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Removal of Methyl Violet in Aqueous Solution on Activated Carbon Based on *Saba senegalensis* Shell Residues

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Abstract

Adsorption on activated carbon is one of the most widely used methods for the removal of dyes. The objective of this study is to valorize the shells of *Saba senegalensis* from local product in Senegal in the form of activated carbon and to test its effectiveness for the removal of methyl violet. The study was carried out in batch mode for a maximum duration of one hour with 100 mL of solution treated at 600 rpm. The results reveal that the granulometry 500 μm gives the best yield with an adsorption rate of 95%, a mass of adsorbent of 0.2 g gives an adsorption capacity of 20 mg/g, the contact time of one hour with a capacity of 5 mg/g. The study also showed that the adsorption process of methyl violet is described by the pseudo-second order kinetic model with correlation coefficient of 0.99. Two adsorption isotherms were studied, and the results revealed that the Freundlich model better describes the adsorption of methyl violet on *Saba senegalensis* shell residue-based activated carbon (SSSRAC). The results indicate that SSSRAC could be used as a low-cost alternative for the removal of textile dyes such as methyl violet.

Keywords

Methyl Violet, Adsorption, Activated Carbon, *Saba senegalensis* Shell

1. Introduction

Dye was described as a large group of industrial chemical with over 700,000 tons of waste produced annually (Jayarajan et al., 2011). It's used in carpet, textile industry, food industry, paper, pharmaceutical industry, and leather industry.

Wastewater produced from factories causes environmental pollution (Konsowa, 2003). One of the most widely used cationic dyes is methyl violet, categorized in phenylmethane cationic dyes. This dye gives an intensive violet color to water when dissolved. Consequently, it reduces the light penetration into water and disrupts the process of photosynthesis (Mittal et al., 2021). Methyl violet has poisonous and mutagenic effect on humans and animals as allergic dermatitis, skin irritation, and mutation in humans. Dyes could be grouped into several types such as direct dyes, reactive dyes, vat dyes, disperse dyes, and azo dyes (Korkmaz et al., 2013).

Currently, some techniques have been developed for removal of methyl violet dye from wastewater as reported by many researchers. For example, ion exchange, biodegradation, oxidation, membrane process, adsorption and solvent extraction were discussed (Kaci et al., 2022; Sarnaik & Kanekar, 1999; Wu et al., 2008). However, most of these methods appear to be very expensive, and difficult to implement techniques, whereas adsorption is an efficient method for the removal of methyl violet. Adsorption is one of the most effective methods for removing different types of colors from waste water using activated carbon and it gives the best result, since commercially available activated carbon is very expensive (Bello et al., 2011). Most adsorbent has been used for removal dyes in waste water, powdered activated carbon is an excellent adsorbent that offers high surface area for the adsorption of organic and inorganic contaminants from water. Any cheap material, with a high carbon content and low inorganics, can be used as a raw material for the production of activated carbone because of their availability at a low price. They can be used for the production of Activated Carbon with a high adsorption capacity, considerable mechanical strength, and low ash content (Savova et al., 2001). Literature survey indicates that there have been many attempts to obtain low-cost Activated Carbon or adsorbent from agricultural wastes such as wheat, corn straw, olive stones, bagasse, birch wood, miscanthus, sunflower shell, pinecone, rapeseed, cotton residues, olive residues, pine rayed, *Eucalyptus maculata*, sugar cane bagasse, almond shells, peach stones, grape seeds, straw, oat hulls, corn stover, apricot stones, cotton stalk, cherry stones, peanut hull and rice straw (Abbas, 2021; Aghababaei et al., 2021; Charoensook et al., 2021; Cheng et al., 2021; Demiral et al., 2021; Thithai & Choi, 2020; Wang et al., 2021). *Senegalensis saba* hulls are refrozen residue in the environment while they contain a large amount of carbon (Demirbas, 2009; Salamata et al., 2020) and other compounds based on silica and carbonate. This study is part of the recovery of its residue as an adsorbent for the removal of methyl violet. The aim of this study is the valorization of *Senegalese Saba* shell residue as adsorbent materials for the removal of dyes.

