





Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is a Publisher's version published in: <http://oatao.univ-toulouse.fr/24475>

Official URL: <https://doi.org/10.4236/jep.2018.92012>

To cite this version:

Bonou, Sidoine and Sagbo, Etienne and Osseni, Sèmiyou Ayélé and Charvillat, Cédric  and Ben-Nissan, Besim and Cazalbou, Sophie  *Adsorption of Textile Dyes on the Shells of Snails <i>Achatina achatina</i> and <i>Lanistes varicus</i> Acclimatized in Benin: Influence of Their Heating Treatment.* (2018) *Journal of Environmental Protection*, 09 (02). 158-174. ISSN 2152-2197

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Adsorption of Textile Dyes on the Shells of Snails *Achatina achatina* and *Lanistes varicus* Acclimatized in Benin: Influence of Their Heating Treatment

S. A. S. Bonou¹, E. Sagbo^{1*}, S. Osseni¹, C. Charvillat², B. Ben Nissan³, S. Cazalbou²

¹Laboratoire de Chimie Inorganique et de l'Environnement (LACIE), Faculté des Sciences et Techniques, Université d'Abomey-Calavi, Cotonou, Bénin

²CIRIMAT Carnot Institute, University of Toulouse, Toulouse, France

³Department of Chemistry and Forensic Science, University of Technology Sydney, Sydney, Australia

Email: *esagbo@yahoo.fr

How to cite this paper: Bonou, S.A.S., Sagbo, E., Osseni, S., Charvillat, C., Nissan, B.B. and Cazalbou, S. (2018) Adsorption of Textile Dyes on the Shells of Snails *Achatina achatina* and *Lanistes varicus* Acclimatized in Benin: Influence of Their Heating Treatment. *Journal of Environmental Protection*, 9, 158-174.

<https://doi.org/10.4236/jep.2018.92012>

Received: December 1, 2017

Accepted: February 24, 2018

Published: February 27, 2018

Copyright © 2018 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The characterization of the shells of snails *Achatina achatina* and *Lanistes varicus* indicates that they contain calcium carbonate (98%) essentially aragonite, and organic matter (2%). The heating at 500°C during three hours (3 h) has destroyed their constitutive organic matter, converted the aragonite form completely into the calcite and reduced their specific surfaces. The effects of these modifications have been revealed in the adsorption in aqueous environment of methylene blue (MB) and methyl orange (MO) which are respectively cationic and anionic dyes. The results showed that the sorption of these dyes on the raw shells is more important than the heated shells. The methylene blue has more affinity for shells than methyl orange. Between these two types of snails, the shells of *Lanistes varicus* have a higher capacity of adsorption. This sorption of the methylene blue is more in relationship with the Freundlich model ($R^2 = 0.984$ for EG and $R^2 = 0.936$ for EA) comparatively to Langmuir model ($R^2 = 0.806$ pour EG et $R^2 = 0.634$ pour EA). If the shells of these snails were calcined before using for the cicatrizing of the human cutaneous wounds in Benin. In the case of the sorption of organic molecule, it will be necessary to avoid submitting them to a preliminary heat treatment.

Keywords

Carbonate of Calcium Biosourced, Organic Matter, Specific Surface, Adsorption, Dyes

1. Introduction

The control and the treatment of the solid waste are a priority of the cleaning up of the environment of living. The selection and the treatment of the solid waste contribute to their valorization. Among the solids waste which were collected in the households and in the markets of Benin, it could have recovered the shells of snails. Research on the valorization of the shells of snails and mollusks is today of actuality, but very little study has been achieved on the possibilities of valorization of the shells of the snails that were consumed in Benin. The shells are especially used in Benin, after calcination for the care of the wounds and human cutaneous burns. These shells are abundant and mixed up to the garbage. Indeed, according to a study achieved in Benin in 2002, 62.5 tons of snail's flesh are delivered every year on the market of Cotonou. This quantity corresponds to 216 tons of shells of snails that rejected per year on Cotonou [1]. It is important to search for interesting applications in order to encourage their transformation and their production. So, after the characterization of the shells of *Achatina achatina* and *Lanistes varicus* acclimatized in Benin, the present study is interested on the potentiality of these shells as biosorbants for the depollution of waters contaminated in organic pollutants.

The substances used here are methylene blue (MB) and methyl orange (MO) respectively cationic and anionic dyes. That will permit to understand the interactions between chemical substances with raw shells and heated shells respectively in aqueous environment in order to know if it is necessary to heat the shells of snail before using it for adsorption of dyes.

2. Material and Methods

2.1. Material

Two types of the shells of snail are studied: the first is constituted by the shells of giant snails *Achatina achatina* and the second are those of ampullar snails *Lanistes varicus*. Their characteristics were determined. They are indicated in the **Table 1**. These mineralogical characteristics have been assessed by X-rays diffraction (diffractometer X D8 Brüker; Brüker AXS GmbH), infrared spectroscopy with Fourier's transformed (Perkin Elmer Spectrum One. UK) and

Table 1. Characteristics of shells of snails.

Type of snails	Name of the sample of snails shells	Chemical composition (%)				Specific surface ($\text{m}^2 \cdot \text{g}^{-1}$)	Point of zero charge (PZC)
		Aragonite (CaCO_3)	Calcite (CaCO_3)	Quartz (SiO_2)	Organic matter		
<i>Achatina achatina</i>	EG	97.21	1.18	-	2.1	1.053	9.1
	EGC	-	100	-	-	0.871	9.4
<i>Lanistes varicus</i>	EA	97.21	1.18	0.2	2.09	1.390	8.9
	EAC	-	100	-	-	0.449	9.5

EGC and EAC correspond to the sample of the EG and EA shells that were submitted to the heat treatment at 500°C during three hours.

thermogravimetric analysis (Setaram Instrumentation, France). The percentage of organic matter is evaluated by thermogravimetric analysis. It corresponds to the loss of mass that recorded between 250°C and 500°C. The specific surface is determined with the help of a device Micromeritics Instrument of Tristar type II 3020 (Micromeritics Instrument Corp. USA). The point of zero charge (PZC) has been determined while using the solid addition method [2] [3].

- **Préparation of the adsorbents**

The powder of shells is sifted on a stitch of 1 millimeter. One part of each is heated at 500°C during 3 hours at the air flow in a hearth.

- **Préparation of solutions of dyes**

Before dissolution, the dyes have been dried at 105°C during 4 hours. For each dye, an initial solution has been prepared by dissolving 100 mg of powder of dye in 1000 mL of deionized water. These solutions have been diluted by 1/10. The measure of the optical density of the solutions prepared permitted to keep the wavelength of maximal absorption for each solution. The characteristics of the molecules of dyes used are indicated below in the **Table 2**.

