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RESEARCH ARTICLE

USE OF DEACTIVATED LICHENS FOR THE ADSORPTION OF TWO TOXIC DYES: CRYSTAL VIOLET AND METHYL RED

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ABSTRACT

This study consisted of using deactivated thallus of the lichen species *Parmotrema dilitatum* as adsorbents in the treatment of water containing crystal violet (CV) and methyl red (MR), two toxic dyes. Scanning electron microscopy (SEM) and Fourier transform spectroscopy (FT-IR) were performed on the deactivated lichens before and after their interaction with the dyes. These analyses showed an affinity of the dyes for the adsorbent. The influence of physico-chemical parameters, related to the experimental environment and the adsorbent, on the removal of the dyes was evaluated. The study showed that the stirring speed for optimal removal of both dyes is 450 rpm. The equilibrium time of adsorption varies according to the nature of the dye. This time is 60 min (short) for the cationic dye (CV) and 100 min (long) for the anionic dye (MR). The amount of dye adsorbed increases as the initial concentration of the target dye increases. Conversely, an increase in lichen mass leads to a decrease in the adsorbed amounts of CV and MR. The high amounts of dyes removed were obtained with the granulometry [125-250 μm] of deactivated lichen powder. The thermodynamic study showed that the adsorption of CV is endothermic while that of MR is exothermic. The pH values of the reaction medium for optimal adsorption were observed at pH = 6 for CV and pH = 3 for MR. For all the physico-chemical parameters evaluated, the study showed that the amount of cationic dye removed is greater than that of the anionic dye.

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INTRODUCTION

Fascinated by the colouring of objects, man has introduced colours into his life since prehistoric times. Indeed, primitive peoples had discovered the dyeing properties of juices (from leaves, fruits, flowers, roots, bark, etc.) and of stains left on their hands after picking up food. In general, colours are obtained from natural sources such as pigments of mineral (coloured earths), vegetable (e.g. madder) and animal (e.g. Tyre Purple) origin or from chemical synthesis (Har and Bharati, 2014). Today, dyes are widely used in industries to colour fabrics, leather, plastics, paper, food products, cosmetics and to produce artistic colours; with the aim of increasing the value of the product on the world market (Aziz et al., 2018). Ivory Coast has not remained on the sidelines of the use of dyes in its industrial sector in recent decades. Unfortunately, the massive use of dyes in this industrial sector has been accompanied by a phenomenon of pollution of its environment (Douagui et al., 2012; Scheren et al., 2004). Indeed, the residues of dyes used in this sector are released into the environment in the form of effluents, without prior

treatment. Some of these dyes are toxic and liable to reach the water table (Şen, 2015) and then cause public health problems (Santiago and Huffman, 2016). Crystal violet (CV) and methyl red (MR) are among these toxic dyes. However, there are several physical, chemical and biological methods of removing these dyes. These methods include electrochemical oxidation (Nidheesh et al., 2018), ozonation (Wijannarong et al. 2013), electrocoagulation (Pirkarami and Olya, 2017), the Fenton photo process (Sohrabi et al., 2017), nanofiltration and reverse osmosis (Nataraj et al., 2009). Unfortunately, some of these disposal methods have revealed limitations related to the production of toxic by-products and the high financial cost of implementation. These limitations make these methods difficult or even inaccessible. To overcome these limitations, scientists are increasingly turning to adsorption methods. These methods are efficient, less expensive and accessible (Ali et al., 2012; De Gisi et al., 2016), as they can remove pollutants without generating hazardous by-products (De Gisi et al., 2016). Several research studies on the removal of dyes from aqueous solutions using the adsorption method have been carried out. Different solid materials such as sawdust (Dulman

and Cucu-Man, 2009), activated carbon (Baysal et al., 2018), clay (Kausar et al., 2018), peanut shell (Liu et al., 2018), nanofibre membranes (Mousavi et al., 2018), alumina and silica (Kannan et al., 2008), banana peel (Munagapati et al., 2018), orange peel (Arami et al., 2005) have been used as adsorbents in various pollutant treatments. However, few dye adsorption studies have been carried out using lichens as adsorbents. Existing studies with lichens have been largely devoted to the adsorption of metals (Chatenet and Botineau, 2001) (Ohnuki et al., 2004). Lichens are plants resulting from the symbiotic association between an alga and a fungus. They are generally used in vivo as indicators of environmental quality (Zoungranan et al., 2018; Zoungranan et al., 2018). The present study aims at evaluating the influence of some physico-chemical parameters in the adsorption of crystal violet and methyl red on deactivated lichens. The physico-chemical parameters evaluated are contact time, stirring speed, initial dye concentration, solution pH, temperature, lichen grind size and lichen mass.

MATERIAL AND METHODS

Sampling: The thalli of the lichen *Parmotrema dilatatum* were collected in the forest reserve of the Lamto ecological station (5.02 °C West and 6.13 °C North). This reserve is 174 km far from the city of Abidjan (Ivory Coast) and located on the Abidjan-Yamoussoukro axis, between Singrobo and Taabo, and stretches along the Bandama River. This space is a natural Park of 2500 ha, with a tropical climate, the average temperature per year is about 28.28 °C, the annual precipitation is around 1194 mm and the rate of humidity is higher than 58%.

