

# **The use of allochthonous tropical peat swamps of Antananarivo for dyes elimination in effluents**

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## **ABSTRACT**

Textile industries play an important role in the economy of developing countries. However, these industries are among the major consumers of water and chemical inputs. They reject considerable quantities of wastewater, the quality of which sometimes threatens the environment due to the inefficiency of the treatment methods used. This is combined with the inaccessibility to the advanced purification technologies because of their high cost. Many low-cost materials have been studied by scientists to treat effluents. The ATP (allochthonous tropical peat) of Antananarivo, Madagascar, has aroused interest in the treatment of wastewater, especially for colored textile effluents. The physico-chemical characteristics of the ATP are determined, then the BLM dye (methylene blue) is used as a model dye for adsorption. After that, treatment tests in the form of filtration are carried out with textile effluent. This study showed that ATP peat is of the mesotrophic type, with an average content of 87% organic matter. Its proton exchange capacity is 66 mmol per 100 g of raw peat. It removes cationic dyes more favorably than anionic ones at pH greater than 4.2, the zero-charge point of peat. The adsorption of BLM, a cationic dye, on ATP is physisorption and endothermic. Dye adsorption by peat ATP follows the Langmuir model. The analysis of the IR spectra showed that the carboxylic function and the phenol group of the peat comes into play on the fixing of the dye. The treatment of effluent taken from the textile industry revealed that ATP improves the pH and the color of the effluent; however, it increases the COD due to the presence of certain organic acids.

*Keywords: tropical-peat, adsorption, textile-dyes, wastewater, pollution, Antananarivo*

## **1. INTRODUCTION**

In the 1980s, peat was increasingly used as a filtering and purifying material in industrial [1] and urban sanitation [2]. Peats have a capacity to adsorb transition metals and polar organic compounds such as dyes from textile effluents. They can be considered as interesting adsorbents, in the region where they are abundant. They do not require any activation [2]. After use, peat can be reused in boilers for steam production [3]. Being considered as "tropical peat", different from conventional peat by its geomorphological and botanical source, the allochthonous peat of the plain of Antananarivo is studied for the first time, for its water purification capacities. In view of the relative abundance of this resource on the one hand, and the preponderant place of textiles in the economy of a developing country on the other, then the study is undertaken to know the capacity of allochthonous tropical peat of

Antananarivo, abbreviated as ATP to treat textile effluent. Indeed, these industries reject relatively huge quantities of water, sometimes coloured and containing other chemical residues, which may harm the environment [4, 5]. Therefore, this study is carried out in order to valorize peat for the treatment of textile effluents. For this purpose, peat is characterized and its exchange and purification capacities are explored, more specifically for the elimination of dyes in effluents. Finally, samples of textile effluents are treated with ATP peat on a laboratory scale.

## 2. MATERIAL AND METHODS

### 2.1 Characterizations of peat

Three localities on the plain of Antananarivo, District of Antananarivo-Atsimondrano, Madagascar were the subject of peat sampling: Fenoarivo, Ambavahaditokana and Anosizato. Firstly, the bulk density of the peat is determined by the method described in Alline A study [6]. The organic matter content of the peat is estimated by gravimetry after calcination at 550°C. Then, the percentage of organic carbons in the peat is obtained by the method of oxidation with potassium dichromate followed by titration with ferrous sulphate. And, the total nitrogen content is evaluated by the Kjeldahl method. The mineral elements in the dried raw peat are analyzed by X-ray fluorescence spectrophotometry. The equilibrium pH of the peat with water is determined by mixing 2 g of 200 µm powder of fresh peat in 50 ml of water distilled for about 20 h, using a stirrer. The pH of the solution is then measured with a pH meter.

Secondly, the zero-charge point of an adsorbent gives an indication of the pH range in which the peat is active with one chemical entity rather than another. In this method, batches of 25 ml of 0.1 M KNO<sub>3</sub> solution are prepared at different pH levels (pH 2 to 12) with dilute sodium hydroxide and acid. A quantity of 0.05 g of peat is added to each container respectively, then they are shaken for 24h. The difference between the initial pH and the pH after 24 h is the ΔpH [7]. The initial pH corresponding to zero ΔpH is the PCZ. Finally, the proton exchange capacity (PEC) is measured using the method developed by Ducafour in 1976 [6].

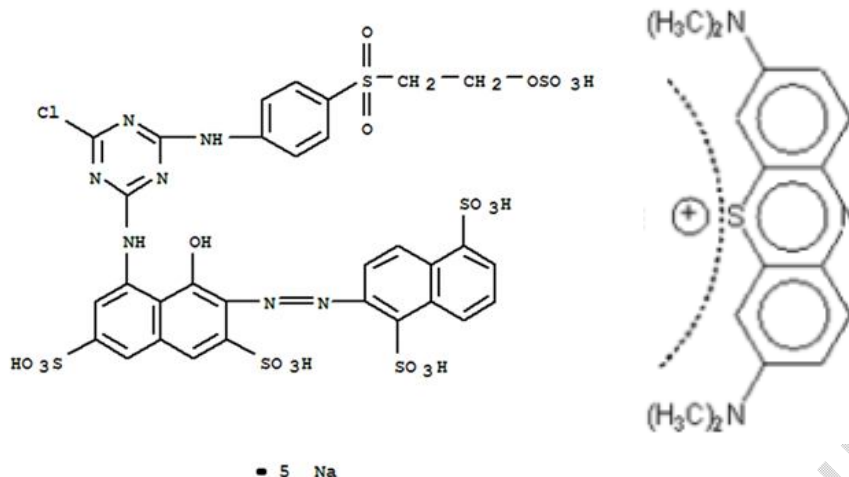
### 2.2 Preliminary dye removal tests on peat

