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Valorization of snail shell (Hélixaspersa) from Tangier-Tetouan region (north of Morocco): an application to eliminate methylene blue

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Abstract: Removal of industrial waste becomes increasingly critical for environmental protection. This study aims to search for effective and less expensive adsorbents in order to remove methylene blue (MB) commonly used in many industrial sectors. To this end, we experiment *Helix aspersa* snail shell as a biosorbent for the removal of MB. The raw snail shells were cleaned, smashed, and characterized afterwards using a scanning electron microscopy (SEM) coupled with an energy dispersive X-Ray analysis (EDX) and by X-ray diffraction. Different parameters were tested in order to identify the optimal conditions for the effective removal of MB. Our experimental results showed that, within the first ten minutes, a remarkable elimination of methylene blue dye reaching a percentage of 82%, with the following optimal conditions; 3.5 g of the adsorbent, initial MB concentration of 20 mg/L, the temperature of 15 °C, and agitation of 250 rpm. This study showed that the use of snail shell waste has inevitably a positive impact on the protection of the environment, in particular, the purification of industrial effluents.

Key words: Snail shell; biosorbent; removal; dye; methylene blue.

Introduction

Dyes are widely used in many industrial sectors including textile, paper, leather, and food industry. Dyes represent enormous risks to human health and the environment. They cause serious problems due to their stability and low biodegradability [1]. Furthermore, once degraded, dyes generate mutagenic or carcinogenic byproducts even more toxic than the dyes themselves [2].

Several research studies have investigated the toxic effects of dyes on human health. Among these dyes, methylene blue is capable of causing very harmful effects on living beings such as breathing difficulties, vomiting, diarrhea, and nausea [3].

Recently, several treatment techniques have been developed [4] such as coagulation/flocculation [5], irradiation [6], filtration [7], photo-degradation by catalysis [8], biological treatment [9], and activated carbon adsorption [10]. The use of activated carbons has many disadvantages generally related to its regeneration difficulty and its relatively high cost [11]. For this reason, several studies focused on finding other low-cost adsorbent materials available locally and made from natural resources including *Coriandrum sativum* seeds [12], orange sawdust [13], chitosan-coated diatomaceous earth to removal heavy metals [14, 15, 16].

Nowadays, the reuse of shell waste (crab, mussels, snail eggs, oysters, etc.) becomes the focus of concern [17, 18]. Given its wide range of applications [19, 20], these natural materials are known for their respect for the environment, their availability, recyclability, and low cost.

The snail shell belongs to the Mollusc (Gastropoda). Several studies have been carried out on the snail shell. The shells were used as a good substitute for commercial CaCO3 [21,22], as a coagulant in the precipitation of the malachite green of the aquatic system [23], or as a source of calcium for the preparation of hydroxyapatite [24,25]. It has as well considerable values in the cosmetics and medicinal fields [26, 27].

The choice of using snail shells is justified by the fact that the production of biomass is less expensive, it allows the valorization of local products, but also it is a safe method to eliminate wastewater pollutants particularly the dyes.

In this work, we studied an adsorbent based on snail shell (*Hélix aspersa*) collected from the region of Tangier-Tetouan (northern Morocco). We used this raw adsorbent for the removal of methylene blue

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dye in synthetic solutions. Different experimental parameters were optimized such as adsorbent mass, temperature, and agitation.

Materials and methods

Experimental

In the context of green chemistry, the snail shell sof *Helix aspersa* were recovered from a snail vendor, (the spicy snail is a traditional recipe very popular in Morocco), located in Tangier and Tetouan (northern Morocco). According to the various samples tested for snail shell, it was found in this study that it is possible to work with the snail shell in its raw state without any pre-treatment.

Preparation of adsorbent

These bio wastes were first washed with tap water to remove surface impurities. Then, it was dried at 110 °C in the oven for 24 hours. Subsequently, they were crushed and sieved to obtain uniform particles. The particles size retained have a diameter between 0.20 and 0.80 mm. The shell powder is packaged in small boxes and stored in a desiccator. (**Picture.1**)

Picture 1: the stages of adsorbent preparation

Methylene blue

Methylene blue is a cationic dye of empirical formula: $C_{16}H_{18}ClN_3S$ (FIG. 1).