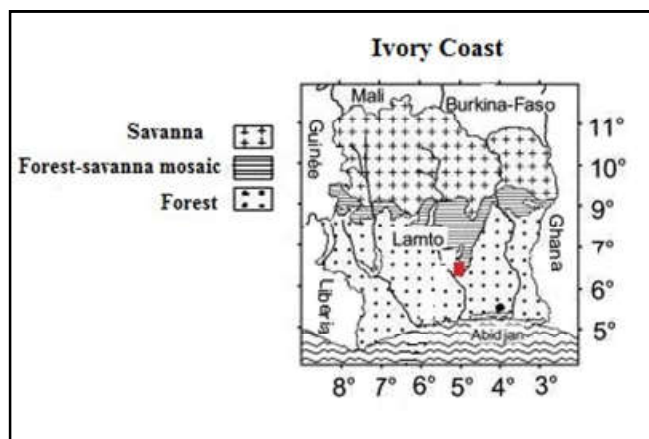


Figure 1. Location of Lamto reserve

Sampling is carried out on mature trees with diameters greater than 20 cm with bark that is not cracked, injured or slanted. Lichens collected are sent to the laboratory.

Lichens deactivation and crushing: In the laboratory, lichens are detached from their substrates and then manually cleaned to remove soil, leaf, dust or insect debris. The thallus is then washed with distilled water. An appropriate amount of lichen is placed in an oven at 80 °C for 48 hours to deactivate them. The deactivated lichens are crushed and sieved.

Characterization of deactivated lichens

IR-TF analysis: The lichen samples were analysed using a Fourier Transform Infrared (FTIR) spectrometer (Bruker

Tensor 27, USA) using the Attenuated Total Reflectance (ATR) technique. The frequency range is 4000 to 500 cm^{-1} . The functional groups present on the biomass of lichens constituting the adsorbent support were determined through the spectra obtained.

SEM analysis: The microstructure of the lichen samples was observed using a scanning electron microscope (JEOL JSM 5800LV). This microscope is equipped with an SDD SAM energy dispersive spectrometer. A specific detector allows cathodoluminescence images to be obtained.

Dyes preparation: Solutions of 500 mg/L of CV and MR dyes, were prepared. We diluted the initial solutions in order to obtain diluted solutions.

The chemical structures and some characteristics of the dyes are given below (Figure 2)

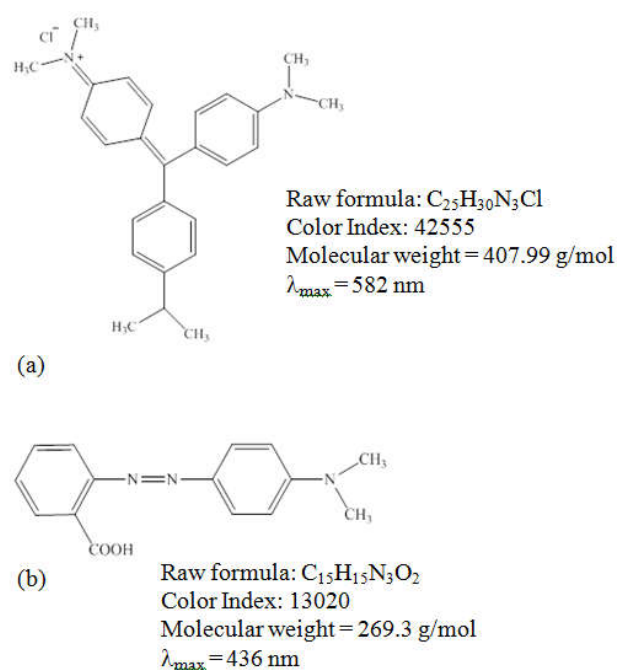


Figure 2. Chemical structures of CV (a) and MR (b)

Adsorption studies

The various evaluations were carried out by bringing the lichens in solution into contact with the dye. The whole was stirred by means of a vibrating shaker (Heidolph Vibramax 100) and then filtered under gravity using Whatman paper, No. 4. The optical densities of the filtrates are read using a UV Visible spectrophotometer (WFJ-752).

The influence of lichen grain size was studied with grain sizes: 125-250 μm , [250-500 μm] and [500-800 μm].

The effect of the stirring speed of the lichen/dye mixture was carried out using the stirrer, vibrating from 150 to 1350 rpm.

The equilibrium time study was carried out in the range of 5-200 min for each dye.

The influence of the adsorbent lichen mass was evaluated by varying the lichen mass from 0.5 to 4g.