2.2. Method

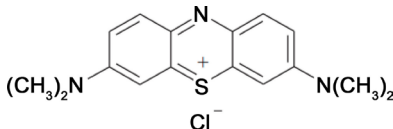
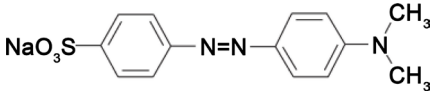
- **Kinetic study of the adsorption**

The first serial of experiments is interested to the kinetic study of the adsorption. Indeed, the adsorption of methylene blue (MB) and methyl orange (MO) according to the time has been made during one hour. The suspensions have mixed under stirring during to 10, 20, 30, 40, 50 and 60 minutes at 250 rpm. The experiments have been realized at 25°C. The suspensions have been constituted by dissolving 2 g of powder in 50 mL of solution of dye. At the end of the mixing, the suspensions have been centrifuged to 4000 rpm during 10 minutes. The quantity of dye in the supernatant has been determined by spectrophotometer UV-Vis (spectrophotometer LANGE DR 500).

The capacity of sorption of the shells has been obtained by the equation:

$$q_e = \frac{(C_i - C_e) \cdot V}{m}; C_i, C_e \text{ and } V \text{ are respectively the initial and final concentrations (mol} \cdot \text{L}^{-1}\text{) and the volume (in liter) of the solution of dye; m. the mass (in g) of}$$

Table 2. Characteristics of dyes.

Dyes	Methylene bleu (MB)	Méthyl orange (MO)
Molecular structure		
Wavelength of maximal absorption (λ_{\max}) and Molecular Weight MW ($\text{g} \cdot \text{mol}^{-1}$)	Methylene blue	Methyl orange
λ_{\max} (nm)	664	464
MW ($\text{g} \cdot \text{mol}^{-1}$)	319.85	327.33

the adsorbent. The solids matrix which are obtained after the centrifugation have been washed with 250 mL of deionized water and have been dried during 12 hours at $80^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. The thus dried powders have been analysed by the infra-red spectroscopy with Fourier's transformed (FTIR).

- **Determination of isotherms of sorption**

The second serial of the experiments consist of the determination of the Langmuir and Freundlich isotherms. In this case, in each serial of the conic flask, it was introduced successively, 5, 10, 15, 20 and 25 ml of the work solution of each dye. The four first erlenmeyers have been completed to 25 ml with the deionized water. 1 g of powder has been put in each solution to form the suspensions. The suspensions are immediately agitated and let to rest during 96 hours to allow the realization of the chemical equilibrium according to the kinetic study. After centrifugation at 4000 rpm during 10 minutes, the measures of absorbance have been done to 664 nm of methylene blue and to 464 nm for the methyl orange for the supernatant. The results have permitted to determine the percentage of adsorption and the Langmuir [4] and Freundlich isotherms [5] have been traced. The percentage of adsorption is defined as being the report of the loss quantity of dye (in mg) in supernatant by the initial quantity (in g) of dye.

3. Results and Discussion

3.1. Electronic Scan Microscopy of the Raw and Heated Shells

The particles that are observed in the MEB before and after heat treatment to 500°C (Figure 8) show the difference of structure and modifications which appear for EG and EA shells.

Thus, during the heat treatment to 500°C , the size of the mineral particles of EG seems practically unaltered in spite of a modification of their arrangement while it appears distinctly a structural and granulometric modification of the particles that compose the EA sample (Figure 1).

Indeed, the creation of strong bridges during the treatment entailed the partial coalescence of the small particles giving denser particles with superior sizes and weaker specific surfaces.

3.2. Buffer Power Zone and Point of Zero Charge of Shells

The point of zero charge and the buffer power zone could permit to choose the appropriate pH of the suspension that could favour the sorption of the cationic or anionic dyes. The results of these parameters are showed to the Figures 2-5.

Curves $\text{pH}_f = f(\text{pH}_i)$ have three parts:

- a first part of pH_i ranging from 2 to 4 where the final pH of the suspensions increases rapidly. This portion would correspond to the reaction between the added acid and the basic functional groups present in the organic matter that coats the calcium carbonate crystals;
- a second part on which the final pH grows very weakly. This part is located

between the values 4 and 9 of the initial pH of the impregnation solutions. In this area, acid-base reactions are very limited and show the buffering capacity

