of surface where the molecules and aggregate of dye would be trapped. We can also call on the theory of Gouy- Chapman on the dual-layer of diffusion which provides that the thickness of this layer would be low with the ionic force what facilitates the bringing together of the molecules of adsorbed and the particles of adsorbent [15].

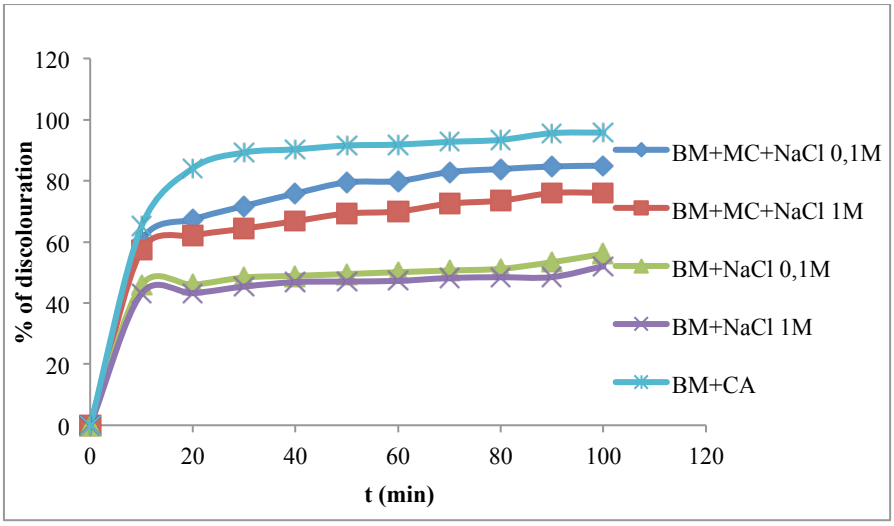

Fig. 13 – Influence of salts on the percentage of colorless of the BM by the coffee ground. (pH=6,4; m = 0.25 G; V = 100 ml; Time of contact = 100min; Agitation = 400 tr/min; C=20mg/l; T = 20 ±2°C)

Isotherm of adsorption

The isotherms of adsorption were studied by agitating a mass of the adsorbent 0.25 G in colored solutions of various concentrations going from 5 to 100 mg/L. The adsorbent and adsorbed it were put in contact during 100 minutes under an agitation of 400 tr/min. The results of the isotherms of adsorption of the dye on the coffee marc are presented on figure 14.

The isotherms show that there is a correlation between the quantity adsorbed of dye to balance (Qe) and the concentration to balance.

According to the classification of the isotherms of adsorption of GILLES [6], the isotherms are of type C sub-group 1; they are in the form of straight lines what means that there is competition between solvent and the aqueous solution to occupy the sites, with always the same division (shares constant). They relate to flexible molecules being able to penetrate far in the pores to move solvents there.

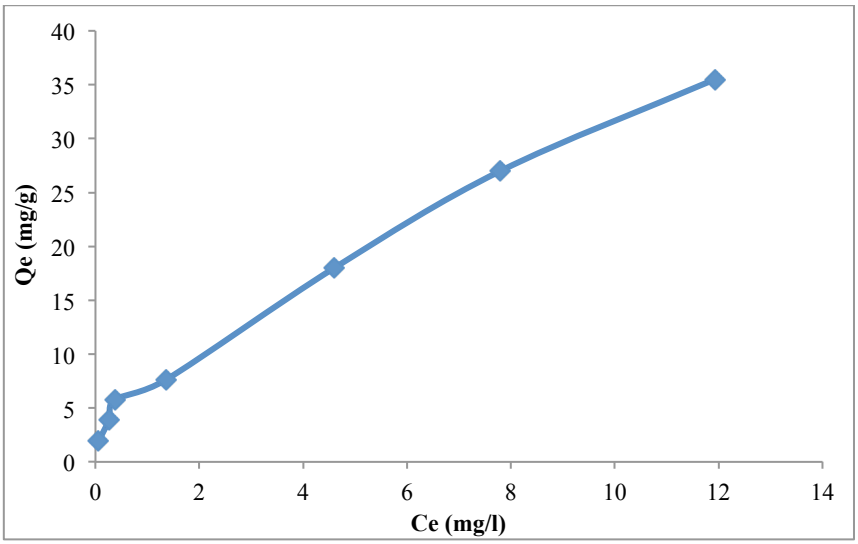

Fig. 14 – Isotherms of adsorption of methylene blue by the coffee ground (. (pH=6,4; m = 0.25 G; V = 100 ml; Time of contact = 100min; Agitation = 400 tr/min; T = 20 ±2°C).

Models of the isotherms of adsorption

Figures 15 and 16 represent the linear transforms of Langmuir and Freundlich respectively; according to these lines we deduced the values from the maximum capacities and the values of the constants of adsorption determined under the above mentioned experimental conditions.