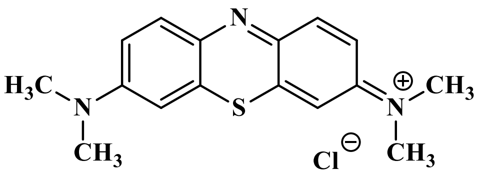

Figure 1. Chemical Structure of Methylene Blue [27]

Its molar mass is 319.852 g/mol. It is soluble in water (50 g/L at 20 °C) and slightly in ethanol (10 g/L at 20 °C). This dye is chosen as a representative model for medium-sized organic pollutants [27]. The used solutions are obtained by dissolving one gram of the methylene blue powder in one litter of distilled water.

Analysis method

The adsorption experiments were carried out by stirring 1g of the snail shell-based biomass that prepared with 100mL of the synthetic methylene blue (MB) solution in an orbital shaker (IKAKScontrol 4000 I), controlling the temperature and agitation.

Samples were taken every 10 min within 60 min, and the suspensions were filtered through 0.45 µm membrane filters (Durapore®-Millipore). The measurements of MB concentrations are made by UV-V is spectrophotometer (Varian Cary® Type 50 UV-Vis) at a maximum wavelength of 662 nm. MB adsorption at equilibrium q_e (mg/g) and percent removals (% removal) were calculated using the equations (1) and (2), respectively:

$$Q_{ads} = \frac{(C_0 - C_{eq})}{m} * V \quad (1)$$

The yield of adsorption:

$$Yield(\%) = 100 * \frac{(C_0 - C_{eq})}{C_0} \quad (2)$$

Q_{ads}: adsorbed amount in mg/g;
C_0: initial concentration of methylene blue in mg/L;
C: equilibrium concentration of methylene blue in mg/L;
V: volume of solution in mL;
m: mass of biomass in g.

Characterization of the shell

The characterization of the snail shell is an important analysis for understanding the behaviour or mechanism of MB elimination. The samples were characterized by the following two methods:

a- The morphology of the snail shell powder was observed using a scanning electron microscopy "Hirox scanning electron microscopy (SEM)"coupled with an Energy Dispersive X-ray analysis system(EDX). The images of the microstructure were obtained with a maximum acceleration voltage of 20Kv.

b- X-Ray diffraction (XRD), the device used is coupled with diffractometer PHILIPS PW 1710. Kα radiation of cooper (λ = 1.5406 Å) was used.

Results and Discussions

Characterization by scanning electron microscopy (SEM)

The observation of the samples by scanning electron microscopy (SEM) allowed us to visualize the morphology of the biomass prepared with snail shell (Figure 2).

The shell of mollusk is generally composed of limestone composed of 95% calcite and calcium carbonate [28].