#### 2.2.1 Dyes

For this experiment, three dyes have used: "Methylene Blue", "Black 2RSE Allilon Polyester dye" and "RED CL 5B", which will be noted respectively as: BLM, BKA and RCL. Both RCL and BKA are anionic dyes but BLM is a cationic dye. These dyes have been supplied by local textile industries. The three dyes RCL, BKA and BLM are prepared respectively at 25 mg.l<sup>-1</sup> with distilled water. The dye solutions are not adjusted for pH, as the initial pH of the solutions are between 6 and 7.60. The 250 ml of dye solutions are poured gently onto the top of the peat filter. Figure 1 shows the chemical structures of the dyes.

(a)

(b)



**Fig. 1. Chemical structures of dyes RCL (a) [8] and BLM (b) [9]**

### **2.2.2 Filtration on ATP peat**

A quantity of 250 g of peat is loaded, without piling ( $0.6\text{g}\cdot\text{cm}^{-3}$ ) up to a height of 7.2 cm and 8.5 cm in diameter. Before use, the peat is washed with 500 ml of distilled water. At the lower end of the filter, the filtrate is collected at an average flow rate of  $75\text{ ml}\cdot\text{mn}^{-1}$ . After a 30 mn rest period, for the sedimentation of suspended matter, the filtrates are analyzed by UV-VIS BECKMAN DU-64 spectrophotometry for the determination of residual dyes. The initial wash solution is used as an analytical blank for this determination.

### **2.3 Effect of pH variation on BLM elimination**

A volume of 100ml of dye prepared with distilled water. The pH is adjusted to different levels with 0.1 N NaOH solution and 0.1 N HCl. Then, a quantity of 0.25 g of ground ATP is added to the dye solution. The solution is stirred at 150 rpm, for 15mn. After 5 mn, time of decantation, 10ml of supernatant is centrifuged at 10,000 rpm for 10mn. Then the limpid supernatant is analyzed on UV-VIS spectrophotometry at 665nm, in order to determine the residual concentration of BLM.

### **2.4 Peat-BLM dye adsorption reaction order**

The adsorption kinetics of the BLM dye on peat is studied by varying the stirring time from 1mn to 50 mn, of a 100 ml solution having an initial concentration of  $25\text{ mg}\cdot\text{l}^{-1}$ . The stirring times are set from 1, 15, 30, and 50 mn, for a quantity of 0.25 g of ATP. The pH of the reaction medium is kept unchanged.

### **2.5 Thermodynamic parameters of adsorption**

The thermodynamic parameters of adsorption are determined from the results of adsorption tests at different temperatures with 100 ml of  $25\text{ mg}\cdot\text{l}^{-1}$  BLM solution. The temperature of the peat-dye system is varied from 12, 20, 30, 40, 50°C. These temperatures are chosen as textile effluents and can reach high temperatures immediately after discharge or very cold when the water stays at a tropical winter temperature. The Residual BLM dye concentrations at equilibrium are determined by UV spectrophotometry.

## 2.6 Isothermal models of ATP-BLM adsorption

By varying the quantities of adsorbent put into the dye solution, after the equilibria, the adsorption isotherm study is performed according to five very common models: Langmuir, Freundlich, Temkin, Dubinin & Radushkevich and Sips. The respective adsorption constants for each model are determined by linearizing the model equations. The comparison of the regression coefficients: sum of square error (SSE) and the correlation coefficient  $r^2$ , allow the identification the best model that would describe the adsorption of BLM on ATP. The tests are carried out without prior adjustment of the pH, at a stirring time of 5mn and at a temperature of 25°C.

## 2.8 Measurement on IR spectrophotometry

The peats recovered after adsorption are dried, mixed with 1% KBr, pressed in pellets and analysed by Fourier Transformer IR spectrophotometry (FTIR) instrument.

## 2.9 Treatment of textile effluents with ATP

A sample of textile effluent from Accord Knits industry is taken for filtration adsorption testing. The pH, conductivity, colour and chemical oxygen demand (COD) are measured before and after the treatment to verify the efficiency of ATP. Peat is used in the same manner as told in previous paragraph (2.2.2).

