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Discolouration Studies of the Slaughterhouse Effluent by Adsorption on Two Adsorbents Made from Species Sawdust of *Triplochiton scleroxilon* and *Milicia excelsa*

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Abstract

The treatment of slaughterhouse effluents is a problem for our municipalities and residents. The objective of this work is to contribute to the protection of the environment through a test treatment of the effluent from the slaughterhouse of cows by adsorption on adsorbents made from sawdust. To achieve this, two adsorbents were produced based on sawdust of Ayous (*Triplochiton scleroxilon*) and Iroko (*Milicia excelsa*), and were characterized. The effluent was sampled in a Ngaoundéré slaughterhouse and then characterized in its turn. Finally, discolouration tests by adsorption of this effluent were carried out. At the end of this work, it appears that both adsorbents produced had an acidic character. They are micro and macroporous with specific surface areas from 14.77 m^2/g to 69.56 m^2/g for Iroko and Ayous, respectively. The effluent from the slaughterhouse of cows sampled in the city of Ngaoundéré is highly conductive and turbid with an organic matter evaluated at 4.15 ± 0.18%. The adsorbent based on sawdust of Ayous is more effective, globally allowed the reduction of more than 70% of all the organic and inorganic loads of the slaughterhouse effluent after treatment. A discolouration rate estimated at more than 90% obtained at the scale of the laboratory, these adsorbents are effective for the treatment of the slaughterhouse effluents. These two adsorbents can therefore be used for the treatment of slaughterhouse effluent in any country in the world.

Keywords: Adsorption, Sawdust, Slaughterhouse effluent of cows, Turbidity, Organic Matter

1. Introduction

Slaughterhouses of cows produce effluents heavily loaded with organic matter, which constitute a significant source of pollution for the environment where they are rejected (Bamba *et al.,* 2009). In addition, producing bad odours and being responsible for the proliferation of mosquitoes, they are also responsible for the asphyxiation of the aquatic ecosystem and the eutrophication of lakes (Rodier *et al.,* 2009). In the classification of pollutant generators, food industries (including slaughterhouses of cows) are considered as the main sources of biodegradable organic pollutants in waters, whether insoluble or dissolved (Labioui *et al.,* 2007). This kind of pollution can be treated by electrocoagulation-flotation with iron electrodes (Khennoussi et al. 2011). This method, although effective, is still expensive. Gongwala *et al.,* (2012) tried to treat slaughterhouse effluent by cold plasma with rampant electric discharge (glidarc) in Yaoundé. They obtained encouraging results on the reduction of BOD_5 and COD. In 2014, these same authors try the same treatment for the elimination of phosphates and nitrates in the effluent of the slaughterhouse, with a despondency assessed at 86% and 42% respectivelly (Gongwala *et al.,* 2014).

Adsorption on porous materials is one of the most effective waste water treatment techniques (Bamba *et al.,* 2009) and easy to implement (Sakr *et al.,* 2014). Adsorption is a process where a solid is used to remove a soluble substance from the water. The adsorbents used are generally activated carbons, activated alumina, silica gels, zeolites, clays (Ngomo *et al.,* 2016; Mouthe *et al.,* 2015; Biké *et al.,* 2013; Ahmad *et al.,* 2009). The adsorbents in general and the activated carbons in particular are of multiple and varied origins. Some such as wood (eucalyptus), bark, wood pulp, coconut husks, coffee scraps, sawdust have been studied (Dabwan *et al.,* 2015; Bamba *et al.,* 2009; Garg *et al.,* 2004; Benaïssa, 2006). Other adsorbents have also been made from straw, coal, olive kernels (Yang *et al.,* 2016), jujube and mango kernels (Pandharipade *et al.,* 2012), bitter almond shell (***Prunus amygdalus***) (Trachi *et al.,* 2014), fruit cores, bamboos, charcoal, lignite, peat and oil residues (N'guessan, 2010), date kernels (Hazourli *et al.,* 2007; Zeroual *et al.,* 2011), rice bran, household waste, fruit peelings.

However, the relevance of an absorbent lies in its use. Because the purpose of using an adsorbent product is the removal of a specific pollutant or a set of pollutants. Indeed, the pollutant load of an effluent varies according to the origin of the latter. The treatment to be provided to the effluent will also depend on the nature of its polluting load. The slaughterhouse effluents have the particularity of being heavily loaded with organic matter which gives them a high degree of turbidity (Labioui *et al.*, 2007). The Cameroon slaughterhouses of cows in general and those of Ngaoundéré in particular have great difficulties in reducing their high turbidity before the discharge of the effluents into running waters (rivers, lac). The present work aims to discolour slaughterhouse effluents through the treatment by adsorption on adsorbent based on sawdust. It will be specifically a question of producing and characterizing two adsorbents based on Ayous and Iroko, carry out adsorption tests on the Methylene Blue (organic pollutant model), then on the sampled effluent from the slaughterhouse in Ngaoundéré.