The influence of the initial concentration was evaluated by varying the initial CV concentration from 10 to 500 mg/L and the MR concentration from 5 to 50 mg/L. The influence of the pH of the solution was studied by varying the pH of the solution from 1 to 12 by moderate addition of a solution of NaOH (0.1 M) and HCl (0.1 M). The thermodynamic study was carried out by varying the temperature from 20 to 60 °C.

The relationship of Jin *et al.* (2008) is used to determine the amount of adsorbed dye Q_{ads} (mg/g). This relationship is given below:

$$Q_{ads} = \frac{C_i V_i - C_f V_f}{m}$$

Where:

C_i (mg/L) is the initial concentration of the dye,
 C_e (mg/L) the final equilibrium concentration,
 V_i is the initial volume (L) of the solution,
 V_f the final volume (L) of the solution,
 m is the mass (mg) of lichens.

RESULTS AND DISCUSSION

IR-TF analysis: The IR-TF analyses were first performed on non-deactivated lichen samples, then on deactivated lichen samples and finally on deactivated lichen samples obtained after CV and MR processing.

The spectra obtained provided information on the nature of possible interactions between functional groups of adsorbents and dye molecules (Figure 3). The non-deactivated lichen sample shows some typical peaks. Wide and strong bands are observed at 3258-3313 cm^{-1} representing the bound hydroxyl groups (-OH) of the alcohols. The peaks observed between 2912-2924 cm^{-1} can be attributed to the C-H stretching vibration. The bands at 1613-1628 cm^{-1} are characteristic of the $\nu_{C=O}$ elongation modes of the CONH groups of proteins and primary amides. The frequencies 1253, 1255 and 1296 cm^{-1} correspond to the elongations of the Ctet-O-Ctri groups of the esters and Ctri-O-Ctri groups of the anhydrides (Ctet means tetrahedral carbon and Ctri trigonal carbon). The frequencies 1313-1374 cm^{-1} indicate the -C=O stretching of the carboxylic acids. The strong bands observed at 1026-1029 cm^{-1} are those of the C-C elongation. For deactivated lichens, the spectrum shows some differences from that of non-deactivated lichens. Indeed, two peaks disappear, one at 1296 and one at 1459 cm^{-1} while the intensities of the bands between 1026 - 1029 cm^{-1} and 1615-1628 have decreased. This means that some functional groups present in the non-deactivated lichen have shifted during the deactivation process. This displacement is explained by the dehydration of lichenic substances (depsides, depsidones etc.) and their decomposition into smaller substances (Mahamad *et al.*, 2015). These different transformations show that there has been modification and/or deactivation of certain functions (ester, carboxylic, alcohol, amide etc.) of the lichenic substances.