1) Model of Langmuir:

$$\frac{x}{m} = \mathrm{Qe} = \frac{\mathrm{a.b.Ce}}{1+\mathrm{b.Ce}}$$

$$\frac{m}{x} = \frac{1}{Qe} = \frac{1+\mathrm{b.Ce}}{\mathrm{a.b.Ce}} = \frac{1}{\mathrm{a.b.Ce}} + \frac{1}{\mathrm{a}}$$

$$a = qm \ \ ultimate\ capacity$$

$$\frac{1}{b} = \mathrm{Kd\ constant\ of\ dissociation\ of\ the\ adsorbent}$$

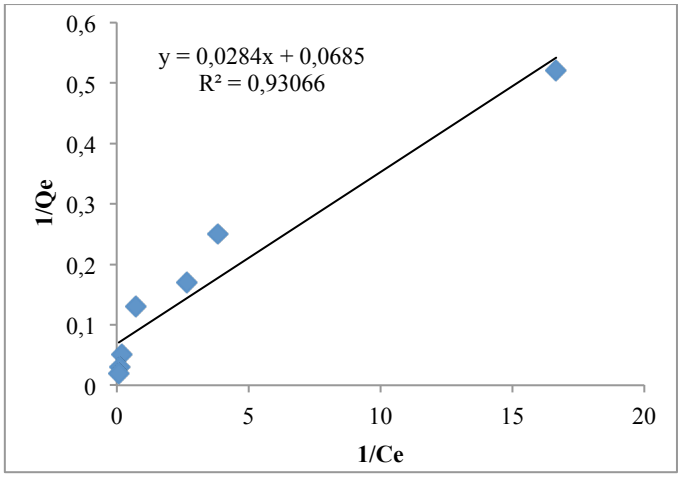

Fig. 15 – Linear transforms of the isotherms of adsorption of Langmuir.

2) Model of Freundlich

$$\frac{x}{m} = Qe = k.\mathrm{Ce}^{1/n}$$

The linearization gives:

Log x/m=Log Qe=log k+1/n log Ce

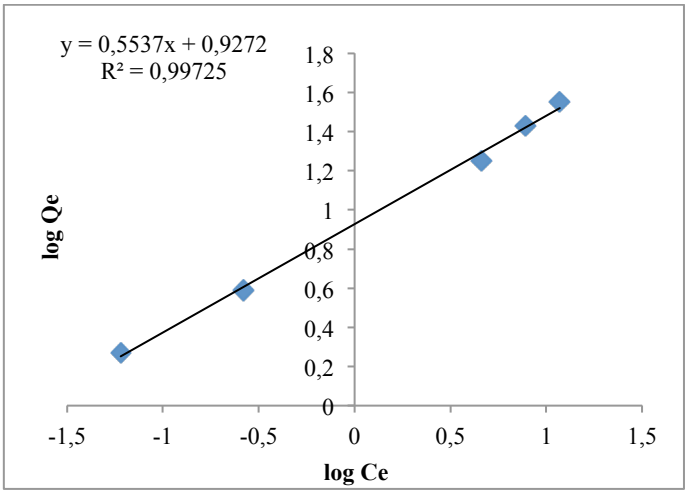

Fig. 16 – Linear transforms of the isotherms of adsorption of Freundlich

The linear representations of the experimental values this process of adsorption enabled us to determine the parameters of balance and the values of the constants of Langmuir and Freundlich calculated by linear regression (Table 7).

Table 7 – Constant of the isotherms of adsorption of Langmuir and Freundlich of the methylene blue on the coffee ground

æ	n	1,8
	1/n	**0,92**
	K_F	**2,52**
	R^2	**0,997**
Langmuir	b	0,67
	q_m	**23,09**
	R^2	0,93
	K_d	1,49

The values of the coefficients of regression indicate that the process of adsorption, of Methylene blue by the coffee ground, is described in a favorable way by the isotherm of Freundlich (with excellent linear coefficients of regression R2 which is very close to the unit).

The parameter of intensity, 1/n, indicates the deviation of the isotherm of adsorption of the linearity.

When 1/n=0, adsorption is linear, i.e. that the sites are homogeneous and that there is no interaction enters the adsorbed species.

When 1/n<1, adsorption is favorable, the capacity of adsorption increases and again sites of adsorption appear.

When 1/n>1, adsorption is not favorable, the connections of adsorption become weak and the capacity of adsorption decreases.

3 Conclusion

The kinetic, thermodynamic studies and the isotherms of

adsorption were carried out to clear up the mode of fixing of the methylene blue on material tested. The experiments highlighted that the coffee marc is very effective for the colorless of water. The percentage of colorless is influenced by the variation of the pH, it can reach 98% for neutral values of pH, on the other hand it is influenced very little by the mass of adsorbent as well as the fixing of the methylene blue on the coffee marc is carried out endothermicly. The addition of salts (NaCl), clearly increases the rate of colorless of the cation dye (methylene blue). And this adsorption will be still better when the content salt increases (NaCl 1M).

The studies continue to seek other less expensive supports which will be combined with the coffee marc in order to in the case of improve the outputs of colorless for a possible use the rejections of textiles and other effluents charged in organic pollutants.

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