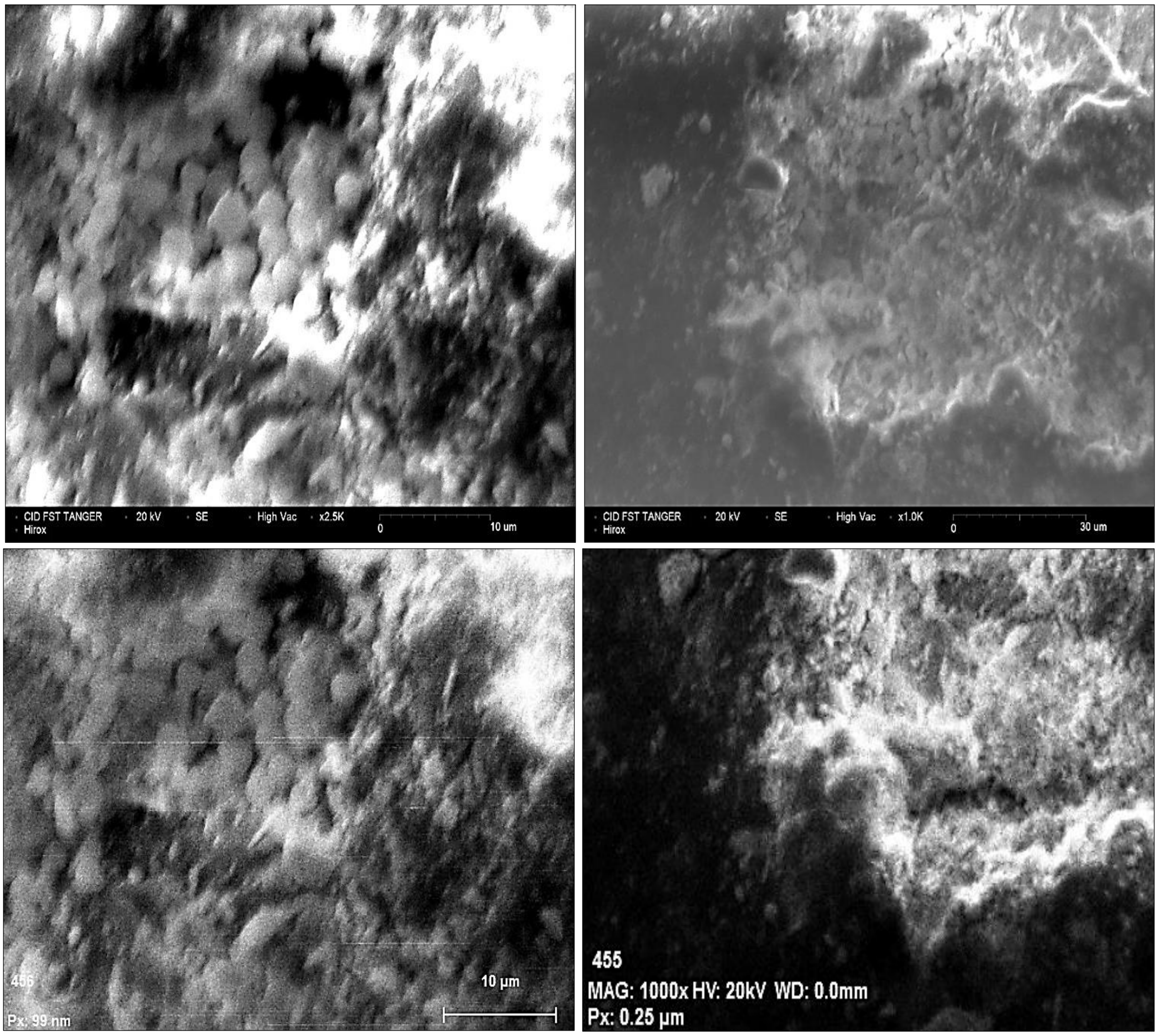

Figure 2. Scanning electron micrographs of the raw snail shell at different resolutions

Figure 2 shows that the shells structure of our sample has a granular morphology. According to previous works [29], this arrangement is called microstructure, and may be present mainly in trigonal polymorphic calcite, or may be present in aragonite, orthorhombic polymorph of CaCO3. Both elements (calcite and aragonite) have an identical chemical composition. This microstructure can be, according to its internal order, prismatic or pearled, lamellar or homogeneous and foliated [29].

In our opinion, and according to Figure 2, we believe that our sample has a pearlescent microstructure. To confirm this result; we performed an X-ray diffraction analysis.

The elemental composition of the snail shell is illustrated by the EDX spectrum in Figure 3.

According to the EDX microanalysis, the main elements are calcium, oxygen and carbon, with weight percentages are respectively 50.59%, 35.27%, and 14.04%. These data are grouped in Table 1.

Table 1. EDX Elemental Analysis (Mass and Atomic Percentage of Snail Shell).

Elements	**Weight %**	**% Atom**
Calcium	50.59	27.21
Carbon	14.04	25.19
Oxygen	35.27	47.52
Silicon	0.10	0.08
Total	100.00	100.00