## 3. RESULTS AND DISCUSSION

### 3.1 Physico-chemical characteristics of ATP

The ATP peat is compact and very dark brown-black in colour. On these first boreholes in the vicinity of Antananarivo, the author observed lenses of allochthonous peat intercalated in clay [10]. Antananarivo peat has a density of 0.89. This relatively high value can be translated, on the one hand, as an advanced decomposition of the organic matter of the peat and on the other hand, by the presence of a clay mixture. Indeed, it is reported that a low density of  $0.05 \text{ g.cm}^{-3}$  is associated with fibrous peat with undecomposed material, whereas well-decomposed materials can have a density of  $0.5 \text{ g.cm}^{-3}$  [11]. The overall composition of ATP peat is given in Table 1 below.

**Table 1. Main constituents of ATP peat**

Compounds	Content %
Organics Carbon	57.53
Organics Total Nitrogen	1.43
Ash	12.88

In its raw state, ATP has a moisture content of 68%. In relation to its dry mass, it contains 87% organic matter, which makes it similar to the brown commercial peat of Heurteauville [6]. The organic carbon content of peat may vary from 12 to 60% depending on the analytical method, the type of organic matter and the level of decomposition [11]. For the present

study, the organic carbon of peat is 18%. This value does not deviate from 20 - 38% organic carbon, in Sarawak, Israel [12].

The organic nitrogen content of ATP peat is 1.43%. When studying peats based on papyrus 0.5% nitrogen was found [13]. Peats developed with reed, sedge and trees generally have 2 or 4 times the nitrogen content than those from sphagnum and eriophorum [11].

The chemical element content of ATP peat is presented in Table 2. Compared to the reference values [11], the ATP elemental concentrations show it characteristic as mesotrophic. This means that it has a character between oligotrophic and eutrophic peat. Indeed, sulfur and potassium contents are respectively three times and ten times lower than in the previous study on peat. Only iron and calcium contents are close to the results of peat analyses found on the studied sphagnum peat [12].

**Table 2. Element contents in mg.kg<sup>-1</sup> in dry peat compared to references**

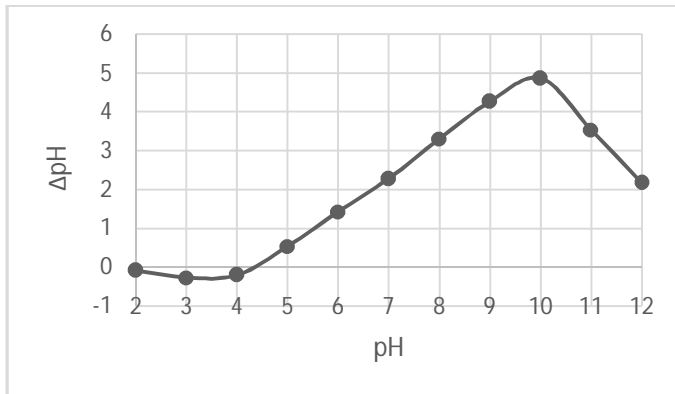
Element	ATP	*Oligotrophic peat	*Eutrophic peat
Calcium (Ca)	6980	3 000	20 000
Copper (Cu)	17	5	10
Iron (Fe)	17 754	1 000	5 000
Manganese (Mn)	153	30	200
Molybdenum (Mo)	15	1	10
Nickel (Ni)	0	5	10
Lead (Pb)	40	10	50
Kalium (K)	932	400	1000
Sulfur (S)	3611	1000	5000
Zinc (Zn)	72	50	500

\*[11]

### 3.3 Equilibrium pH of peat and zero charge point

The equilibrium pH for ATP is 4.35. This pH is linked to the quantity of organic acids that are essential constituents of the peat but also to the strength of its acid functions. Oligotrophic brown peat has a significantly lower pH than eutrophic blond peat, respectively 4.0 versus 5.75 [6]. This result confirms the mesotrophic character of ATP, described earlier.

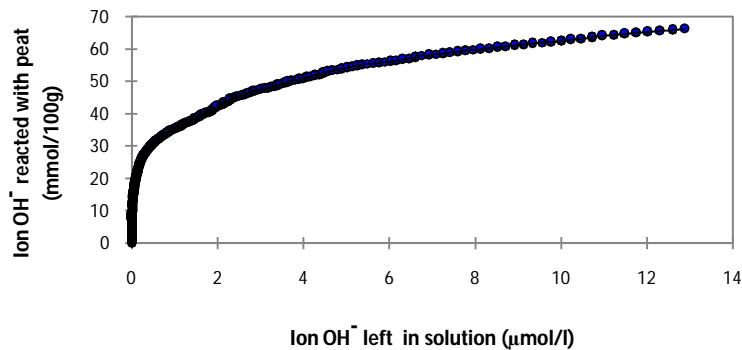
According to the curve of  $\Delta\text{pH}$  as a function of the initial pH (Figure 2), the PCZ would be in the vicinity of pH 4.2. The  $\text{pH}_{\text{PZC}}$  corresponds to the pH where the  $\Delta\text{pH}$  curve crosses the abscissa axis. If  $\text{pH} > \text{pH}_{\text{PZC}}$  the adsorption of cations is favourable and if  $\text{pH} < \text{pH}_{\text{PZC}}$  the adsorption of anions is favoured [14].