2. Material and Methods

2.1. Preparation of the Absorption Material

Saba senegalensis hulls were used as raw material as adsorbent in this study. After washing, they were dried in the oven at a temperature of 105˚C for 24 hours. After the grinding operation, the obtained powder was impregnated with a mass of phosphoric acid (H_3PO_4) equal to the quantity of adsorbent. This was placed in a muffle furnace at 400˚C for 1 hour. Finally, the carbon was neutralized using a sodium carbonate solution (Na_2CO_3) with a concentration of 100 g/L.

2.2. Methods

2.2.1. Characterization of the Adsorbent

- **Elementary composition**

For the analysis of the adsorption material, we used an X-ray fluorescence spectrometer (Niton XLT900s). Indeed, a mass of 1.2 g of the sample was weighed, mixed with 0.12 g of additive better known as "binder" in order to obtain a good pellet.

- **Granulometry**

The determination of the particle size of the material was carried out using a series of manual sieves with different pore sizes: >160 μm, >400 μm, >500 μm, >800 μm. The sieving operation consists in manually shaking the whole above a container or a support to avoid any loss.

2.2.2. Experimental Procedure

The removal of methyl violet on the activated *Saba senegalensis* hull powder made it possible to determine the optimal parameters for adsorption of the dye on the adsorbent material (**Figure 1**).

The study parameters are: particle size, contact time, adsorbent mass, dye concentration, solution pH and temperature. For each test, a constant volume of 100 mL of colored solution is brought into contact with the adsorbent in an Erlenmeyer flask (250 mL). The mixture is agitated for a period of 60 min at ambient temperature, with the exception of the tests on the contact time and the temperature where these two parameters respectively are not fixed. UV-visible spectrophotometry was used as a technique for the determination of methyl violet concentration before and after adsorption at a wavelength of 585 nm. Thus, the quantity (q_t) of adsorbed dye is given by the following relationship:

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

The percentage of discoloration (R) is calculated by the following relationship:

Figure 1. *Saba senegalensis* materials.

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

With:

q_t: the fixed quantity of colorant per gram of adsorbent (mg/g) at time t; C_0: initial concentration of dye (mg/L); C_t: concentration of dye over time (mg/L); V: volume of the used solution (L); m: mass of adsorbent used (g).

3. Results and Discussion

3.1. Chemical Characterization of the Material

The elementary chemical composition of the adsorption material is shown in Table 1.

The chemical composition of the adsorption material shows that the contents of the toxic elements are below the detection limit and a composition of the low mineral elements.

3.2. Adsorption of Methyl Violet on *Saba senegalensis* Shell

3.2.1. Effect of Particle Size

Four types of absorbent particle sizes were used to study their effects on methyl violet adsorption (Figure 2).

For the study of the effect of particle size adsorption rates greater than 90% are observed. The rate of removal of methyl violet is greater for particle sizes between 500 and 800 µm. The particle size between 500 and 800 µm is therefore considered to be the optimum adsorbent particle size with a removal percentage of 94.93%.

Table 1. Chemical composition of *Saba senegalensis* shell powder.

Elements	Pb	Al	Cu	Fe	Mn	Ca	Si	Zn	Cd	K	P	As
%	<LD	<LD	0.06	0.04	0.15	1.10	5.77	0.01	<LD	9.73	0.23	<LD

LD: Limit of detection.