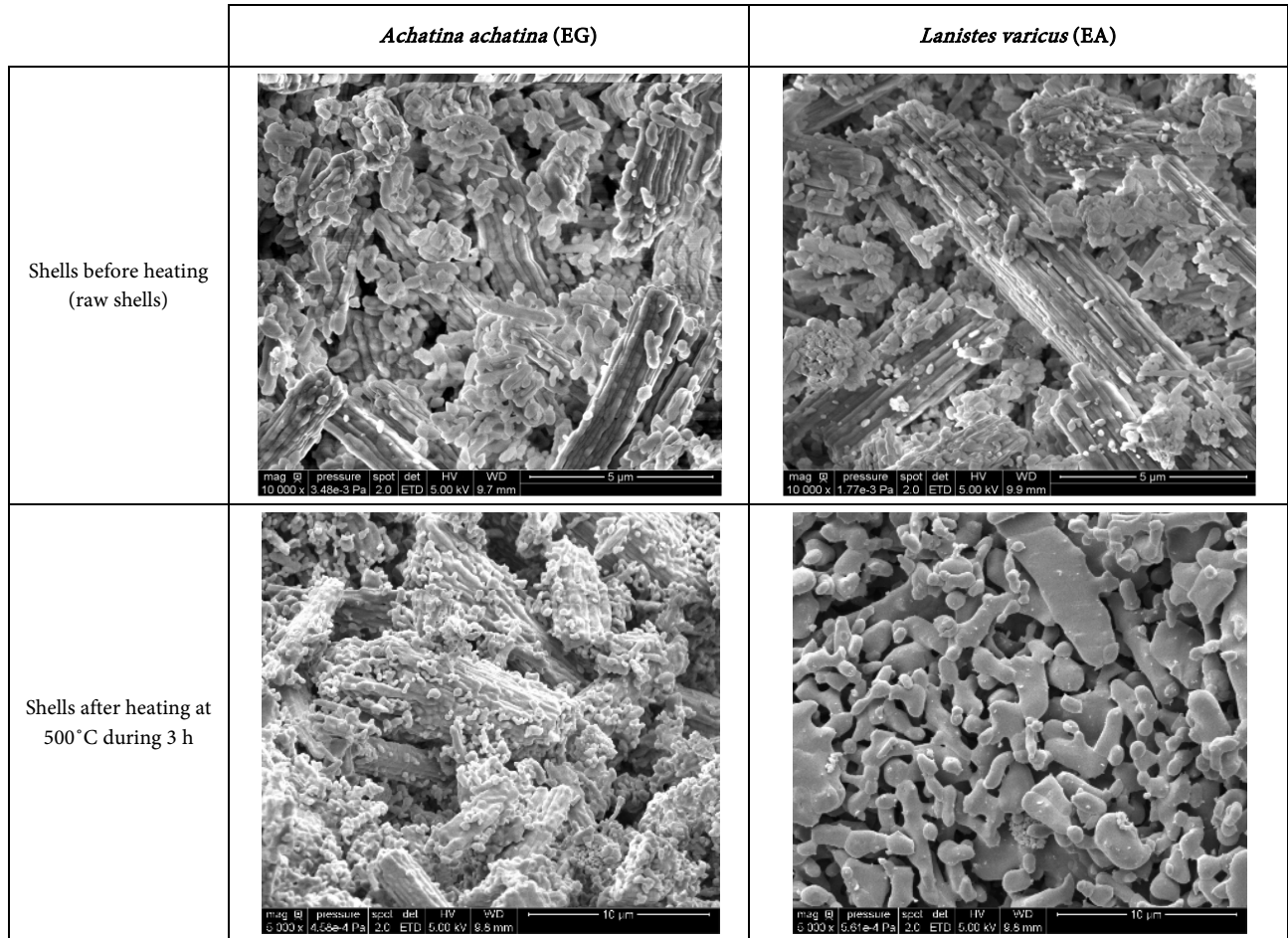


Figure 1. Images MEB of shells of *Achatina achatina* (EG) and *Lanistes varicus* (EA) before and after heating at 500°C during 3 hours.

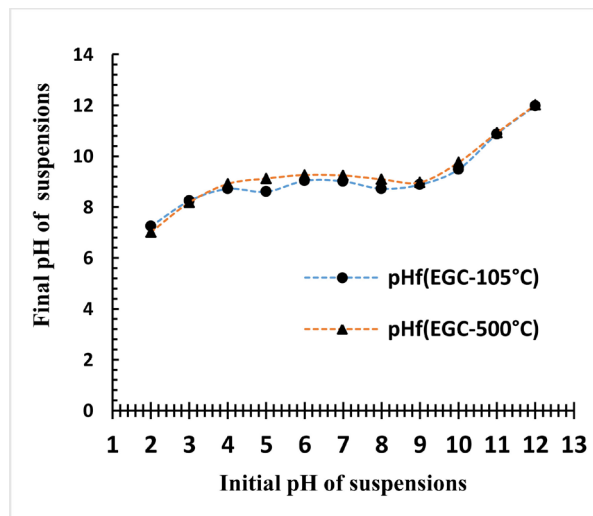


Figure 2. Evolution of pH of EG and EGC suspensions as function of the pH of initial solutions.

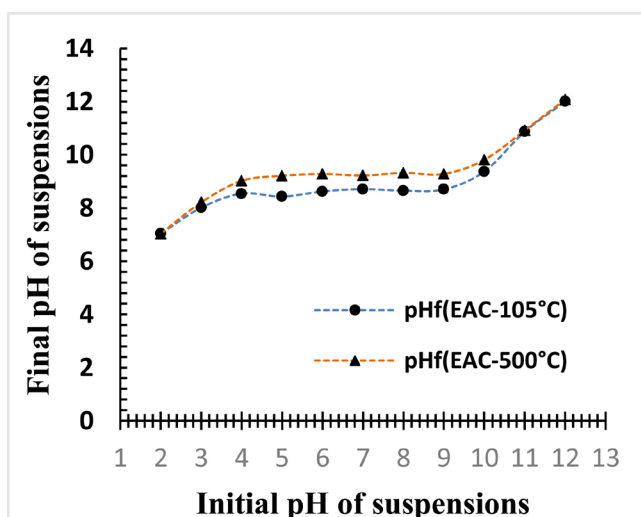


Figure 3. Evolution of pH of EA and EAC suspensions as function of the pH of initial solutions.

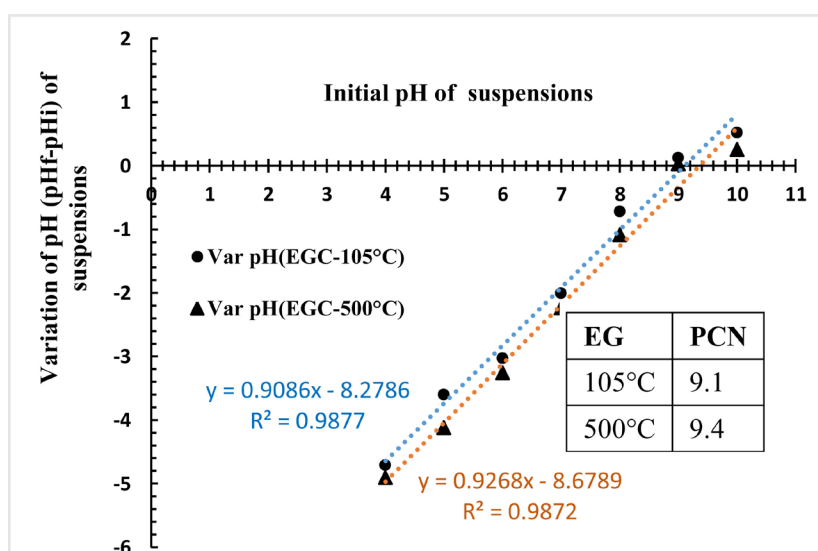


Figure 4. Variation of pH of EG and EGC suspensions as function of the pH of initial solutions.

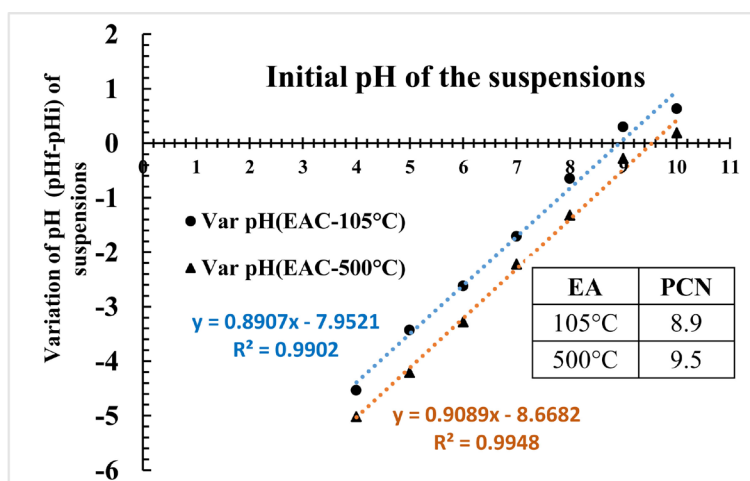


Figure 5. Variation of pH of EA and EAC suspensions as function of the pH of initial solutions.

of snail shells because such a large variation in pH ($\Delta\text{pH}_i = 5$) induces a very small variation of the final pH ($\Delta\text{pH}_f < 1$). Assuming that all the acidic and alkaline functions of the organic framework have reacted in the first range of pH_i, the small variation in the final pH observed would be due to the manifestation of the buffering capacity of the carbonate ions present both in raw and heated (to 500°C) shells.