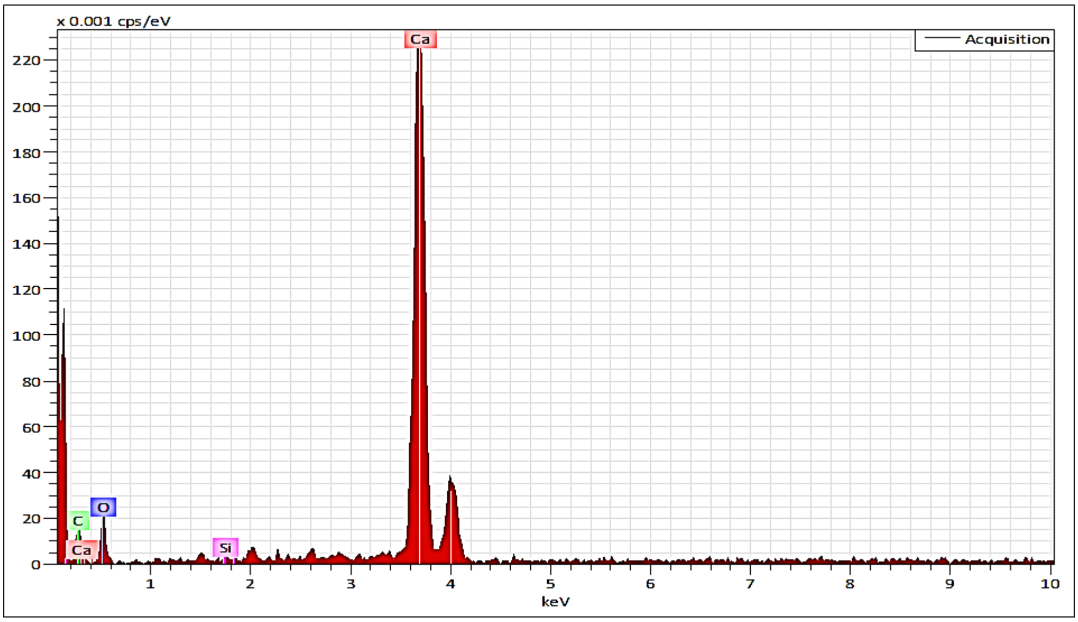

Figure 3. Representation of the energy dispersive X-Ray peaks (EDX) of the raw shell.

X-Ray Diffraction (XRD)

The X-ray diffraction analysis results of the raw shell are presented in Figure 4. Table 2 reports the crystallographic parameters of the raw shell. The latter crystallizes in a hexagonal system. Having a constant lattice orthorhombic crystal system, a = 4.940 Å, b = 7.940 Å, c = 5.720 Å and unit cell volume V=224.36 Å. By comparing values a, b, and c of this biomass by those reported in the literature, it is suggested that the crystalline phase present in the shell is aragonite. These results confirm that the presence of aragonite in the shells is in agreement with the bibliographic works [28]. We can agree that the shell used in this study is composed mainly of polygonal aragonite crystals. X-ray diffraction was used to confirm the microstructure of our sample.

Table 2. Crystallographic parameters of the raw shell.

Formula	$CaCO_3$
Name	Calcium Carbonate
Name(mineral)	Aragonite
Name(commun)	$_{Y}$-$CaCO_3$
Lattice	Orthorhombic
Mol.weight	100.09
Volume[CD]	224.36
Dm	2.94
I/Icor	-1.000
A	4.940
B	7.940
C	5.720
$^{a}/_{b}$	0.62217
$^{c}/_{b}$	0.72040