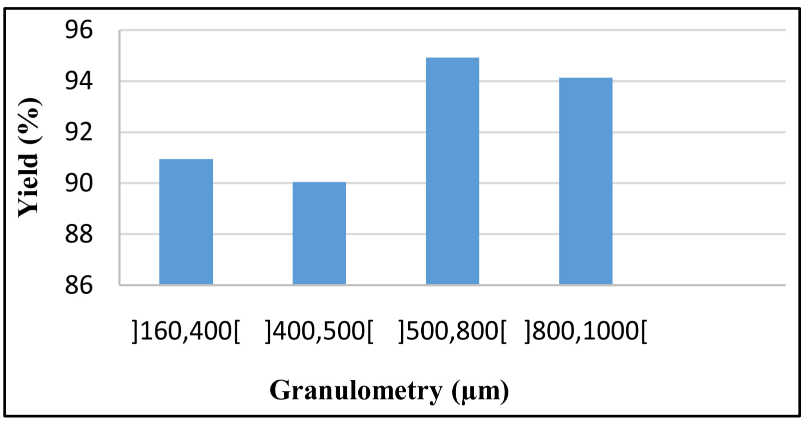

Figure 2. Rate of removal of methyl violet after 60 min according to the size of the particles (M_{ads} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

3.2.2. Contact Time Influence

Figure 3 represents the evolution of the adsorption capacity of the absorption material and the removal rate of methyl violet as a function of contact time.

The results indicate that the removal rate increases progressively during the first 30 min (reaching 89.64% or a capacity of 4.48 mg/g) due to the availability of active sites on the surface of the adsorbent. , and slowly up to 40 min with a capacity of 4.71 mg/g and a dye removal efficiency of 94.18%, then stabilizes during the remaining time. The optimal contact time for our adsorption is 40 minutes.

3.2.3. Influence of Adsorbent Mass

Figure 4 describes the evolution of the adsorption efficiency of methyl violet and the adsorption capacity of the material as a function of the mass of the adsorbent.

The results show that the rate of removal increases according to the mass until reaching its maximum value of 94.93% for 1 g of adsorbent thereafter we note that the rate is relatively constant in spite of weak reductions.

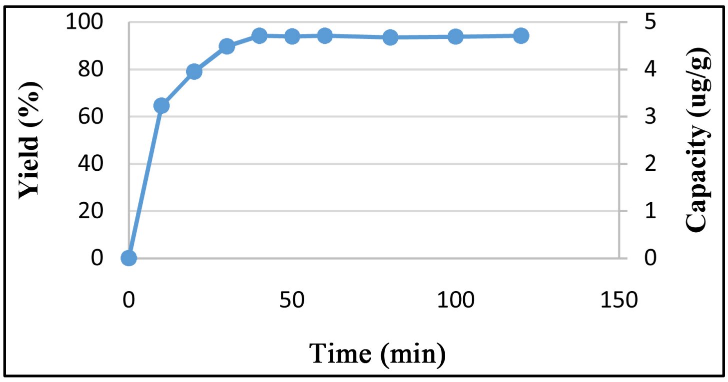

Figure 3. Methyl violet removal rate and adsorption capacity of the material as a function of contact time (M_{ads} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

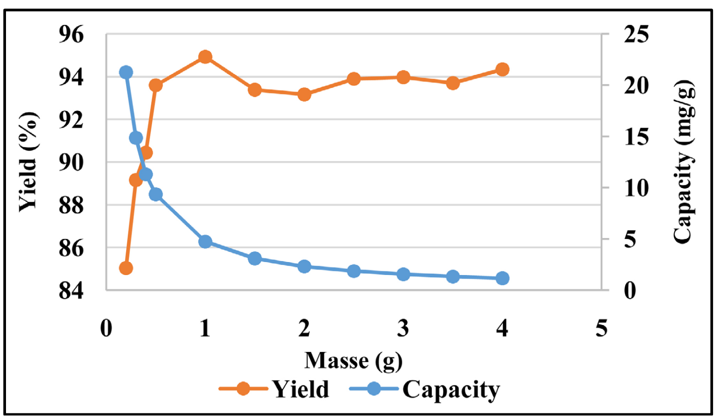

Figure 4. Methyl violet removal rate and adsorption capacity after 60 min as a function of adsorbent mass (M_{ads} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

3.2.4. Influence of Solution pH on Adsorption

Figure 5 corresponds to the results of tests on the effect of pH in relation to the removal of methyl violet in solution on the absorption material.