**Fig. 2. Curve for the zero charge point determination of ATP**

### 3.4. Proton exchange capacity

The PEC reflects the proton exchange capacities of the peat. Because of the simplicity of its implementation and for the reference that it can be used for ion exchange capacities in general. This measurement does not depend on the pH and the total concentrations of ions chosen for its determination. It is therefore an intrinsic value. The PEC is determined as the maximum amount of ion  $\text{OH}^-$  expressed in mmol/100g of peat, which can be deduced from the curve below (Figure 3). The PEC found for ATP peat is 66mmol of  $\text{OH}^-$  per 100 g of raw peat, i.e., 204.9 mmol/100g of dry peat.



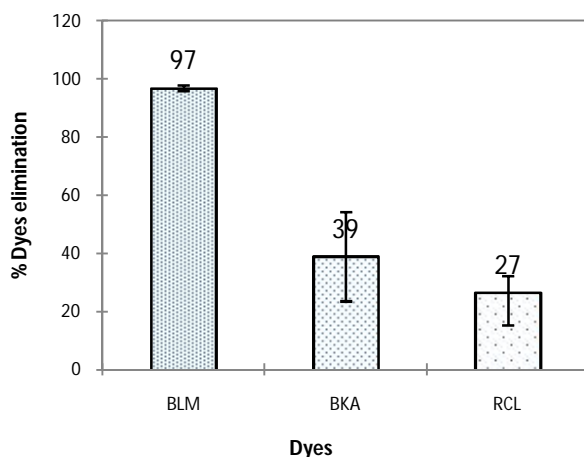
**Fig. 3. Variation of the amount of  $\text{OH}^-$  ion reacted with peat as a function of remaining  $\text{OH}^-$ , for the determination of PEC**

In previous studies, brown peats have a higher PEC than white peat, with values of 164 and 105 mmol/100g of dry matter respectively. This difference reflects the higher advanced decomposition of brown peat and its enrichment in humic and fluvic acids [11]. This implies that the allochthonous peat of Antananarivo would contain more compounds with acid characters compared to the blond peats and brown peats already studied.

### 3.5 Removal of dyes by peat

#### 3.5.1 Preliminary test for the removal of BKA, RCL and BLM dyes by ATP

The result of the preliminary dye removal tests by filtration on ATP (Figure 4) shows a very high affinity of BLM with peat. Its average removal percentage reaches 97%. This is due to the positive charge it contains. Latvian sphagnum peat moss (SPM) removes cationic organic contaminants rapidly, including malachite green dye [15]. SPM is less effective in removing acid and reactive dyes. Thus, dyes such as "acidic black 1", "acidic red 27", "reactive black 5" and "reactive orange 16" are adsorbed in low amounts of 29.1%, 2.3%, 1.3%, and 15.2%, respectively [16].

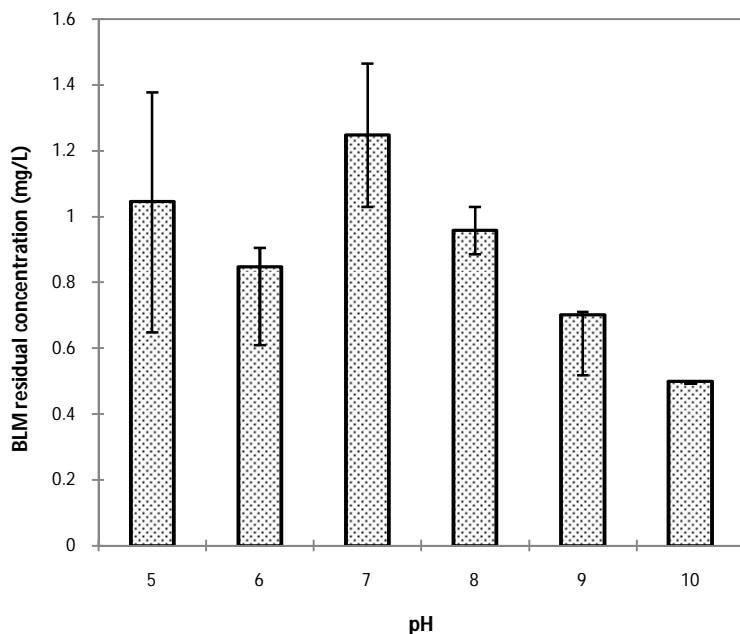


**Fig. 4. Percentage of BLM, BKA and RCL dyes removed by filtration on ATP**

The BKA dye is eliminated at 40%, probably because of its low solubility; thus, the insoluble microparticles are blocked in the interstices of the peat, despite their negative charge density. RCL is a very soluble dye and is only slightly retained with an average rate of 27%.

### **3.5.2 Removal of BLM as a function of pH**

In the following, the study focuses on the adsorption of the dye BLM on ATP. According to the dye adsorption rates on ATP peat at different pH levels (Figure 5), BLM removal seems better at basic media. The amounts of adsorbed BLM are  $95.8\% \pm 1.30$ ,  $95\% \pm 1.23$  and  $98\% \pm 0.48$  respectively at pH 5, 7 and 10. These results correlate well with the results obtained on the zero charge point of ATP peat. For the rest of the study, the pH of the solution is not adjusted.