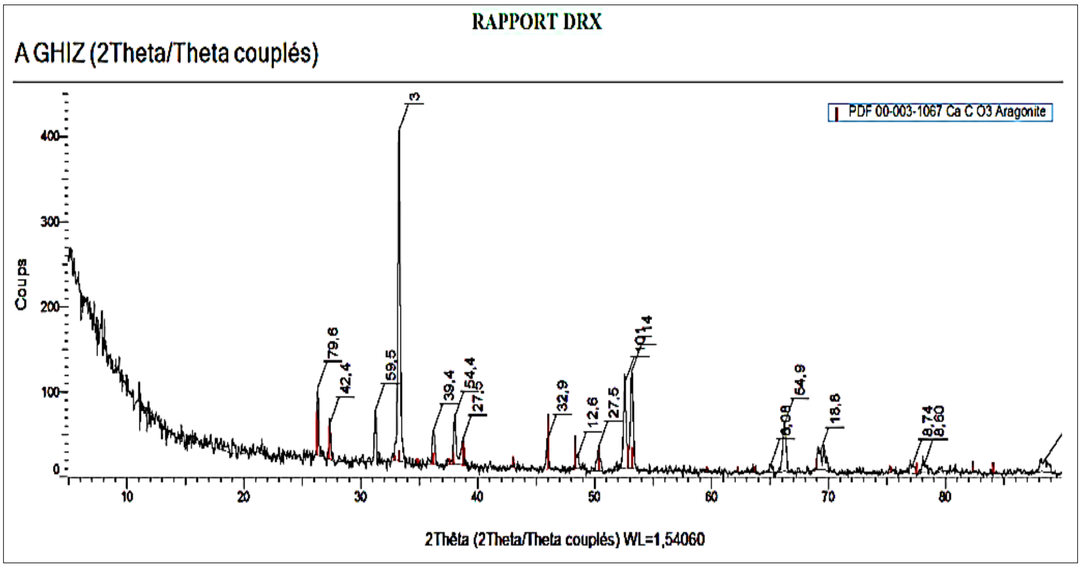

Figure 4. X-ray diffractogram of the raw snail shell used

Adsorption test of methylene blue by a snail shell

The choice of samples

In order to evaluate the optimal adsorption capacity of methylene blue by the snail shell, a series of samples was prepared by varying the mode, time, and heating shelf (Table 3).

Table 3. The different samples tested for the snail shell.

Samples(T°)	300°C /h						400°C/h	0°(raw)
Time spent in the oven (h)	1h	2h	3h	4h	24h	48h	24h	0h

Adsorption test

According to Table 3, a series of experiments were conducted using 100 mL of the 20 mg/L methylene blue solution, to which different samples of the activated and raw shells were added. The objective of this experiment is to optimize the elimination rate in order to obtain efficient adsorption of methylene blue using the raw and activated shell at a different temperature.

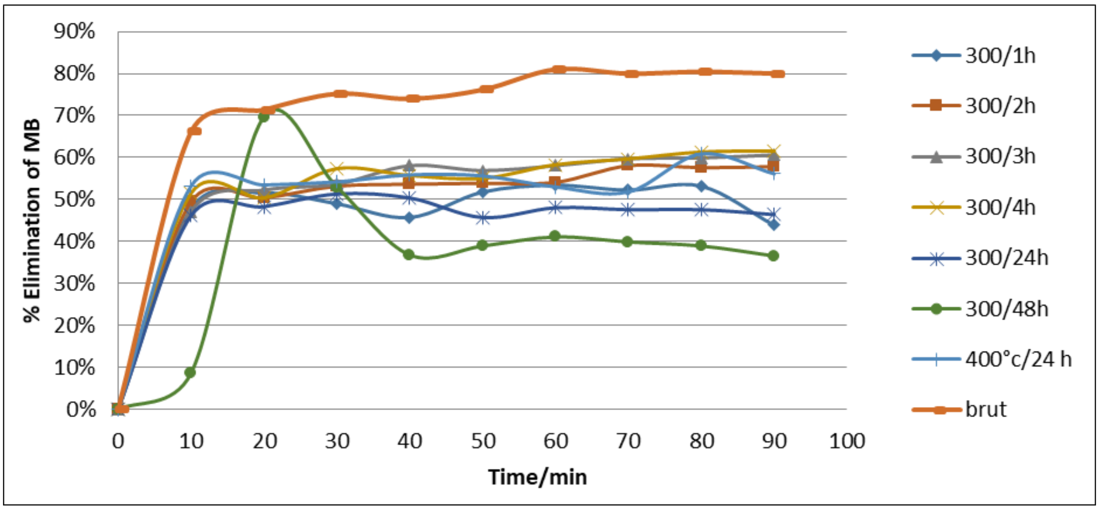

Figure 5. Adsorption test samples of raw and activated snail shells on the adsorption of MB dye.

Figure 5 shows that raw snail shine staining rates are higher compared to those obtained by adsorption on activated shells. Results show that the temperature of shell activation has a negative influence on the adsorption capacity of MB. This result can be due to the nature of the interactions of different samples with MB.

For economic reasons, the subsequent study of the MB dye adsorption process will be performed using raw snail shells without any prior treatment, and look for the optimization of several experimental parameters.