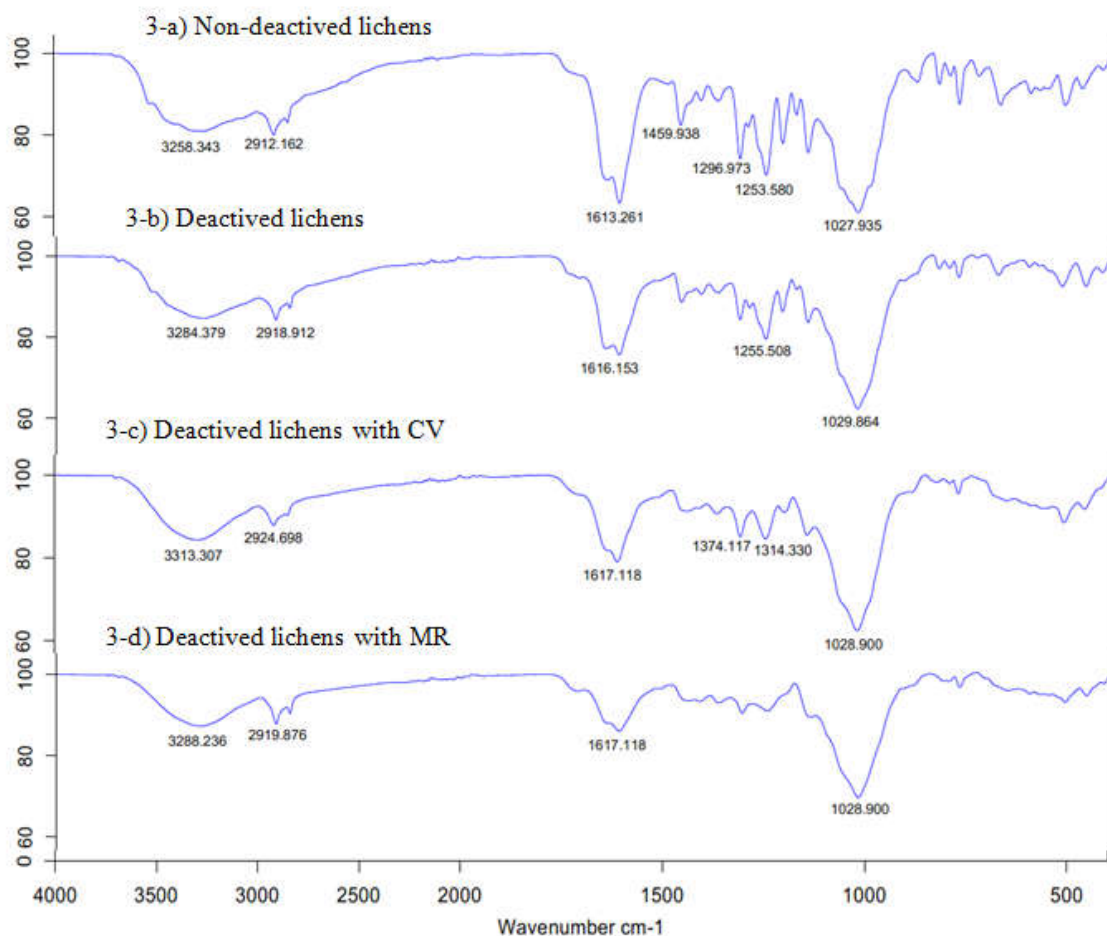


Figure 3. IR spectra of non-deactivated lichens (3-a), deactivated lichens (3-b) and deactivated lichens obtained after dye treatments (3-c with CV and 3-d with MR)

modifications. Indeed, the stretching vibration of the OH group increased from 3284 cm^{-1} to 3313 cm^{-1} in the case of CV adsorption and from 3284 cm^{-1} to 3286 cm^{-1} in the case of MR. These results show that electrostatic interactions between dye molecules and hydroxyl groups occurred on the surface of the deactivated lichen biomass. The change in intensity observed around $1613\text{--}1628\text{ cm}^{-1}$ is due to the interaction between the amide functions of the lichen adsorbent and the dyes. A peak due to the C-O stretch is observed at 1374 cm^{-1} for deactivated lichens obtained after CV treatment. For deactivated lichens obtained after MR treatment, a disappearance of peaks was observed between $1253\text{--}1372\text{ cm}^{-1}$. This disappearance is due to the interaction of carboxyl groups on the surface of deactivated lichens with dye molecules (Gül *et al.*, 2019). Also, whatever the treated dye, changes in frequency were observed in the case of C-H groups present on the surface of deactivated lichens. The results on the deactivated lichens obtained after treatment of the dyes show that the C-O, C-H and COOH groups are mainly involved in the adsorption processes of the CV and MR dyes (Subbaiah *et al.*, 2011).

deactivated lichens obtained after treatment of the dyestuffs. Figure 4 shows a change in surface morphologies between non-deactivated lichens (Figure 4-a) and deactivated lichens (Figure 4-b). This change is mainly in the spatial distribution of the lichen particles. Non-deactivated lichens have a fibrous and compact surface whereas deactivated lichens have a granular and porous surface reflecting a multiplication of adsorption sites. The granular and porous structure of deactivated lichens is due to the disappearance of certain lichenic substances. This result corroborates that of the IR-TF analysis concerning the disappearance of peaks in the spectrum of deactivated lichens. This indicates that the deactivation of the *Parmotrema dilatatum* species enhances its adsorption potential. The SEMs of deactivated lichens from dye treatment are shown in Figs 4-c and 4-d. Compared to non-deactivated lichens, deactivated lichens obtained after dye treatment show a pore choking phenomenon and a more compact surface structure. The observed increase in compactness is explained by the phenomenon of chain reconstitution due to the trapping of dye molecules by several adsorbent particles.