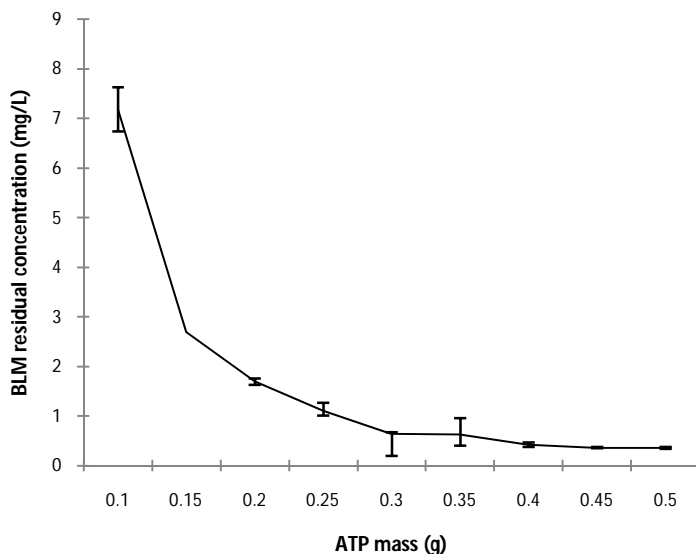


**Fig. 5. Residual concentration of BLM after adsorption at different pH level**

The removal of Malachite green, a cationic dye by SPM had shown a maximum (100%) adsorption from pH 3 to pH 7, and then decreases to 85% at pH 9 [17]. These results are in contradiction with what was found in this study. This would be due to the difference in experimental methods. Methylene blue with  $pK_a > 14$  [18] is positively charged on the entire studied pH range and it will be attracted well onto sorbent's negatively charged sites because of electrostatic attraction [9]. Deprotonated product of  $-COOH$  group, through electrostatic interaction was the most reasonable mechanism for the sorption of positively charged methylene blue from aqueous solution [9]. The electrostatic interactions play a dominant role in the adsorption mechanism when the free electrons of the dye molecule present in aromatic rings interact with chemical species present on the surface of the peat [19].

### **3.5.3 Effect of peat mass variation and isothermal adsorption equations**

The residual concentrations of BLM dye at each variation in peat mass of peat are displayed in Figure 6. These data allow the study of adsorption according to different isothermal equation models.



**Fig. 6. Variation of the average equilibrium concentrations ( $C_e$ ) of BLM as a function of the amount of ATP in grams in adsorption tests**

Comparison of the values of the regression constants  $r^2$  and SSE between the models (Table 3) showed that the Langmuir isotherm best describes the adsorption of BLM on ATP. Indeed, among the other models, the correlation coefficient  $r^2 = 0.98$  corresponding to the Langmuir equation is the highest and the SSE = 0.004 is the lowest. Thus, the dyes adsorb on the peats forming an energetically homogeneous monolayer surface [20]. According to the Langmuir model, the maximum concentration of BLM that can be adsorbed on peat is  $19.97 \text{ mg.g}^{-1}$ . The maximum adsorption of Methylene Blue on clay is  $40 \text{ mg.g}^{-1}$  at the same initial concentration of  $25 \text{ mg.l}^{-1}$  at  $40^\circ\text{C}$  [21].

**Table 3. Linear equations, regression coefficients and constants relating to the five adsorption models**

Isotherm	Linearized equation		Correlation coefficient ( $r^2$ )	Sum of square error (SSE)
Langmuir	$C_e/Q_e = 0.048 + 0.05 \cdot C_e$	(1)	0.987	0.004
Freundlich	$\log Q_e = 0.95 + 0.35 \cdot \log C_e$	(2)	0.800	0.15
Dubinin & Radushkevich	$\ln Q_e = 2,48143 - 0.32 \cdot [\ln(1 + (1/C_e))]^2$	(3)	0.484	1.96
Sips	$\ln[Q_e/(Q_{\max} - Q_e)] = 0.78 + 1.69 \cdot \ln C_e$	(4)	0.609	47.14
Temkin	$Q_e = 9.84 + 3.62 \cdot \ln C_e$	(5)	0.861	53.52

$C_e$ : Concentration of BLM dye in solution at equilibrium;  $Q_e$ : Quantity of BLM adsorbed at equilibrium;  $Q_{\max}$ : Maximum quantity of dye adsorbed.

### 3.5.4 Effects of temperature variation and enthalpies of adsorption

As the temperature of the adsorption medium increases, the amount of BLM adsorbed increases. Overall, this shows the endothermic nature of the adsorption of BLM on ATP peat.