- a third part on which the final pH of the suspensions grows very rapidly while being alkaline and which has an upward concavity. In this area, the calcium carbonate crystals are saturated by the hydroxide ions provided by the basic solution.

The evolution of the pH as a function of the initial pH shows that the suspensions of the shells have a neutralizing power of the acids. This neutralizing power is due to carbonate ions. In a water of pH = 7 at 25°C, the pH of the suspensions at 2 g/L of the EG and EA shells are around 8.4 and 8.6 respectively and indicate that these particles contained in the shell powders have an affinity for the hydrogen ions of the water that once attached to the particles make the suspension basic. Moreover, the presence of organic matter regulates the decarbonation in acidic medium of the shells and shows for the suspensions a buffer zone extending from pH = 4 to pH = 9 and in which the suspensions retain almost constant pH values between 8 and 9. Indeed, the presence of the organic matter which covers the layers of aragonite crystals slows the decarbonation by reacting firstly itself with the acid. In addition, the suspensions of the powders resulting from the heating at 500°C are more alkaline than those of the raw powders. This increase of alkalinity is justified by the destruction of the layer of organic matter which releases the carbonate ions which are better protonated in water. The powders of heated shells, become essentially mineral, put in solution can play the function of regulator of acidity by their alkaline character, and this better than the powders of raw shells.

$\text{pH}_f - \text{pH}_i = f(\text{pH}_i)$ curves permitted to determine the point of zero charge (PZC) for the different suspended shells. The results indicate that the pH of the point of zero charge for EG (9.1) and EA (8.9) shells are greater than 7. The values obtained for powders heated at 500°C (9.4 for EGC-500°C and 9.5 for EAC-500°C) are higher than those powders heated to 105°C. Thus, the suspensions of the powders of raw and heated shells are basic. These powders can be used as antacids. The grafting of anionic molecules and the grafting of the cationic molecules on the shell powders can be a priori favourable, respectively, to the lower and higher pH than the value of the PZC determined for the suspensions of the shells.

3.3. Capacity of Sorption of Methylene Blue and the Methyl Orange on the Raw and Heated Shells

3.3.1. Influence of the Concentration of the Solution of the Dye

The **Figure 6** indicates the evolution of the quantity of methylene blue (MB) that fixed by gram of raw or heated shells according to the initial quantity of methylene

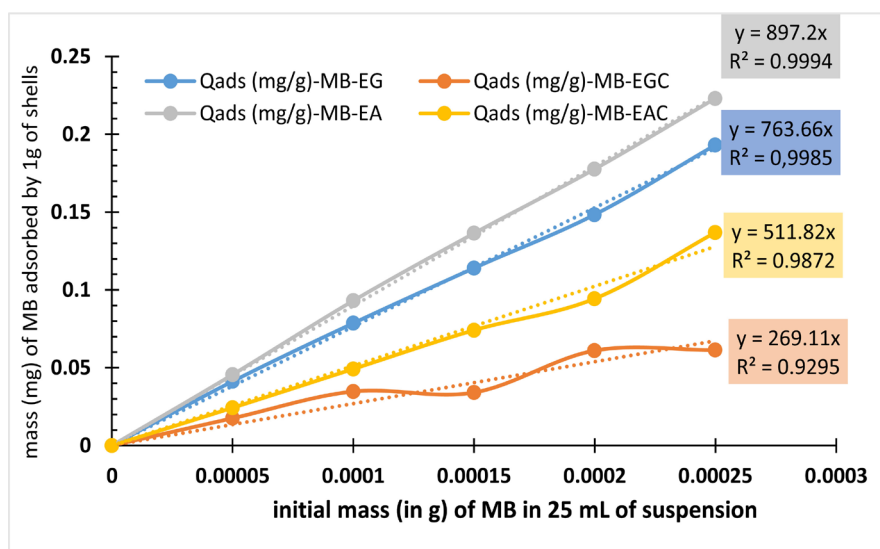


Figure 6. Evolution of the quantity of methylene blue fixed on the different shells (EG, EGC, EA and EAC) according to the initial mass of MB.

blue that is present in 25 ml of solution.

The results show that the raw shells adsorb methylene blue more than methyl orange. The MB absorption on the shells of ampullar snails (EA) is better than those of shells of giant snails (EG). Otherwise, for a same mass of shell powder, the quantity of methylene blue that adsorbed increases when the concentration of methylene blue in the initial solution increases. This increase is linear with coefficients of regression $R^2 = 0.999$ for EA and $R^2 = 0.998$ for EG. For the heated shells, these coefficients are $R^2 = 0.987$ for EAC and $R^2 = 0.929$ for EGC.

However, the percentage of adsorption is lower than 100% whatever the mass of dye in the initial solution. It shows that the adsorption of the methylene blue is not total and there is an equilibrium that settles between the quantity of dye that adsorbed and those free in solution. The increase of the quantity of MB according to the concentration can be due to the effect of the ionic strength that acting would allow the molecules of methylene blue to reach in depth the layers of organic matter and the beds of calcium carbonate. The molecules of methylene blue certainly have an affinity for the organic matter that presents in the shells than the free calcium carbonate.

The **Figures 7-10** show the percentage of adsorption (%) of the methylene blue and the methyl orange in the achieved suspensions that let to rest during 96 hours.

These results indicate that the rate of the adsorption is function of the ionic strength. For the initial concentrations that are experienced, it appears that the minimal rate of the adsorption is 74% for the EG shells against 89% for the EA shells; 23% for EGC against 47% for EAC.

The heating to 500°C entailed a destruction of the organic matter, a reduction of the specific surface and a recrystallization of the carbonate of calcium of the

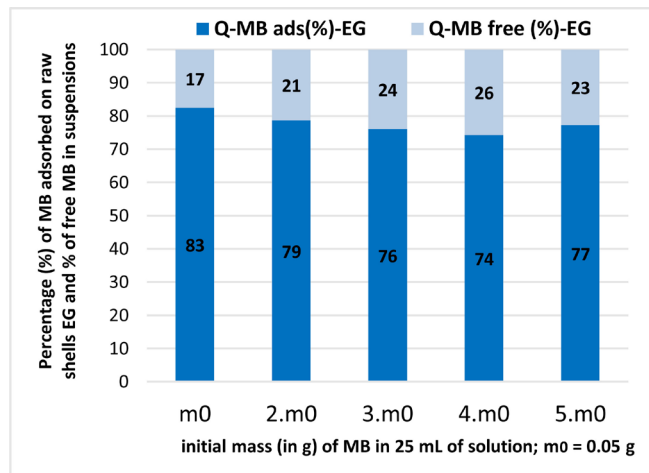


Figure 7. Distribution (%) of methylene blue on the raw shells EG and in suspensions as function of the initial mass of MB in 25 mL of solution.