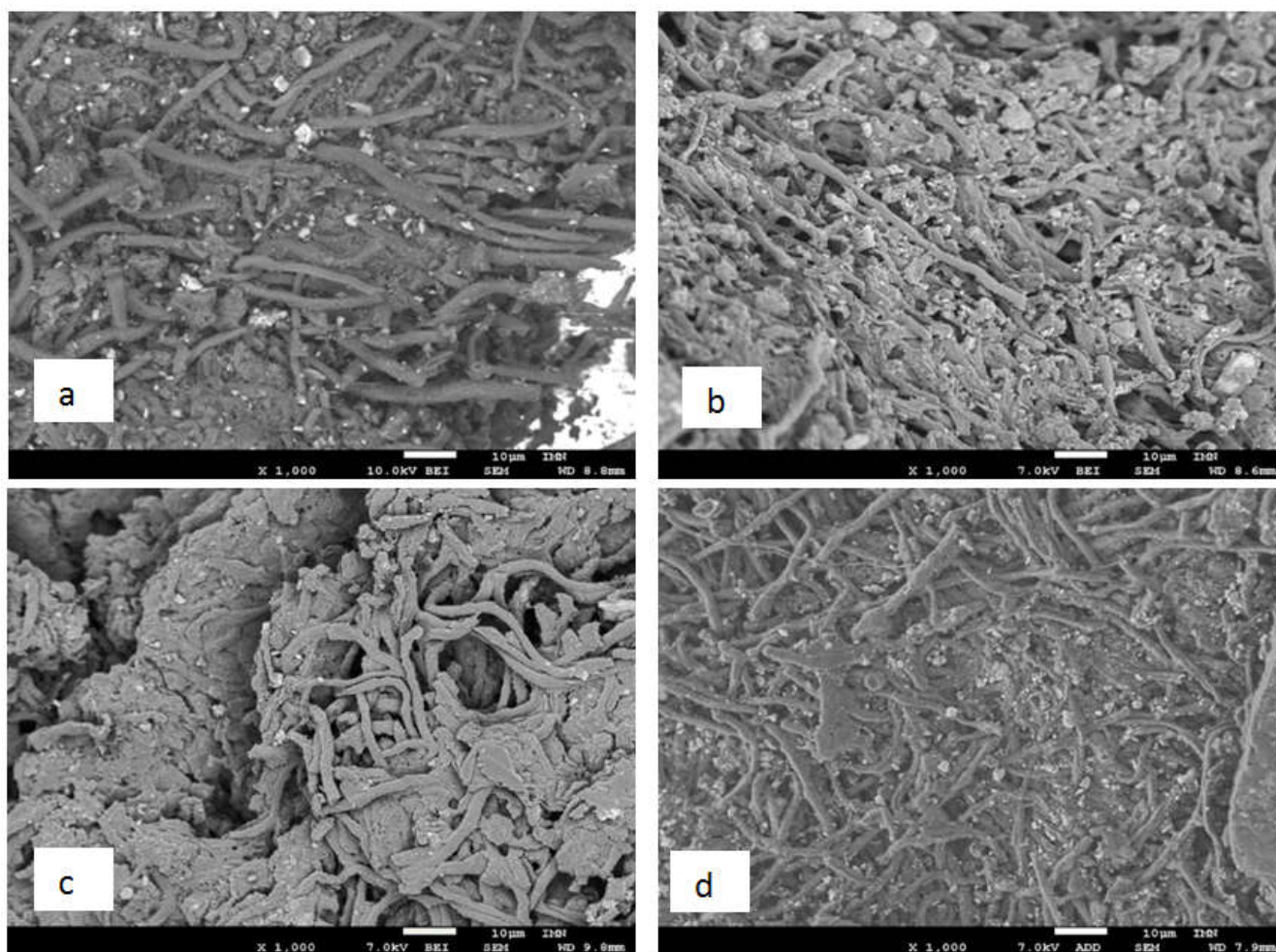


Figure 4. Scanning electron microscope (SEM) of non-deactivated lichens (4-a), deactivated lichens (4-b) and deactivated lichens obtained after dye treatments (4-c with CV and 4-d with MR)

SEM analysis

Examination of the surface morphologies of the adsorbents (Figure 4) was carried out using scanning electron microscopy (SEM).

This examination established the differences in surface morphology, non-deactivated lichens, deactivated lichens and

Choking is related to interactions between dye molecules and functional groups on the surface of deactivated lichens (Gül *et al.*, 2019), confirming that the CV and MR dyes have been adsorbed. In the end, the analysis of the IR-TF spectrum and the SEM of the adsorbents justified the choice of deactivated lichens for further work.

Agitation speed effect

The influence of stirring speed on the adsorption of dyes by deactivated lichens was evaluated (Figure 5).

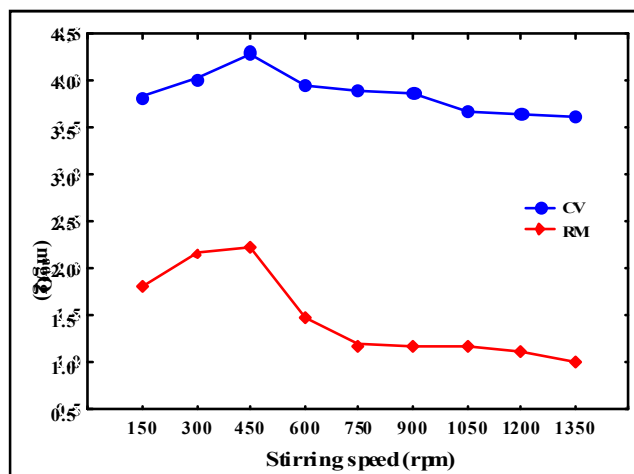


Figure 5. Amount of dye adsorbed according to the stirring speed

The best amounts of adsorbed CV and MR were obtained at 450 rpm. When the stirring speed increases from 150 to 450 rpm, the amounts of CV and MR adsorbed increase, above 450 rpm, a drop in adsorption capacity is observed. Ekmekyar *et al* (2006), in their study of copper (II) biosorption by non-living *Cladonia rangiformis* lichens, reported that an increase in stirring speed leads to an increase in mass transfer rate and a decrease in boundary layer thickness. This decrease, in boundary layer thickness results in a reduction in surface film strength (Benefield *et al.*, 1982) facilitating, dyes adsorption on the desactivated

lichens surface. The low adsorption above 450 rpm is due to the elevation of stirring speed which makes the suspension non-homogeneous and therefore a difficulty for the dye molecules to be fixed on the surface of the desactivated lichens.