Figure 5 shows an increase in yield from 94.18% to 95.48%, respectively for the values of pH = 4 and pH = 5. According to the results observed, the removal of methyl violet is more appropriate in an acid medium.

3.2.5 Influence of Temperature

The results in Figure 6 represent the adsorption percentages of methyl violet on the material at different operating temperatures.

We noted a minimum adsorption rate of 94.93% at 25˚C and a maximum retention rate at 80˚C for 99.05%. Indeed, the increase in temperature promotes the mobility of methyl violet ions but also the penetration of these ions on the different active sites of the material.

3.3. Methyl Violet Adsorption Kinetics

The kinetics of adsorption allowed us to know the type of kinetic model chosen for the adsorption, the results of the experiments are mentioned (Figure 7).

Results obtained by applying the pseudo-second-order kinetic model are shown in Figure 8.

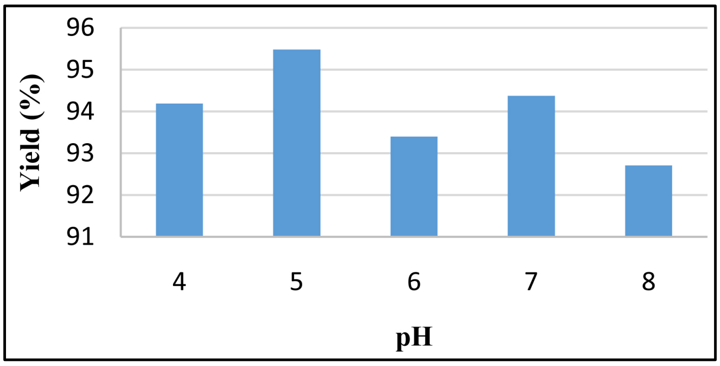

Figure 5. Methyl violet removal rate after 40 min as a function of the pH of the solution (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

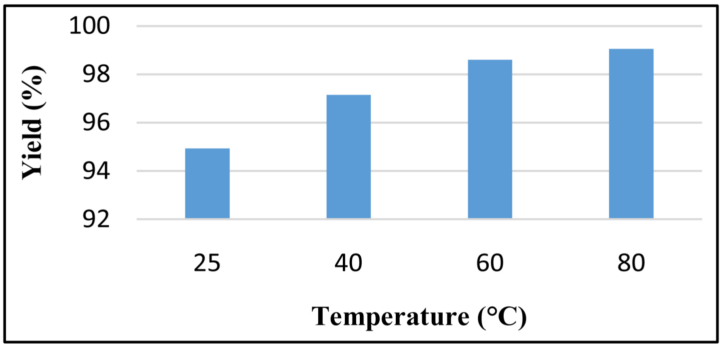

Figure 6. Rate of removal of methyl violet on the material after 60 min as a function of temperature (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

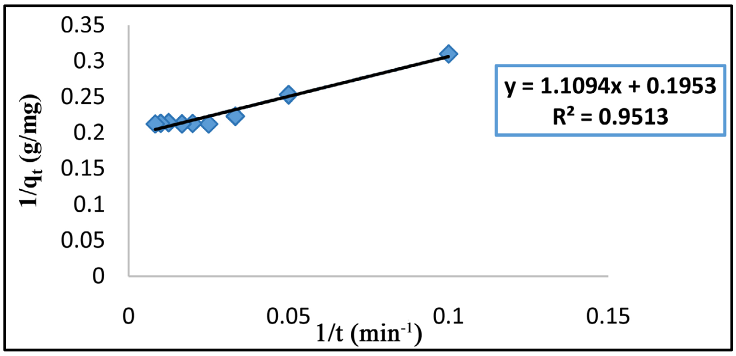

Figure 7. Modeling of the pseudo-first order adsorption kinetics of methyl violet (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