2. Material and Methods

2.1 Substrate of Adsorbent Materials

2.1.1 Substrate Sampling

The adsorbents used in this work are produced from two species of sawdust, Ayous (*Triplochiton scleroxilon*) and Iroko (*Milicia excelsa*). The choice to use sawdust as a substrate for the production of adsorbents was motivated by its availability in Cameroon in general and Ngaoundéré in particular, its abundance and proximity. The choice of these substrates also comes within the framework of the valorization of local waste. Thus, the sawdust samples were taken from two different sawmills in the city of Ngaoundéré. To be sure of having only the desired species, the sampling was made the same day on a pile of sawdust generated following the sawing (cutting) only (about 5000 boards) of the species Ayous firstly (1st sawmill) and Iroko afterwards (2nd sawmill).

2.1.2 Production of Adsorbents

Both adsorbent materials were produced following the modified method of Kra *et al.,* (2015). Indeed, the samples were dried in an oven for 24 hours, then ground and sieved with a sieve of 1 mm mesh diameter. They were then mixed with a solution of 1N H_3PO_4 with a ratio 3.5 g per 20 ml. The mixture remained at room temperature for 24 hours and the resulting solutions were filtered. The solid fractions were oven dried at 105 °C for 24 hours. The dry substrates were introduced into reformable porcelain crucibles and introduced into a furnace (brand Nabertherm) where they were pyrolyzed for 1h30 at a maximum temperature of 500

℃. At the outlet of the oven, the adsorbents obtained were cooled in a desiccator and then washed several times with deionized water to remove the maximum H_3PO_4 which served as an activator, until the pH stabilized. After washing, the adsorbent materials were again dried in an oven at 105 °C for 24 hours, then crushed and sieved using a 200 µm sieve. The adsorbents obtained were packaged in glass jars.

2.1.3 Characterization of Adsorbents

2.1.3.1 Fourier Transform Infra-Red Spectroscopy (FTIR) and Scanning Electron Microscope (SEM)

The surface morphology of the two adsorbents was determined by SEM according to the modified method used by Tsamo and Kamga (2017). Indeed, 2 mg of the dry adsorbent was mixed with 1 ml of chloroform. After stirring, the solution obtained was analysed by SEM, brand FEI QUANTA 200. The Infra-Red of the adsorbents was performed according to the modified method of Kibami et al. (2017). For this purpose, 2 mg of dry adsorbent was directly analysed by Fourier transform infra-red spectrometry (iS50RAMAN brand). Each sample were recorded in the wavenumber range of 4000-400 cm^{-1}.

2.1.3.2 Iodine Index

The iodine index of the adsorbents was determined according to the modified method used by Soleimani and Kaghazchi (2014). In fact, 0.5 g of each dry adsorbent was mixed with 50 ml of an iodine solution (0.1 N) in a beaker. After stirring in a jar-test (Raypa brand) at 250 rpm for 5 min, the mixture was filtered and 10 ml of the filtrate were pipetted and introduced into a conical flask with 0.5 ml of a 1% prepared starch solution. The solution tinted to dark blue and the reaction between iodine and starch was titrated with sodium thiosulfate ($Na_2S_2O_3$ at 0.1N) until complete bleaching of the mixture. The iodine index was calculated from the following formula.

$$\text{iodine index} = \frac{(\mathrm{V_b} - \mathrm{V_e}) N_{sthio} \,\mathrm{x}\, \mathrm{M_{I_2}} \,\mathrm{x}\, 1{,}5}{\mathrm{m_A}}$$

$\mathbf{V_b}$ = volume of sodium thiosulfate used for the blank (mL); $\mathbf{V_e}$ = volume of sodium thiosulfate used to determine the iodine solution after adsorption (mL); $\mathbf{N_{sthio}}$ = normality of sodium thiosulfate (0.1N); $\mathbf{M_{I2}}$ = molecular mass of Iodine (253.81 g/mol) and $\mathbf{m_A}$ = mass of adsorbent used (0.5 g).

2.1.3.3 Methylene Blue Index

The determination of the Methylene Blue Index was inspired by Kra *et al.*, (2015). Indeed, 0.2 g of each adsorbent was mixed in a beaker with 100 ml of a methylene blue solution at 20 mg/L. After 1h30min of stirring in the jar-test (at 250 rpm), representing the maximum time to reach equilibrium, the adsorbent was separated from the solution by filtration. The absorbance of the filtrate was measured on a UV/visible spectrophotometer (Jenway brand) at 664 nm. But before, a range of calibration solutions had been prepared with concentrations varying from 0 to 10 mg/L of methylene blue in steps of 1 mg/L and analysed at the same wavelength. The residual dye concentration was determined using the calibration line. The methylene blue number or the adsorption capacity of the adsorbent was calculated from the formula below.