Effect of grain size: The determination of the best particle size is a parameter for the physical characterization of the adsorbent. Figure 6 shows the different amounts of dyes adsorbed on deactivated lichens at different grain size levels.

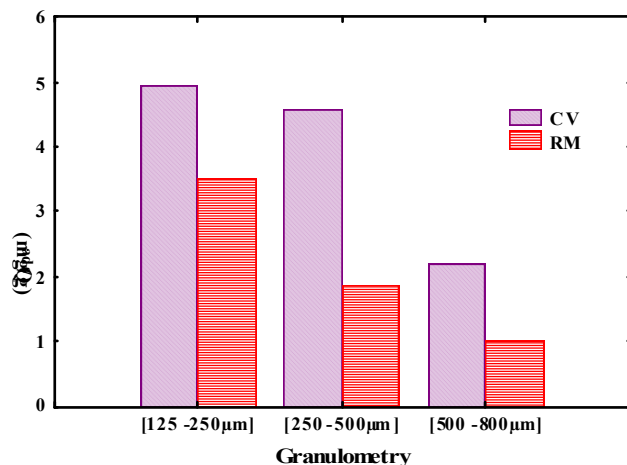


Figure 6. Amount of dye adsorbed by grain

The best amounts of adsorbed dyes are observed at the particle size level [125-250 μm], they are 4.96 mg/g for CV and 3.51 mg/g for MR. The small particle size improves the efficiency

of dye adsorption. This is due to the interlayer structure of the fine fractions (Duong *et al.*, 2009) of deactivated lichens. The efficiency of small particle sizes had also been observed by authors Duong *et al* (2010) and Sangster *et al* (2015) in different studies. However, these authors reported that the amounts of adsorbates adsorbed with small particle sizes may be a function of the type of adsorption, functional groups and physico-chemical properties of the medium. In addition, a study of the effect of particle size was conducted by Luo *et al* (2019). These authors obtained results close to those found in this study. Indeed, in a study on the adsorption of two antibiotics (norfloxacin and tetracycline) by suspended solids in lakes, these authors found that the smaller fraction 63-150 μm had the greatest adsorption capacity for antibiotics, while the fraction greater than 300 μm had a lower adsorption capacity.

Initial concentration effect: The results of the study of the concentration effect of CV and MR dyes are shown in Figure 7. In this Figure it can be seen that the amounts of dyes adsorbed by the deactivated lichens increase with the increase of the initial concentration of the dye.

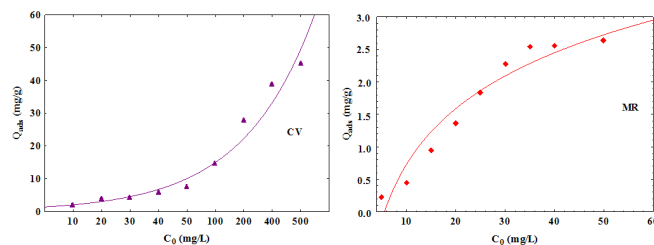


Figure 7. Amount of dye adsorbed according to initial dye concentration

The increase in the amount of adsorbed dye can be explained by the increased driving force caused by the concentration gradient. This driving force causes dye molecules to diffuse to the active sites of the adsorbent and thus increases the mass transfer to the surface of deactivated lichens (Hor *et al.*, 2016; Pathania *et al.*, 2017). Papita *et al* (2012) and Khan *et al* (2018) in recent studies concerning respectively CV and MR adsorptions, had also observed similar results. Another study by Kulkarni *et al* (2018) on the lichen species *Dermatocarpon vellereceum* reported that the amount of dyes adsorbed by this species also increased with increasing the initial concentration of the dye. In addition, the study by Ekou *et al* (2017) on copper and iron adsorption by the species *Parmotrema dilatatum*, also revealed an increase in the amount of metal adsorbed with increasing initial metal concentration. However, this study demonstrated the existence of an adsorption maximum beyond which, any increase in the initial metal concentration resulted in a desorption process.

Effect of contact time: The results about contact time of lichens with dyes solutions are shown in Figure 8. It can be seen that as the time increases, the quantities of dyes adsorbed increase until they reach a plateau that reflects the chemical equilibrium of adsorption. The chemical equilibrium of adsorption corresponds to the occupation of the majority of sites by the dye molecules (Shukla *et al.*, 2002). Equilibrium is reached after 60 minutes for CV and 100 minutes for MR.