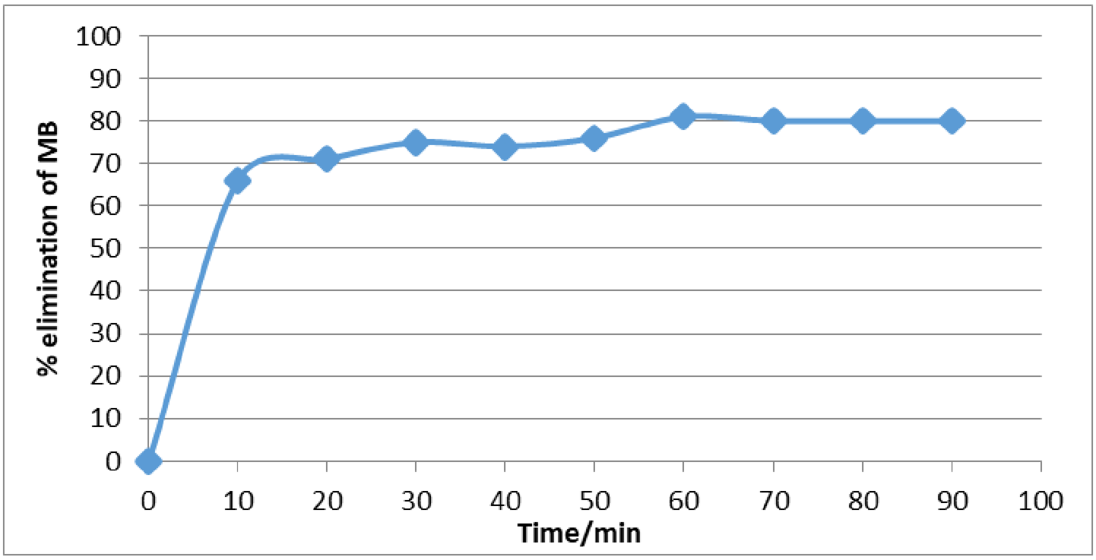

Figure 6. The adsorption kinetics of MB

Time effect of contact

To determine the time necessary to reach the MB adsorption equilibrium, experiments were carried out on a 1g of the snail shell and a volume of 100mL of MB of concentration equal to 20mg/L, with stirring at 200 rpm at room temperature. Figure 6 illustrates the percentage of changes in MB removals as a function of time.

The curve in Figure 6 shows that the adsorption kinetics of MB has two distinct stages; the first one is characterized by rapid adsorption during the first 10 minutes, this is due to the adsorption of MB at the surface of adsorbent's particles which can be explained by the high number of activated sites available. In the second stage, the occupation of deep adsorbent sites requires the diffusion of the adsorbed molecule within the microspores of adsorbent. As the recovery rate of the surface increases, accessibility to available sites becomes more and more difficult. Consequently, adsorption speed becomes slower until reaching the equilibrium after the majority of active sites were occupied by MB ions.

All these results told us that the equilibrium would be established after 60 minutes. Beyond this time, the adsorbed amount remains substantially constant. Therefore, in the rest of our study, we will work with a 60-minute equilibrium time.

Mass effect

The mass effect of the adsorbent was studied for 60 min at room temperature by varying the mass of the snail shell from 0.5 g to 5 g, on a MB solution (100 mL, 20 mg/mL), stirring speed is at 200 rpm (Figure 7).