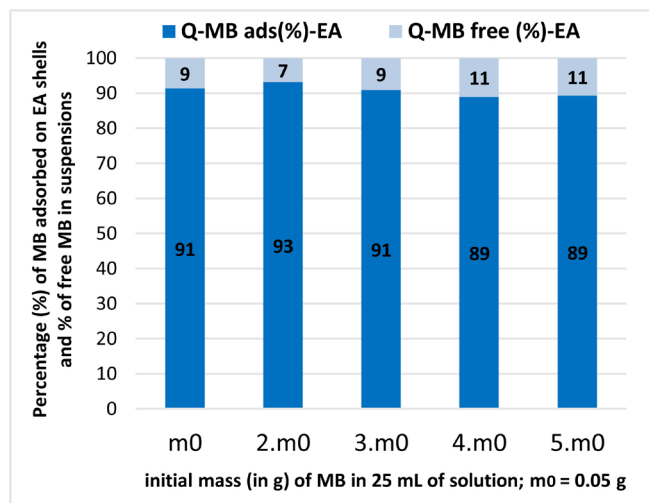


Figure 8. Distribution (%) of methylene blue on the raw shells EA and in suspensions as function of the initial mass of BM in 25 mL of solution.

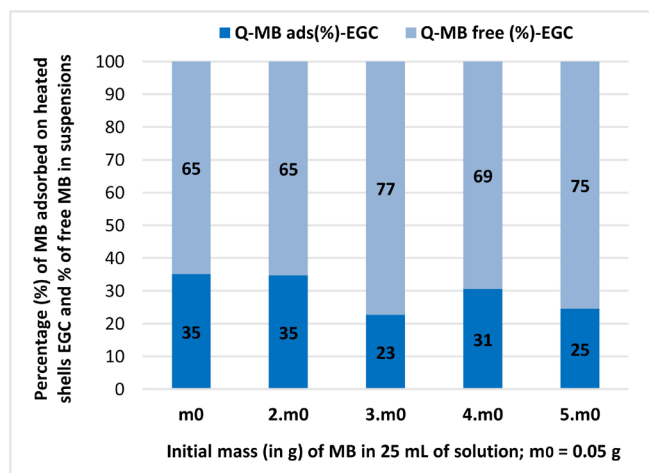


Figure 9. Distribution (%) of methylene blue on the heated shells EGC and in suspensions as function of the initial mass of BM in 25 mL of solution.

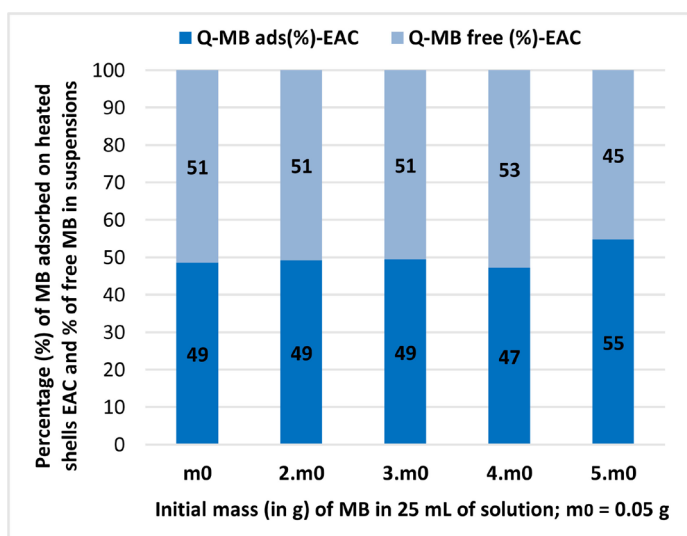


Figure 10. Distribution (%) of methylene blue on the EAC shells and in suspensions as function of the initial mass of BM in 25 mL of solution.

shells. Both of these variations contributed to the reduction of the number of site of adsorption of the shells. With the heated shells, devoid of organic matter and having the same crystalline phase (calcite), it was noticed that the heated shells EA that henceforth had the weakest specific surface (EAC) have adsorbed methylene blue more than the heated EGC shells. It could be deduced that the presence of the organic matter and the specific surface are not the only factors of which depend the adsorption of methylene blue on the shells. The new morphology of the particles of EA henceforth denser with a weak specific surface reduced the rate of adsorption but in the same time, the cavities created between these particles offer possibilities of trapping of the molecules of methylene blue during the sorption. It could justify the fact that the heated shells EAC keep the molecules of methylene blue more that the heated shells EGC.

3.3.2. Isotherms of Sorption of Methylene Blue by the Shells EG and EA

The **Figures 11-14** are the isotherms of Freundlich and Langmuir that are obtained in these experiments.

3.3.3. Sorption du Methyl Orange

The results of the sorption of methyl orange are indicated in the **Figures 15-19**.

These results show that there is almost no adsorption of methyl orange on the raw shells. However, in the case of the heated shells, it is noted an increase of the adsorption rate until 24% for the EGC shells against 3% for the EA shells. This indicate that the methyl orange as anionic dye, develop a repulsion towards the organic matter more than the carbonates of the shells.

The elimination of this organic matter favoured a weak adsorption on the heated shells EGC that presented a more important specific surface than the heated shells EAC. The molecular size of methyl orange added to the repulsion of the negative charges [6] [7] would not have permitted the trapping of the mo-

lecules of methyl orange in the cavities developed by the particles of the heated shells EAC. The survey of adsorption achieved on the EG shells and EA with methylene blue (MB) and the methyl orange (MO) chosen like elements of references

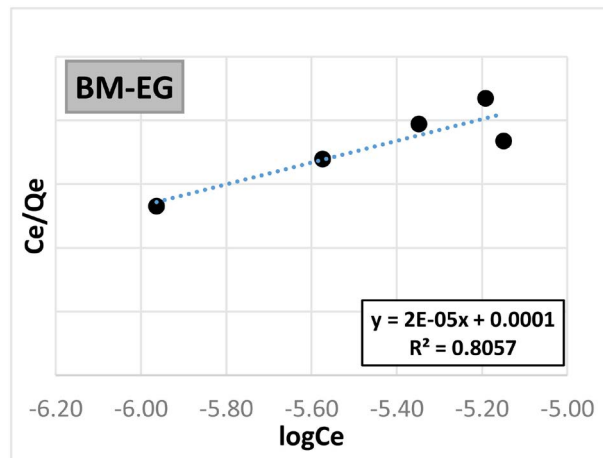


Figure 11. Isotherm of Langmuir of the sorption of methylene blue on raw shells EG.