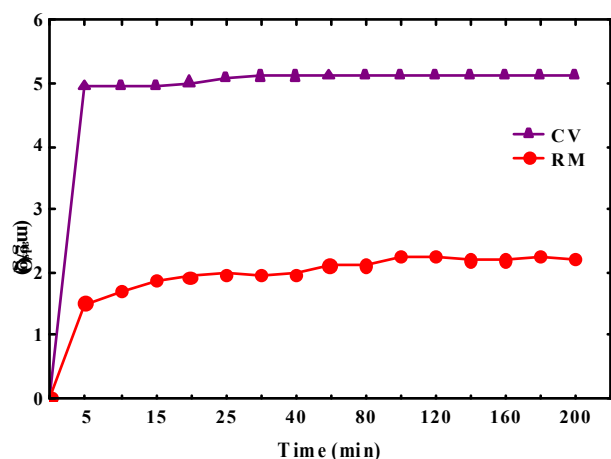


Figure 8. Amount of dye adsorbed according to contact time in solution

The maximum amount of CV adsorbed at equilibrium is 5.14 mg/g and 2.24 mg/g at MR. After the chemical equilibrium, the active sites of the deactivated lichens are saturated. There is then a phenomenon of insignificant dye uptake by the lichens. This results in a constant adsorption capacity over time (Figure 8).

Effect of deactivated lichens mass: In adsorption process studies, the mass of the adsorbent is a descriptive parameter of the adsorption kinetics. Indeed, study the mass makes it possible to determine the optimal mass of the adsorbent required for a given initial concentration (Eris and Azizian, 2017) of dye. The dye removal tests were carried out on different masses of deactivated lichens. The results of these tests are presented in Figure 9.

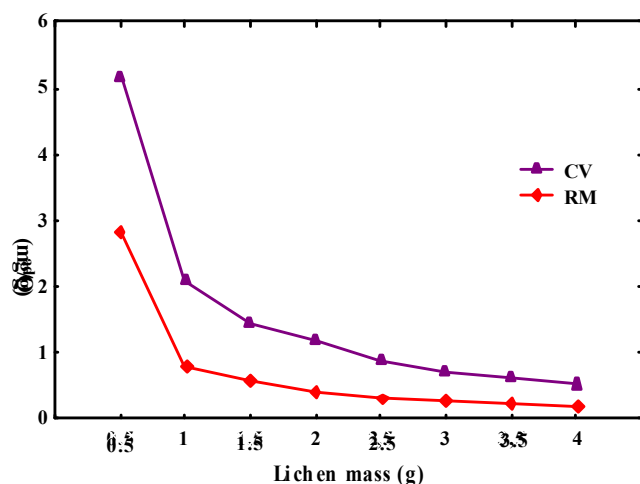


Figure 9. Amount of dye adsorbed according to the mass of deactivated lichens

The analysis of Figure 9 shows that the amount of adsorbed dye decreases as the mass of deactivated lichens increases. When the mass of lichens varies from 0.5 to 4 g, there is a drop in the amount of dye removed. Thus, for CV the amount removed drops from 5.182 to 0.524 mg/g and for MR from 2.824 to 0.208 mg/g. It thus appears that when the mass of the adsorbent is low, the quantity of adsorbed dye molecules is high. This is due to the fact that for low masses the active sites are easily accessible. In the opposite case of high masses, these

active sites become difficult to access by the dye molecules due to the formation of biomass aggregates (Karthikeyan *et al.*, 2007). These biomass aggregates form a screen that makes it difficult to access the active sites (Sarma *et al.*, 2016). Authors Shoukat *et al* (2017) and Khan *et al* (2018) in their studies concerning respectively CV and MR dye removal by adsorption, has observed that the amount of dyes removed also decreased with increasing mass of the adsorbent in solution.

Effect of temperature: Temperature variation affects adsorption capacity (Fatemeh *et al.*, 2017) and can help determine the mechanism of the adsorption process. The results of the study of the influence of temperature on the adsorption of CV and MR by deactivated lichens are presented in Figure 10.