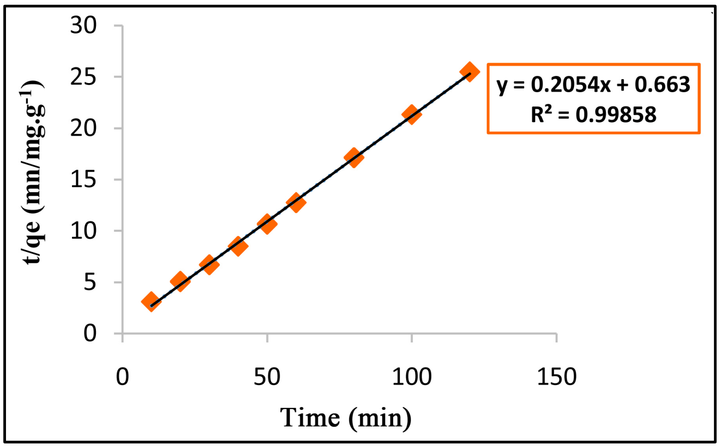

Figure 8. Modeling of the pseudo-second order adsorption kinetics of methyl violet (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

These results show a linear variation of t/qt as a function of t. The parameters of the two kinetic models are grouped in Table 2.

The table shows us that the *Lagergren* equation is not applicable in the case of the discoloration of the methyl violet solution and its regression coefficient is R^2 = 0.95 while the adsorption kinetics of methyl violet reproduced by the pseudo-second order kinetic model gives a significant correlation coefficient R^2 = 0.99.

3.4. Methyl Violet Adsorption Isotherms

The monitoring of the evolution of Qe as a function of Ce according to the classification of Giles et al., the evolution of 1/Qe as a function of 1/Ce according to the Langmuir model and of the evolution of logQe as a function of logCe according to the Freundlich model made it possible to calculate the maximum adsorption capacity as well as the adsorption parameters according to the mathematical models. The results obtained are respectively illustrated in Figures 9-11.

- **Classification of Giles et al.**

The evolution of the curve in Figure 9 would correspond to form C according to the classification of Giles et al.

Table 2. Pseudo-first and pseudo-second order kinetic parameters for the retention of methyl violet.

Kinetic models	q_e (exp) in $mg \cdot g^{-1}$	q_e (th) in $mg \cdot g^{-1}$	Correlation coefficients (R^2)	Speed constants (K_1, K_2)
Pseudo first order	4.71	5.12	0.95	5.68 min^{-1}
Pseudo second order	4.71	4.87	0.99	0.064 $g \cdot mol^{-1} \cdot min^{-1}$

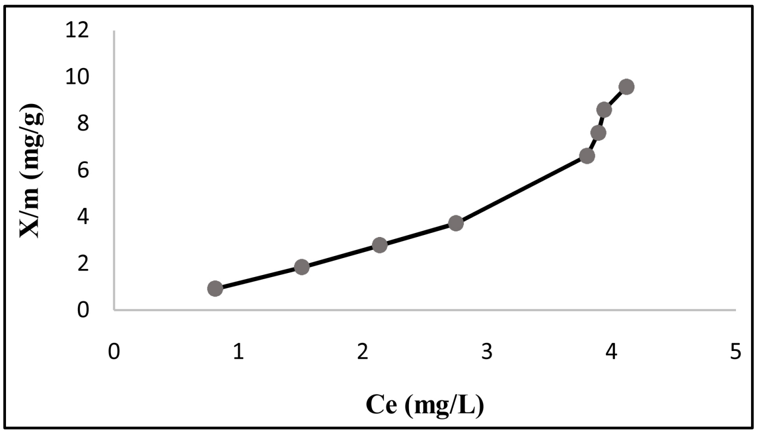

Figure 9. Methyl violet adsorption isotherm (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