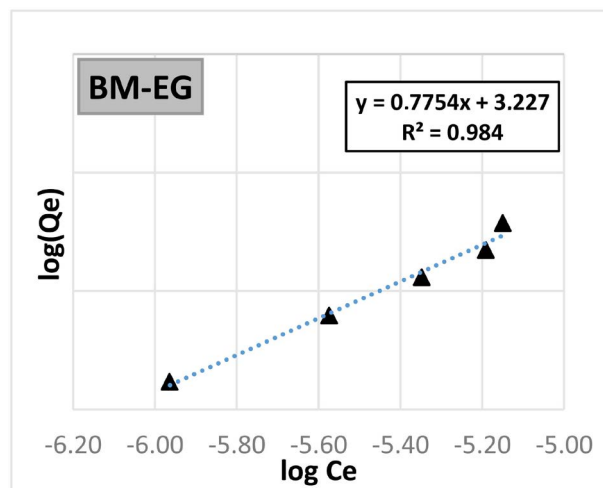


Figure 12. Isotherm of Freundlich for the sorption of methylene blue on raw shells EG.

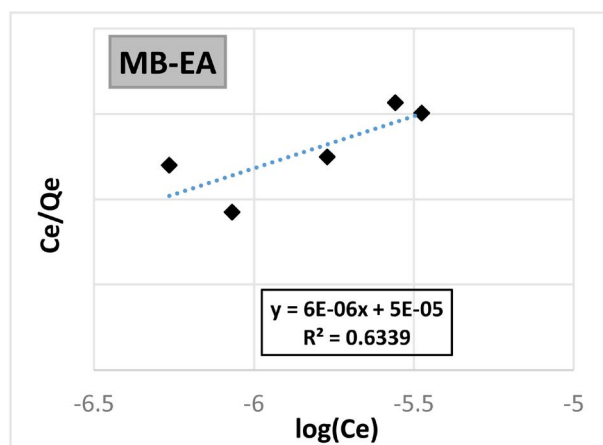


Figure 13. Isotherm of Langmuir of the sorption of methylene blue on raw shells EA.

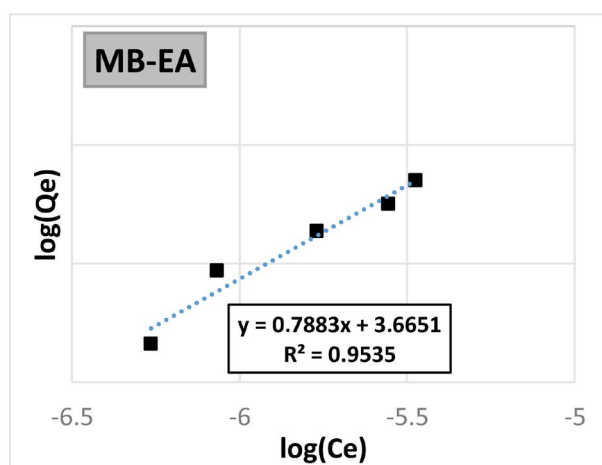


Figure 14. Isotherm of Freundlich for the sorption of methylene blue on raw shells EA.

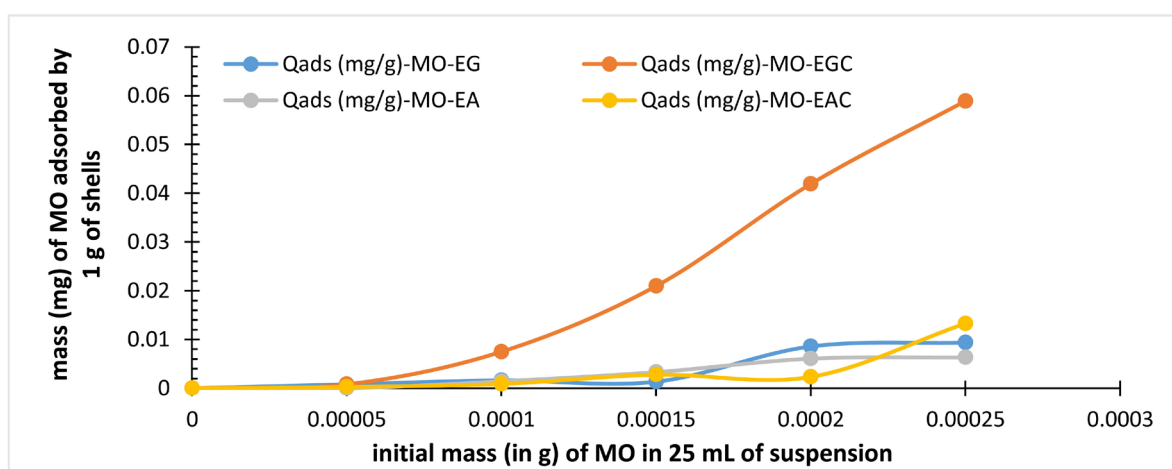


Figure 15. Evolution of quantity of methyl orange (MO) adsorbed on different shells as a function of initial mass of MO.

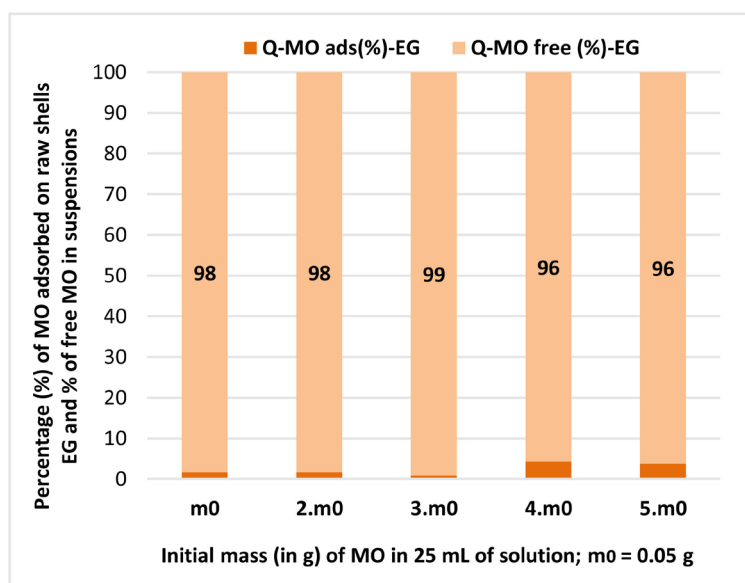


Figure 16. Distribution (%) of methyl orange on the raw shells EG and in suspensions as function of the initial mass of MO in 25 mL of solution.