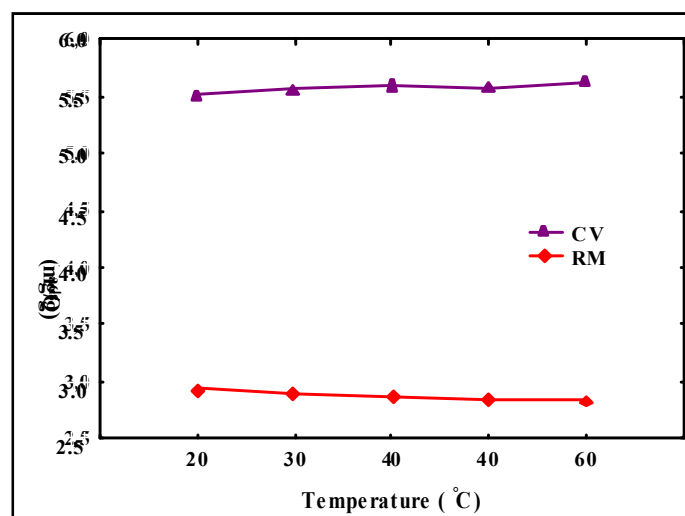


Figure 10. Temperature effect on CV and MR adsorption

Examination of Figure 10 reveals that the amount of CV removed increases with increasing temperature, whereas with the MR dye, the increase in temperature appears to be a limiting factor in its adsorption on deactivated lichens. The increase in adsorption capacity with increasing temperature reflects an endothermic process (Ngulube *et al.*, 2017; Elmoubarki *et al.*, 2015; Chinoune *et al.*, 2016). In the case of CV, the increase in temperature of the medium results in an increase in the diffusion rate of the dye molecules, allowing them to rapidly cross the outer boundary layer and reach the deactivated lichens internal sites of adsorption (Miyah *et al.*, 2018). It is also possible that temperature contributed to the disaggregation (Karaca *et al.*, 2008) of the biomass permitting greater accessibility to CV molecules to the active sites. Authors Shoukat *et al* (2017) observed that the amount of CV adsorbed on a bio-composite decreased with increasing temperature. However, for the MR dye, the increase in temperature would limit the diffusion rate of the molecules. However, the work of Guyo *et al* (2017) reported an improvement in the amount of MR eliminated with elevation of temperature.

Effect of solution pH: The pH value of the dye is an important factor in understanding the adsorption process. It influences the adsorption capacity (Moyo *et al.*, 2013) and determines the retention mechanism of the adsorbate (Bozbaş and Boz, 2016). In general, the effect of pH can be described using the pH_{PCZ} (pH of the zero charge point or pH of the zero charge point). The pH_{PCZ} is the pH value for which the net

charge of the adsorbent surface is zero. The pH_{PCZ} of the deactivated lichens of this study had been determined in our previous studies and it was 6.5 (Dobi-brice *et al.*, 2018). This pH_{PCZ} value means that the surface of the adsorbent is positively charged at pH values below 6.5 and negatively at pH values above 6.5 (Miyah *et al.*, 2017). The results of the effect of pH on the adsorption capacity of deactivated lichens are presented in Figure 11.

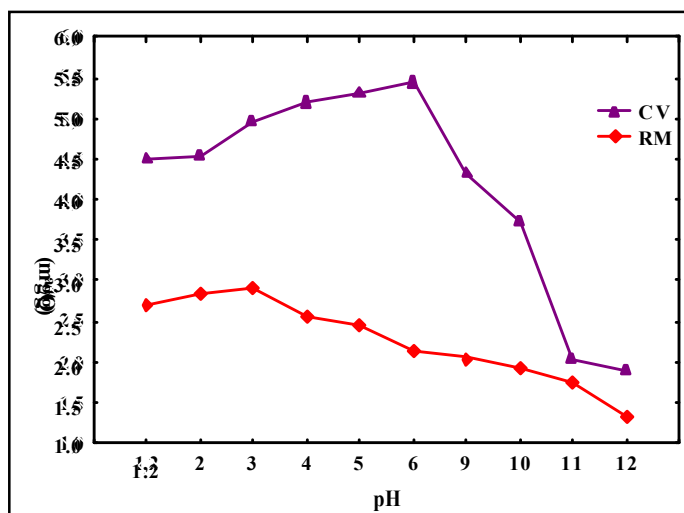


Figure 11. Effect of pH on CV and MR adsorption

This figure shows that the maximum adsorbed amounts are obtained at pH 6 and 3 respectively for CV and for MR dyes. In a strongly acidic medium, the surface of the deactivated lichens is positively charged ($pH < pH_{PCZ}$). This surface is therefore unfavorable to the adsorption of the cationic CV dye and favorable to that of the anionic MR dye, through electrostatics attractions phenomena (Abramian and El-Rassy, 2009; Ngulube *et al.*, 2017). As the pH increases towards pH_{PCZ} , the number of positively charged sites decreases while the number of negatively charged sites increases, this fact progressively promotes adsorption of CV to a maximum (at $pH = 6$). Beyond this maximum, the quantity of dye drops while the surface tends towards a strong negativity. This could be explained by a steric hindrance effect linked to the structure and size of the CV dye molecule. This hindrance appears to be a factor limiting access to the negative sites on the deactivated lichens surface.

CONCLUSION

The study evaluated the influence of a few physico-chemical parameters on the adsorption of two toxic dyes (crystal violet and methyl red) using deactivated lichens as adsorbents. Lichens of the species *Parmotrema dilatatum* have been previously deactivated and characterized by IR-TF and SEM. From the various evaluations, it appears that the physico-chemical parameters affect the amounts of dyes removed and the intrinsic adsorption mechanism differently. Chemical equilibrium of adsorption is reached after 60 for CV min and 100 min for MR. The stirring speed of 450 rpm appears to be the optimal speed for good removal of both dyestuffs. Increasing the initial dye concentration increases the removal capacity of the dye. Also, the [125-250 μm] grain range [125-250 μm] resulted in the maximum amounts of dyes removed being 4.96 mg/g for CV and 3.51 mg/g for MR. The rise in temperature is favourable for the removal of CV but limits that

of MR. In view of this influences, deactivated lichens are good adsorbents for the removal of toxic dyes such as CV and MR. However, the study is conducted in the laboratory with small volumes of solutions, it would be interesting to applied adsorption methods using large volumes of solutions to be treated. Column adsorption method with a fixed bed of deactivated lichens could be a good alternative.

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