The standard enthalpy  $\Delta H^\circ$  and the entropy  $\Delta S^\circ$  of adsorption can be determined from the Vant'Hoff equation:

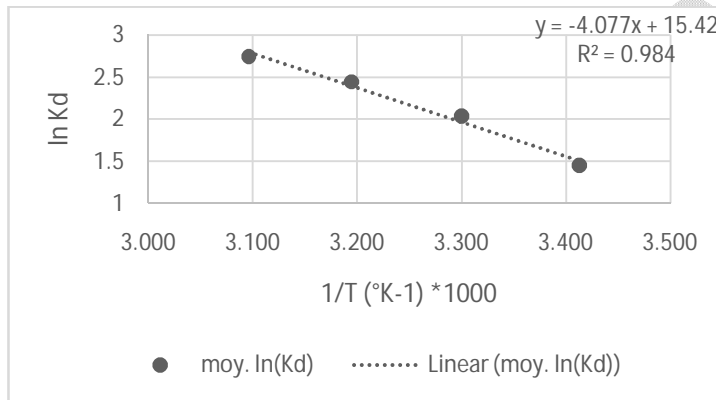
$$\ln(K_d) = (\Delta S^\circ/R) - [\Delta H^\circ/(R \cdot T)] \quad (6)$$

Knowing that:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (7)$$

$$K_d = Q_e/C_e \quad (8)$$

$K_d$  is the distribution coefficient and R is the ideal gas constant. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are obtained from the slope and the intercept of  $\ln(K_d)$  versus  $1/T$  (figure 7).



**Fig. 7. Linear regression line representing  $\ln K_d=f(1/T)$**

The endothermic nature of the process is confirmed by the positive value of the free enthalpy  $\Delta S^\circ$  [22, 23]. The positive value of  $\Delta S$  shows the affinity of the adsorbent towards the dye [23]. The negative value of  $\Delta G^\circ$  indicates the spontaneity and low activation energy of the system. The  $\Delta G^\circ$  value below  $-80 \text{ kJ}\cdot\text{mol}^{-1}$ , confirms physical adsorption on the peat, while chemisorption is associated with a  $\Delta G^\circ$  value between  $-400$  and  $-80 \text{ kJ}\cdot\text{mol}^{-1}$ . In another way,  $\Delta H^\circ > 80 \text{ kJ}\cdot\text{mol}^{-1}$  indicates chemisorption while  $\Delta H^\circ < 80 \text{ kJ}\cdot\text{mol}^{-1}$  indicates physisorption [24].

Since the ATP-BLM system displays a Gibbs free energy  $\Delta G^\circ = -2.01 \text{ kJ}\cdot\text{mol}^{-1}$ , a negative value and less than  $80 \text{ kJ}\cdot\text{mol}^{-1}$  in absolute value, and an enthalpy  $\Delta H^\circ = 33.88 \text{ kJ}\cdot\text{mol}^{-1}$  less than  $80 \text{ kJ}\cdot\text{mol}^{-1}$ ; therefore, the adsorption of the BLM on the ATP peat would be of the physisorption type. On the other hand, the positive free enthalpy  $\Delta S^\circ = 128 \text{ J}\cdot\text{mol}^{-1}$  also indicates that the adsorption is endothermic.

Table 4 compares the values of the adsorption energies obtained during this study with those of the other "Adsorbent-dye" adsorption experimented by other authors. Thus, the values of enthalpies and entropies found in the system "peat-cationic dyes" (Malachite green

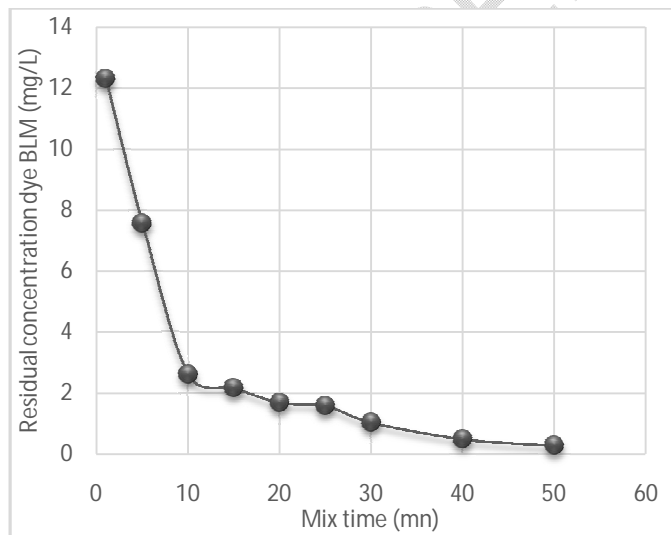
and crystal violet) are in the same order of magnitude. For the “clay-methylene blue” system [21], a value of  $\Delta G = -23.60 \text{ kJ.mol}^{-1}$ , is ten times greater than for the other “peat-cationic dye” systems. This difference would be due to the adsorption temperature condition which is  $40^\circ\text{C}$  with clay versus  $25^\circ\text{C}$  for the other studies.