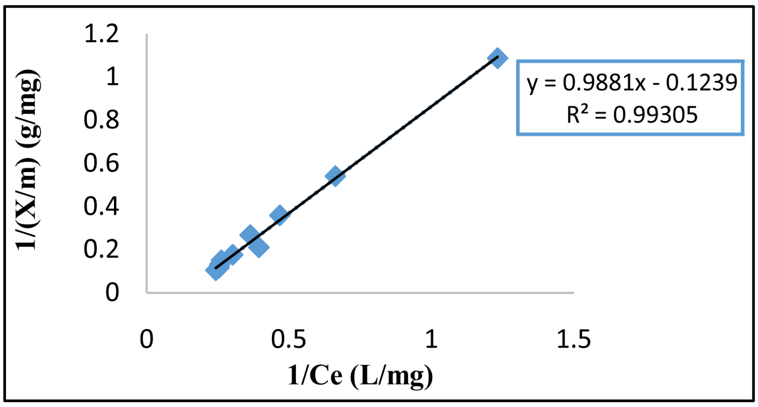

Figure 10. Methyl violet adsorption isotherms according to the Langmuir model. (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

- **Langmuir Isotherm**

Figure 10 indicates a correlation coefficient (R = 0.99), however we see that the ordinate at the origin of the equation of the line is negative (−0.1239) which is physically impossible. Indeed, in the literature this phenomenon is explained as being the result of low residual concentrations, which implies that the equilibrium curve is generally very close to a straight line.

- **Freundlich isotherm**

The equation has a correlation coefficient $R^2 = 0.9691$. The linear representations of the experimental values of this adsorption process made it possible to determine the equilibrium parameters and the values of the Langmuir and Freundlich constants calculated by linear regression (Table 3).

According to these results in Table 3, we can conclude that:

- The Freundlich model better describes methyl violet adsorption;
- Adsorption is favorable because the material support can be considered as a good adsorbent for the removal of methyl violet in aqueous solution;
- According to the Freundlich model, the phenomenon of methyl violet adsorption refers to non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption.

3.5. Thermodynamic Parameters

The evolution of $\ln k_d$ as a function of 1/T in Figure 12 allowed us to deduce the thermodynamic quantities relating to the adsorbent/adsorbate system studied (Table 4).

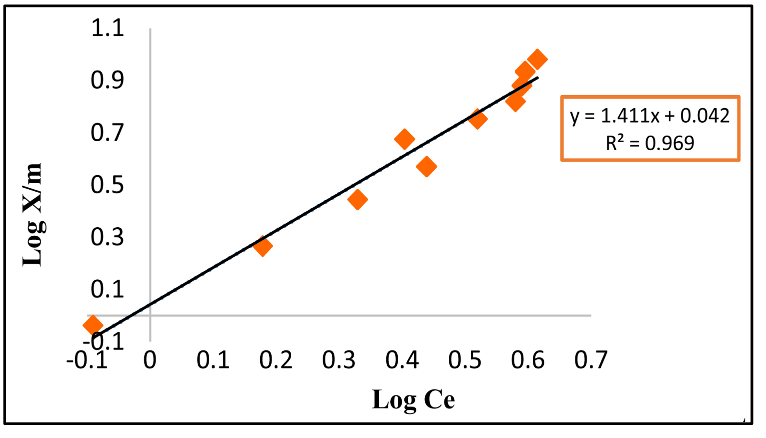

Figure 11. Methyl violet adsorption isotherms according to the Freundlich model. (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