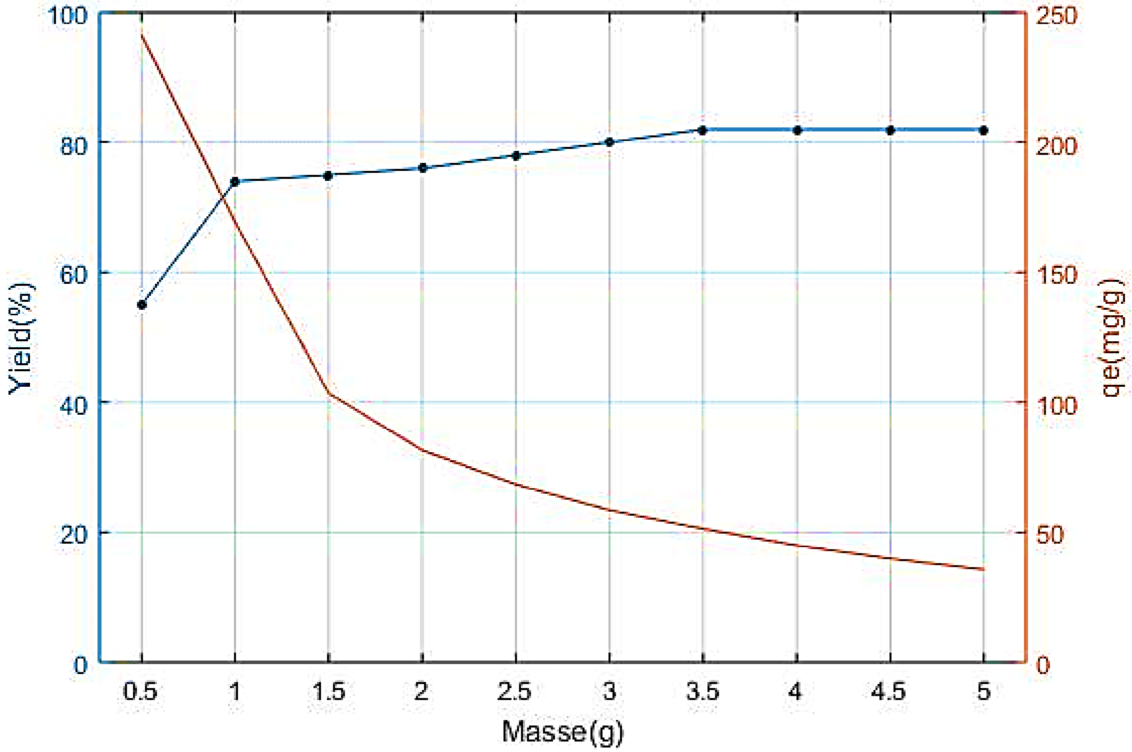

Figure 7. Percentage of elimination of MB as a function of shell mass

The results of Figure 7 show that when we increase the mass of the adsorbent from 1 g to 5 g the percentage of methylene blue removal increases to reach 82% for 3.5 g/100mL of adsorbent. From 3.5g of biomass, the percentage of MB elimination is no longer evolving and remains constant. This behavior may be due to the number of adsorption sites, which increases with the amount of adsorbent to a mass of 3.5g/L, from which the number of sites becomes stable [30]. These results can be explained as follows; at the beginning of the experiment, there is high availability of both adsorbent biomass and activated sites, in which more MB ions can be attached to those sites. At equilibrium, there is no enough available site for MB ions. Therefore the elimination process is no longer evolving and remains constant.

Stirring speed effect

In order to study the influence of the stirring speed on the adsorption of MB, we set the following operating conditions: volume of MB 100 mL, shell mass 3.5 g and contact time 60 minutes at room temperature.

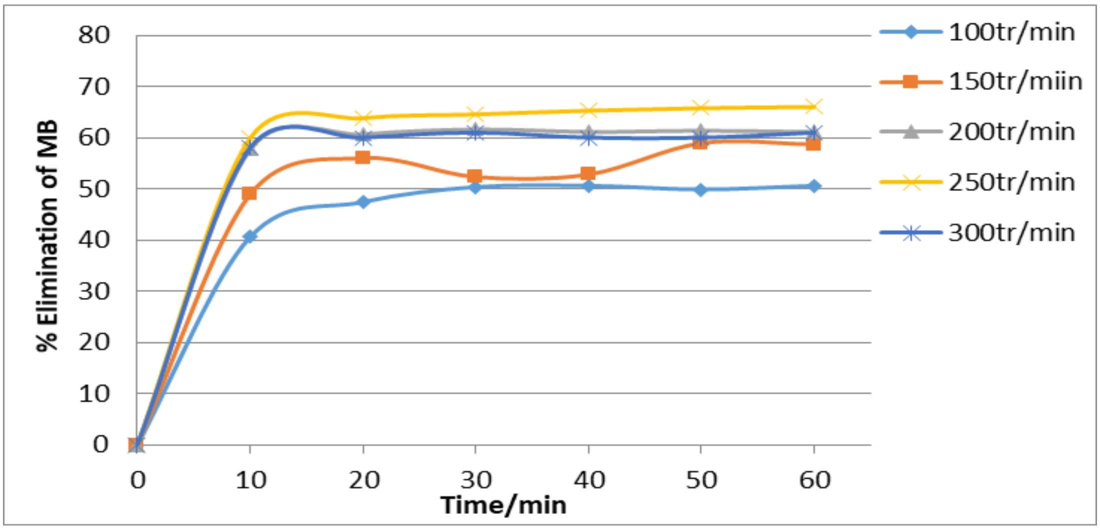

Figure 8. Influence of stirring rate on methylene blue adsorption.