**Table 4. Comparison of enthalpy and entropy values of different adsorbent/dye pairs**

Adsorbent/Dye (Temperature)	Initial Conc. ( $\text{mg.l}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJ.mol}^{-1}$ )	$\Delta S^\circ$ ( $\text{J.mol}^{-1} \text{K}^{-1}$ )	$\Delta H^\circ$ ( $\text{kJ.mol}^{-1}$ )	References
ATP/BLM ( $25^\circ\text{C}$ )	25	-2.01	128	33.88	Present study
Peat/Crystal Violet ( $25^\circ\text{C}$ )	10	-2.3	136.9	37.3	[12]
Clay/ BLM ( $40^\circ\text{C}$ )	24	-23.60	150	25.24	[21]
Peat/Malachite green ( $25^\circ\text{C}$ )	30	- 4.3			[17]

### 3.5.5. Kinetic study of BLM adsorption on peat

The variation of the residual concentrations of BLM dyes as a function of the stirring time of the peat-dye mixture (Figure 8) shows that between 10 and 50 mn, dye residual concentrations vary only between 2 to  $0.5 \text{ mg.l}^{-1}$ .



**Fig. 8. Variation of the residual concentration of BLM according to the mix time**

Two kinetic models are tested according to the equilibrium concentration data corresponding to each stirring time. The pseudo first order of the adsorption reaction rate is verifiable when plotting the regression line from equation below:

$$\text{Log } (Q_e - Q_t) = \text{Log } Q_e - (k_1/2.303) *t \quad [25, 26] \quad (9)$$

And for pseudo-second-order, the corresponding equation is:

$$t/Q_t = [1/(k_2 Q_e^2)] + (1/Q_e) *t \quad [25, 26] \quad (10)$$

By definition  $Q_t$  is the quantity of dye adsorbed per gram of peat at each instant  $t$ .  $Q_e$ , fixed at  $9.9 \text{ mg.g}^{-1}$  is the maximum quantity of dye adsorbed relative to the experimental conditions.  $k_1$  and  $k_2$  are the rate constants expressed in  $\text{mn}^{-1}$  and in  $\text{g.mg}^{-1}.\text{mn}^{-1}$  respectively.

Linear regression from these equations gave  $r^2 = 0.8887$  and  $r^2 = 0.9997$  respectively for pseudo-first-order and pseudo-second-order. The adsorption of BLM on peat is therefore pseudo-second-order and the rate constant is  $0.062 \text{ g.mg}^{-1}.\text{min}^{-1}$ . The systems “peat-crystal violet”, “peat-malachite green” and “clay-methylene blue” respectively gave the same order of reaction [21, 27]. However, rates constants are different.