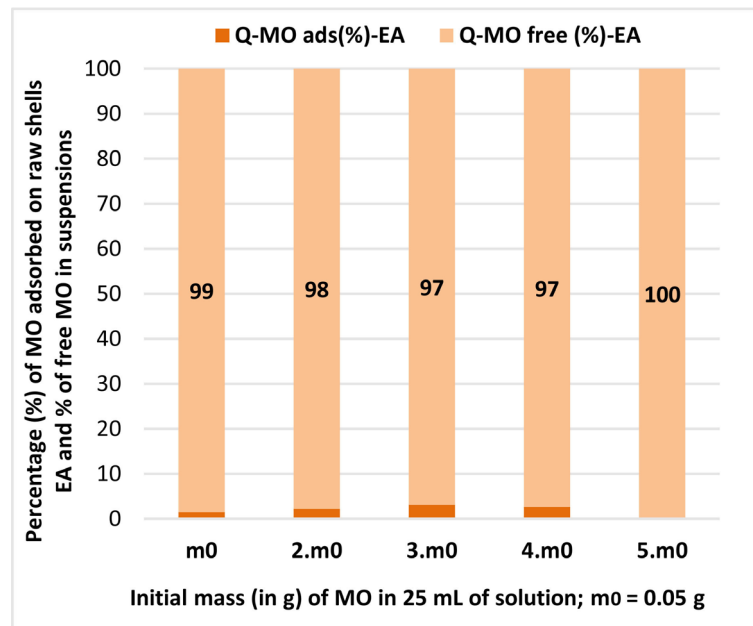


Figure 17. Distribution (%) of methyl orange on the raw shells EA and in suspensions as function of the initial mass of MO in 25 mL of solution.

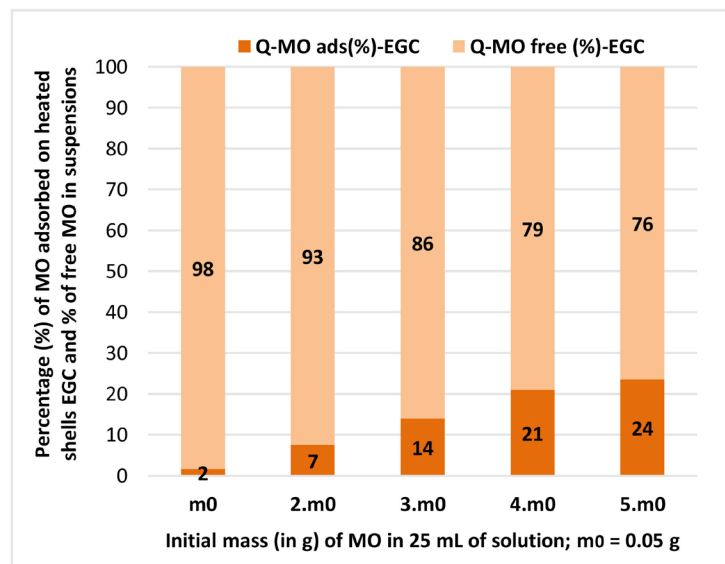


Figure 18. Distribution (%) of methyl orange on the heated shells EGC and in suspensions as function of the initial mass of MO in 25 mL of solution.

of stains cationic and anionic put in evidence a large affinity of EA for the cationic compounds.

The adsorption of methylene blue on the shells of EG and EA follows the model of Freundlich ($R^2 = 0.98$ for EG; $R^2 = 0.95$ for EA) better than the one of Langmuir ($R^2 = 0.81$ for EG; $R^2 = 0.63$ for EA). Indeed, the model of Freundlich justifies that an adsorption is in multilayered and explain why for a same quantity of shells (adsorbent), the quantity of dyes fixed increases with the initial concentration of the dye.

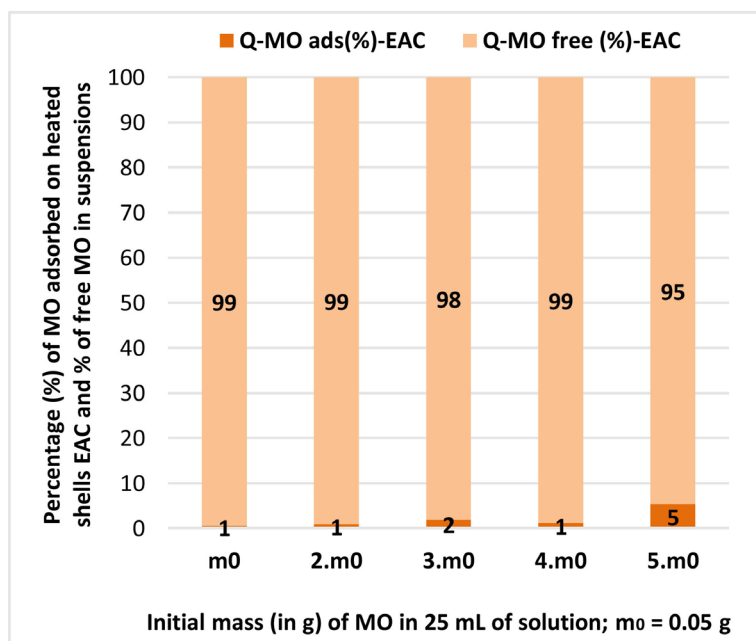


Figure 19. Distribution (%) of methyl orange on the heated shells EAC and in suspensions as function of the initial mass of MO in 25 mL of solution.

3.3.4. Kinetic Study of Adsorption of Methylene Blue and Methyl Orange on the Shells of Snails EA and EAC

The kinetic study of adsorption of methylene blue (MB) achieved on the EA powders before and after heat treatment to 500°C during 3 hours, show that the heat treatment has an influence on the capacity of the adsorption of these shells (**Figure 20**).

Besides, this survey prove that the capacity of adsorption is important in the first minutes with about 63% of MB adsorbed during the 10 first minutes against about 76% adsorbed at the end of 60 minutes (13% supplementary adsorbed in 50 minutes). Thus, if 63% of MB are adsorbed by EA during the 10 first minutes, only 11% are adsorbed by the heated shells (nearly 6 times less). In the same way, only 17% of MB are adsorbed by the heated shells at the end of 60 minutes against about 76% adsorbed by the raw shells. These differences are multi-factorial and are due to the modifications induced by the heat treatment (reduction of the specific surface of 64%, disappearance/denaturation of the organic matter, transformation of the aragonite to calcite).

3.4. Infra-Red Spectroscopic Analysis of the Residual Powders of the Shells

The infrared spectroscopic analysis of the residual shells powders, that are washed and dried, don't show strips of vibrations that one could assign to the presence of methylene blue fixed on the shells (**Figure 21**).

The **Table 3** indicates the frequencies of IR vibrations of the vestigial powders and the one of the raw shells.