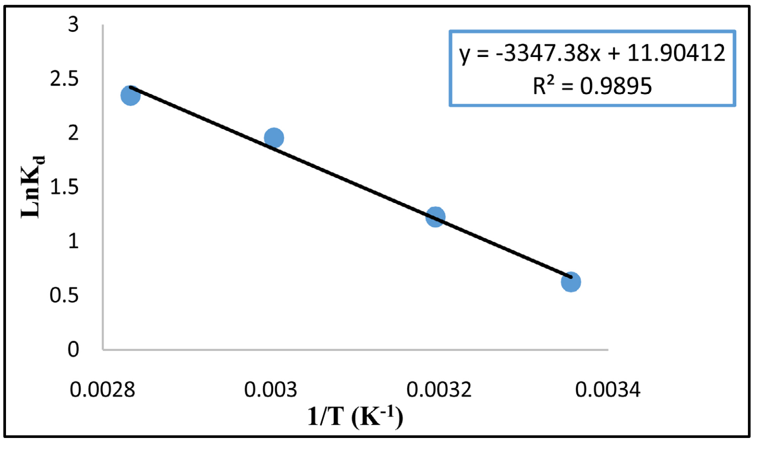

Figure 12. Effect of temperature on methyl violet adsorption distribution constant. (M_{abs} = 1 g, C_0 = 50 mg/L, V = 100 mL and T = 27˚C).

Table 3. Parameters of the adsorption isotherms of methyl violet on the material.

Isotherms	Parameters	Values	Hypotheses
Langmuir	Q_{max} (mg/g)	−8.1	- monolayer,
	K_L ($L \cdot mg^{-1}$)	−0.13	- number of adsorption sites;
	R_L	−0.19	- 1 site = 1 molecule;
	R^2	0.99	- no mobility and interaction of the molecules.
Freundlich	K_F ($mg^{(1-n)} \cdot L^n \cdot g^{-1}$)	1.101	- heterogeneous surface,
	n	0.70	- no mobility and interaction of molecules on the surface
	Q_{max}	17.61	
	R^2	0.97	

Table 4. Thermodynamic parameters of methyl violet adsorption.

Time (K)	K_d	ΔG° ($KJ \cdot mol^{-1}$)	ΔH° ($KJ \cdot mol^{-1}$)	ΔS° ($KJ \cdot mol^{-1}$)	R^2
298	1.871	−1.552	-	-	-
313	3.407	−3.190	27.830	98.970	0.989
333	7.063	−5.412	-	-	-
353	10.454	−6.888	-	-	-

The negative values of ΔG° (**Figure 4**) confirm the feasibility of the process and the spontaneous nature of the adsorption of methyl violet on the support of activated *Saba senegalensis* material. The decrease in the value of ΔG° with increasing temperature indicates that adsorption becomes more favorable at high temperatures. The positive value of ΔH° indicates that the reaction of the process is endothermic. This result confirms the effect of temperature. The positive value of ΔS° suggests that some structural changes have occurred on the adsorbent, and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process. In addition since ΔS° = 98.97 KJ/mol, and therefore, is between −40 KJ/mol and 800 KJ/mol then we can conclude that we are in the presence of chemisorption.

4. Conclusion

The objective of this study was to develop an activated carbon adsorbent based on *Saba senegalensis* shells, in order to proceed with the treatment of an aqueous solution loaded with a synthetic dye (methyl violet) using the adsorption technique. The characterization of the adsorbent used allowed us in part to understand the behavior of the latter during the treatment of the colored solution. The performance of the tests made it possible to record the following results:

- The dye removal rate on the material support is optimal respectively for the following values: a contact time of 40 min, an adsorbent mass of 1 g, an initial concentration of 100 mg/L, a pH = 5, pH = 7 and a temperature of 80˚C;

- The kinetic study shows that the mechanism of the adsorbent can be described by the pseudo-second-order kinetic model;
- The plot of the adsorption isotherms shows that the Freundlich model better represents the adsorption of methyl violet with a maximum adsorption capacity of 17.61 mg/g;
- The adsorption isotherm of methyl violet is of type C according to the classification of Gille et al.;
- The thermodynamic study confirms the feasibility and spontaneity of the process as well as its endothermic nature. It makes it possible to know that the adsorption of methyl violet on the material is chemisorption.

Thus, the results showed an adsorbent potential of *Saba senegalensis* hulls for the removal of dyes in aqueous solutions. It is an accessible and low-cost material, especially during the winter period in the Sahelian countries.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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