Several agitations were tested as shown in Figure 8. For a low agitation (from 100 to 150 rpm), the percentage of MB removal is less than 60%. For a moderate agitation (~250 rpm), the adsorption was optimal and reached more than 70% removal of MB. However, for high agitation (>=300 rpm), the removal rate of MB is reduced.

Effect of temperature

In order to obtain an optimal temperature for better adsorption by snail shells, tests have been made using a thermostatic orbital stirrer to maintain the desired value between 15 °C and 40 °C).

The experiments were carried out by adding 1 g/L of the shell to the MB solution (100 mL) and a stirring speed of 250 rpm.

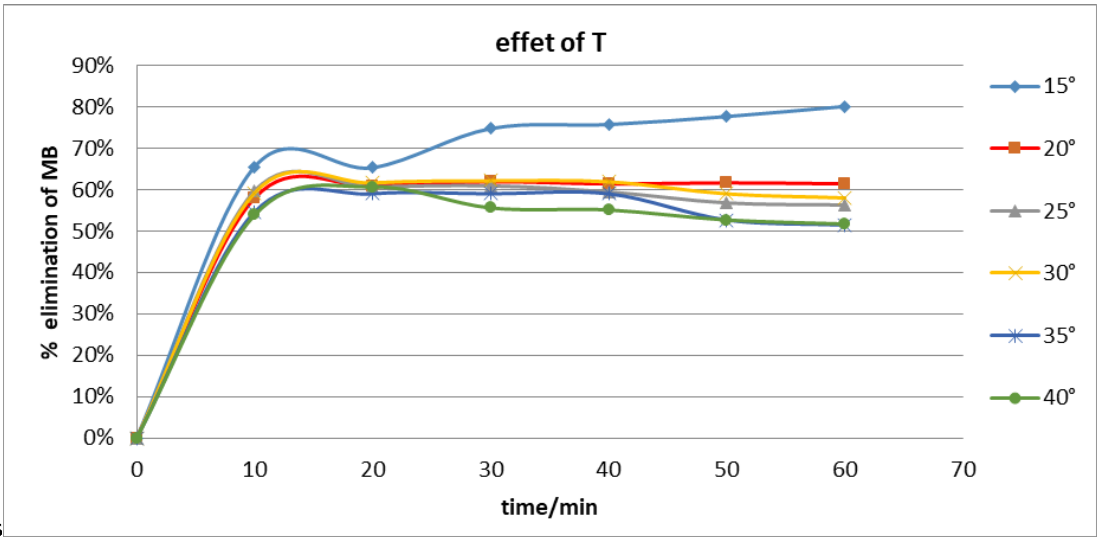

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Figure 9. Effect of temperature on the adsorption of the MB by the snail shell

Figure 9 shows that the best results are obtained at a temperature of 15 °C. It can be concluded that the increase in temperature decreases the rate of MB removal, indicating that the reaction is exothermic.

The reason for the decreasing removal of MB at high temperature is the increased solubility of MB ions in the solution at high temperature, which weakens the interaction forces between MB ions and active sites in the shell snail. As a result, MB ions are more difficult to adsorb at high temperatures. Therefore, the low temperatures are favorable for the removal of MB ions by snail shells. Therefore, high temperature hinders the progress of the adsorption phenomenon [31].

Conclusion

In this study, a new raw snail shell material was tested, without any treatment (thermal or chemical), by a simple, cost-effective, and quick method to minimize the costs of dye pollution treatments — industrial methylene blue on the one hand, and the other hand a recovery of bio-waste used.

The optimal conditions for better elimination can be summarized as follows: temperature of 15°C, agitation of 250 rpm, and 3.5 g of biomass corresponding to the elimination of 82% of MB.

The results obtained are promising and encouraging to consider a complete study in order to show that the adsorbent chosen for this study is effective and could be used as an economic adsorbent for industrial effluents.

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