The strips of vibrations observed are those of the calcium carbonates. They

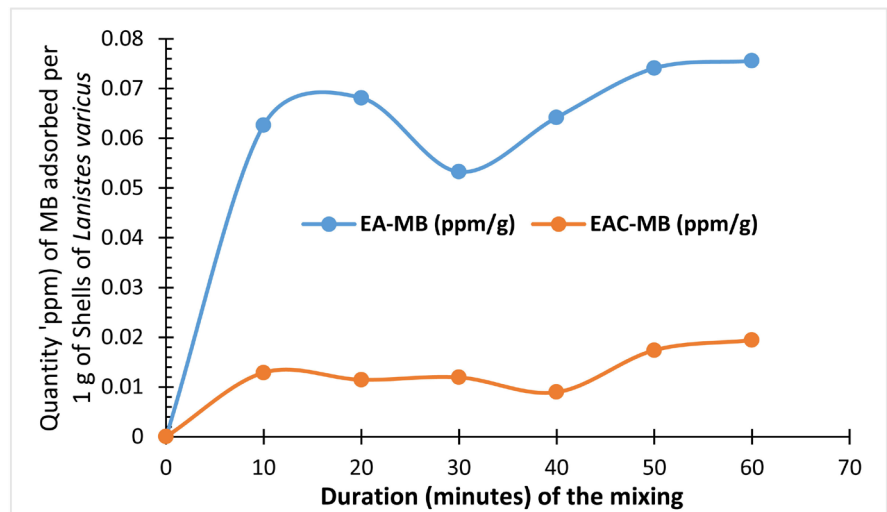


Figure 20. Quantities of BM fixed on *Lanistes varicus* shells as function of the duration of the mixing.

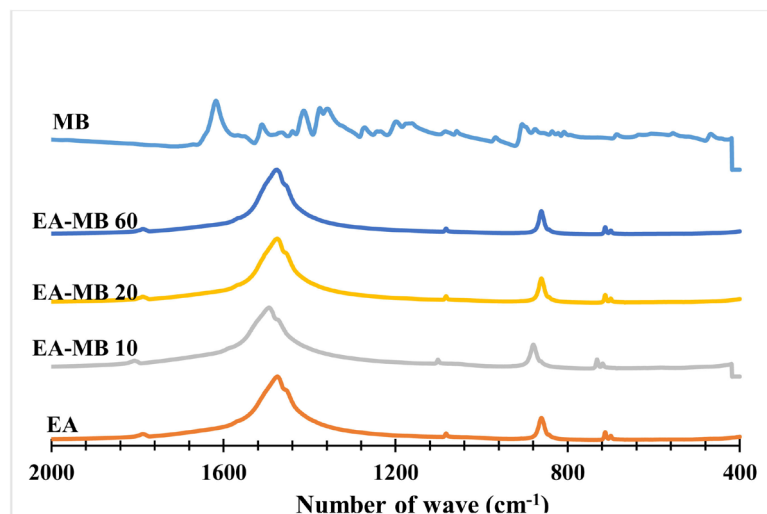


Figure 21. Infra-red spectrum of residual powders of *Lanistes varicus* shells after the adsorption of methylene blue.

Table 3. Frequency (cm⁻¹) of the vibration strips observed in infrared on the residual powders during the adsorption of methylene blue.

Frequency (cm ⁻¹)							Vibration associated
EA	EA-BM10	EA-BM20	EA-BM30	EA-BM40	EA-BM50	EA-BM60	
1787.86	1788.2	1787.95	1787.7	1788	1787.78	1787.75	$\nu_1 + \nu_4 (\text{CO}_3^{2-})$
1474.99	1475.19	1475.36	1475.84	1475.54	1476.01	1475.88	$\nu_3 (\text{CO}_3^{2-})$
1082.74	1082.72	1082.82	1082.83	1082.77	1082.82	1082.81	$\nu_1 (\text{CO}_3^{2-})$
861.09	860.93	861.16	861.29	861.03	861.13	861.28	$\nu_2 (\text{CO}_3^{2-})$
712.82	712.77	712.84	712.83	712.8	712.82	712.82	$\nu_4 (\text{CO}_3^{2-})$
699.91	699.82	699.91	699.92	699.86	699.9	699.91	$\nu_4 (\text{CO}_3^{2-})$

didn't undergo any meaningful displacements comparatively to the raw shell. The stage of abundant rinsing of the residues with water permitted to shell powder, to get rid of the molecules of methylene blue. Therefore, during the adsorption, there was not establishment of strong links between the molecules of methylene blue and the particles of shells.

This study shows that the sorption of methylene blue on the shells of the snails *Lanistes varicus* is not a chemisorption but rather a physisorption.

4. Conclusion

The survey achieved on two types of shells of snails of Benin (*Achatina achatina* and *Lanistes varicus*) permitted to show that the shells of these mollusks are constituted in the majority of calcium carbonate as aragonite (98%) and organic matter (2%). The methyl orange, an anionic dye, is not almost adsorbed in these shells because it develops a repulsion towards the organic matter and the carbonates of the shells. Besides the specific surfaces of the shells are decreased by a heat treatment to 500°C, which entailed a reduction of their capacity to adsorb the methylene blue, a cationic dye. The raw powders of shells of *Lanistes varicus* present a capacity of adsorption about 93% of methylene blue. In the same way, the shells of *Achatina achatina* adsorb methylene blue but their capacity of adsorption is less important than those of the shells of *Lanistes varicus*. This adsorption is more correlated with Freundlich model than Langmuir model. The shells of these mollusks could be used as no expensive biosorbent for the treatment of the sewages polluted by the organic dyes like methylene blue. These results completed with further applications will encourage, in evidence, the promotion of snails growing in Benin.

References

- [1] Sodjinou, E., Biaou, G. and Codjia J.C. (2002) Caractérisation du marché des escargots géants africains (achatines) dans les départements de l'Atlantique et du littoral au Sud-Bénin. *Tropicultura*, **20**, 8388.
- [2] Oladoja, N.A. and Aliu, Y.D. (2009) Snail Shell as Coagulant Aid in the Alum Precipitation of Malachite Green from Aqua System. *Journal of Hazardous Materials*, **164**, 1496-1502. <https://doi.org/10.1016/j.jhazmat.2008.09.114>
- [3] Balistrieri, L.S. and Murray, J.W. (1981) The Surface Chemistry of Goethite (α -FeOOH) in Major Ion Seawater. *American Journal of Science*, **281**, 788-806. <https://doi.org/10.2475/ajs.281.6.788>
- [4] Langmuir, I. (1916) The Adsorption of Gasses on Plane Surface of Glass, Mica and Platinum. *Journal of the American Chemical Society*, **40**, 1361-1368. <https://doi.org/10.1021/ja02242a004>
- [5] Freundlich, H.M.F. (1906) Uber Die Adsorption in Losungen. *Zeitschrift für physikalische Chemie*, **57**, 385-470.
- [6] Hameed, B.H., Ahmad, A.A. and Aziz, N. (2009) Adsorption of Reactive Dye on Palm-Oil Industry Waste: Equilibrium. Kinetic and Thermodynamic Studies. *Desalination*, **247**, 551-560. <https://doi.org/10.1016/j.desal.2008.08.005>

- [7] Elmoubarki, R., *et al.* (2014) Adsorption of Textile Dyes on Raw and Decanted Moroccan Clays: Kinetics, Equilibrium and Thermodynamics. *Water Resources and Industry*, **9**, 16-29. <https://doi.org/10.1016/j.wri.2014.11.001>