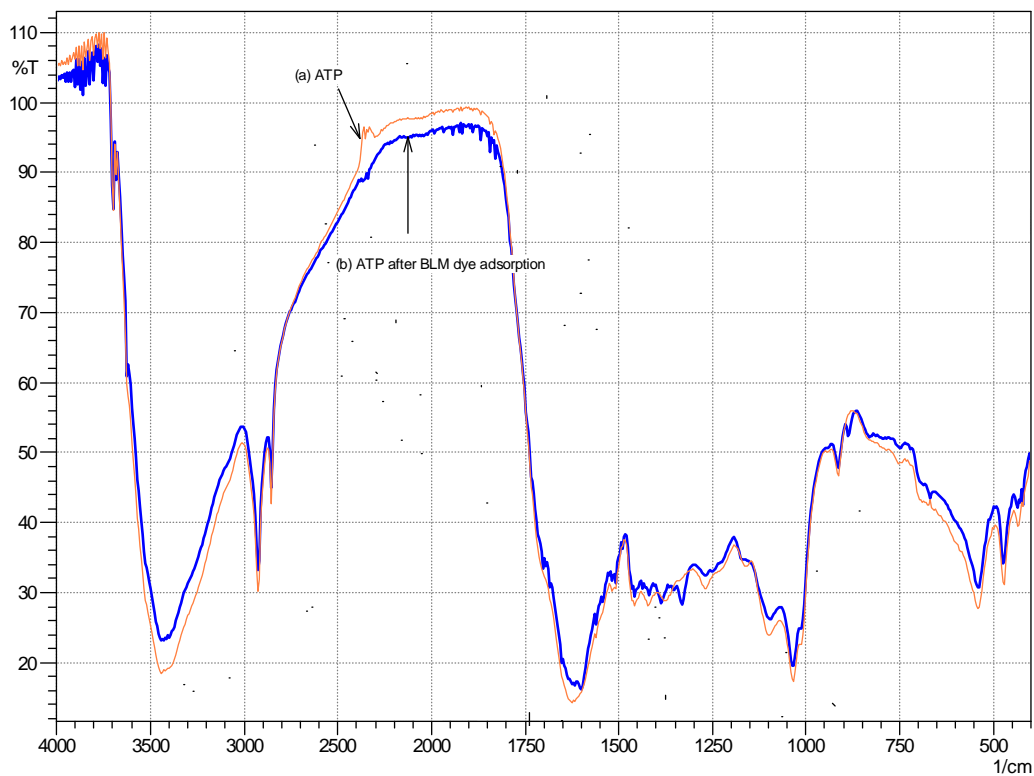
### 3.6 FTIR spectra analysis

#### 3.6.1 Spectrum of ATP peat alone

The spectra of the raw peat and those of the peat after adsorption of BLM dye at two different concentrations (Figure 9) are displayed simultaneously in order to clearly highlight the differences. The ATP peat spectrum shows characteristic bands corresponding to common peat functional group. Thus, the carboxylic group is remarkably noted by the presence of a very broad and intense band at  $3427 \text{ cm}^{-1}$  and at  $1624 \text{ cm}^{-1}$ . These bands represent, respectively, the vibrations of the OH bonds of the carboxylic functions involved in hydrogen bonds and the stretching or deformation vibration of the C=O bond, but also of the C-N bond of the peptides. The presence of bonds corresponding to the CH<sub>3</sub> group is also noted by a fine and less intense band at  $2920 \text{ cm}^{-1}$ . The bands at  $2850$  and  $2852 \text{ cm}^{-1}$  testify to the asymmetric and symmetric stretching vibrations respectively of the aliphatic C-H bonds [28]. Finally, the bands at  $1119$  and  $1032 \text{ cm}^{-1}$  reflect the existence of the C-O bond in phenols and in the C-O ether function in celluloses [29].

On the one hand, the bands at  $1082$  and  $1038 \text{ cm}^{-1}$  can be attributed to C-OH bonds of the polysaccharide, Si-O-Si, Si-OH, or free silica [30]. On the other hand, the bands at  $786$  and  $689 \text{ cm}^{-1}$  mainly signal the vibration of Si-O-Si bonds. However, ATP does not display these last two bands [31]. This would imply that the bands at  $1100$ ,  $1010$  and  $1032 \text{ cm}^{-1}$  observed on the analyzed peat would exclusively indicate the C-O bonds of ethers and phenols of the polysaccharides. Therefore, the ATP peat sample analyzed would therefore contain little or no silica.

Peat ATP also displays bands at  $912$ ,  $539$ ,  $471$ , and  $433 \text{ cm}^{-1}$  and acute bands at  $3695 \text{ cm}^{-1}$  which would represent O-H, N-H, or X-H bonding. These functions stay free from hydrogen bonds.



**Fig. 9. Transmittance (%) IR spectra of peat ATP alone (a) and peat ATP after adsorption of BLM (b)**

### **3.6.2 ATP spectrum after BLM adsorption**

The spectrum of ATP peat containing methylene blue differs from that of peat alone by the appearance of a peak at  $1387\text{cm}^{-1}$ . This appearance would characterize the binding of BLM at the level of the carboxylic function of the peat. The presence of BLM on peat could also be highlighted by the appearance of new peaks at  $1330\text{cm}^{-1}$  and  $885\text{cm}^{-1}$ , which correspond respectively to the vibrations of the C-S bonds and those of the substituted aromatic benzene rings of the methylene blue. The relatively significant decrease in the intensity of the band at  $1260\text{cm}^{-1}$  also confirms the formation of the dye bond with the acid functions of the peat.

On the other hand, the decrease in intensity of bands at  $1374\text{cm}^{-1}$  and at  $1159\text{cm}^{-1}$  which represents the tertiary alcohols -C-OH and the phenols of peat, would be due to the hydrogen bond between these alcohol functions and hydrogenated branches of BLM.

### 3.7 Textile effluent treatment tests with ATP peat

The values of some physico-chemical parameters of distilled water and textile waste water, before and after their passage through a layer of peat, are shown in Table 5. According to this result, it appears the passage through the peat increases the chemical oxygen demand (COD) and at the same time makes decrease the pH media of the water. Although peat adds color and conductivity, when tested with distilled water, it is shown that ATP removes much of the color and lowers the conductivity when treating textile effluent. And even if the permissible limit values for textile industry discharges are exceeded, this does not cast doubt on the effectiveness of peat. Indeed, other types of non-cationic compounds and dyes could be present in the effluent and would not be intercepted by ATP. This means that of ATP should be combined with other methods that can remove these non-cationic compounds.

**Table 5. Physico-chemical analysis of distilled water and textile waste water, before and after their passage through a layer of peat**

	Distilled water	Filtrate Distilled water	Wastewater	Filtrate wastewater	*Permitted limit
<b>pH</b>	5.32	4.65	10.05	5.35	6 – 9
<b>Conductivity (µs/cm)</b>	1,3	277	4850	3497	-
<b>Colour (Pt-Co mg/l)</b>	0	45	780	93	20 ≤
<b>COD (O<sub>2</sub> mg/l)</b>	0	154	164	203	50 ≤

\*International standard for discharge of effluent containing dyes [32]

### 4. CONCLUSION

Colors in textile effluent can be removed by allochthone tropical peat from Antananarivo, Madagascar. However, its application needs improvement to reduce the release of other compounds to the treated water. And the use of allochthone tropical peat may be combined with other methods for the elimination of all other hazardous compounds.

### CONSENT (WHERE EVER APPLICABLE)

Not applicable

### ETHICAL APPROVAL (WHERE EVER APPLICABLE)

Not applicable

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