$$\text{MB index (mg/g)} = \frac{(C_i - C_f) \times V}{m_A}$$

$\mathbf{C_i}$ = initial concentration of methylene blue (MB) in the solution; $\mathbf{C_f}$ = concentration of MB in the solution after adsorption; **V** = volume of MB solution; $\mathbf{m_A}$ = mass of adsorbent

2.1.3.4 Mass Effect of Adsorbents on Methylene Blue

To study the influence of the mass of the two Ayous and Iroko adsorbent materials produced on an initial concentration of MB, the same mass range of the two adsorbents was introduced in 100 mL of MB at 20 mg/L for 1h30min of stirring. Residual concentrations were measured using a UV / visible spectrometer at 664 nm.

2.1.3.5 Determination of the Specific Surface Area of the Adsorbent Materials Produced

The determination of the specific surface (S_{MB}) area of the adsorbents is conventionally based on measurements of adsorbent adsorption capacity for adsorbates of known characteristics. In this case, it has been decided to determine the adsorption capacity of S_{BM} on the monolayer of our adsorbents from the adsorption isotherm. Indeed, for the determination of S_{BM} (m^2/g), 0.8 g of Ayous and 1.4 g of Iroko were brought into contact with a solution of methylene blue of varied concentration (15 to 150 mg/L in steps of 15 mg/L) in a series of beakers. After 1h30min of stirring time in the jar-test, the residual MB absorbance of each solution in the series was measured by UV-Visible spectrophotometer at 664 nm. The results obtained, made it possible to draw the equilibrium adsorbed quantity curve (Q_e) as a function of the equilibrium concentration (C_e). From the following Langmuir equation in the linear form:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q\infty} + \frac{1}{Q\infty . K_L}$$

The maximum adsorption capacity of the monolayer Q∞ was deduced from the slope and the intercept at the origin C_e/Q_e = f (C_e). The specific surface (S_{MB}) area is given by the following relationship:

$$S_{BM} = \frac{Q_\infty . s}{M_{BM}} N_A$$

Q∞ = ultimate adsorption capacity (mg/g); $\mathbf{C_e}$ = equilibrium concentration (mg/L) ; $\mathbf{Q_e}$ = equilibrium adsorption capacity (mg/g) ; $\mathbf{K_L}$ = Langmuir constant, **S** = the area occupied by a MB molecule (175 $Å^2$) ; $\mathbf{N_A}$ = Avogadro's number ($6{,}02 \times 10^{23}$ mol^{-1}) and $\mathbf{M_{MB}}$ = molar mass of methylene blue (319.5 g / mol).

2.1.3.6 Surface Function of Adsorbent Materials Produced

The determination of the acidic surface functions of our adsorbents was made according to the Boehm method implemented by Bamba *et al.*, (2009). For each sample, 1 g of the dry adsorbent was introduced into three different conical flasks each containing 50 ml of a concentration solution (0.25 N) of bases $NaHCO_3$, Na_2CO_3 and NaOH. After 48 hours of stirring and filtration, the excess of basic solution in each filtrate was back-titrated with a solution of hydrochloric acid (0.25 N HCl). In these various reactors, sodium hydrogen carbonate ($NaHCO_3$) neutralises the carboxylic groups, sodium carbonate (Na_2CO_3) neutralises the carboxylic groups and lactone groups, and sodium hydroxide NaOH neutralises the carboxylic, lactone and phenolic groups.

Total basicity was determined according to the same principle as for acidic functions. In fact, 1 g of the adsorbent was brought into contact with 50 ml of a solution of HCl (at 0.25 N). After 48 hours of stirring, the excess of the HCl solution (0.25 N) after filtration was determined by the NaOH solution (0.25 N). The acid and base content was determined using the formula below:

$$N_o V_o - N_f V_o = N_{eqgR}$$

With $\mathbf{N_0.V_0}$ = the number of gram equivalents before the reaction ; $\mathbf{N_f.V_0}$ = the number of gram equivalents after the reaction and $\mathbf{N_{eqgR}}$ the number of gram equivalents reacted.

2.2 Sampling and Characterization of the Effluent of the Slaughterhouse to be Treated

The effluent was taken at the exit of the slaughterhouse of Ngaoundéré the 1st. It is the largest slaughterhouse of cows in operation right now in the city of Ngaoundere. It is a slaughter structure of more than twenty animals a day. The effluent was taken very early in the morning (6h45min), at which time felling took place. The sampling point is located downstream from the felling section, precisely between the point of slaughter and the point of discharge in the river downstream of the structure. The sample was then transported to a cooler at the Chemical and Environmental Engineering Laboratory at the University of Ngaoundéré where its undergoes physico-chemical characterization. Organic matter was determined by oxidation with potassium dichromate ($K_2Cr_2O_7$) in an acidic medium using the method of the Quebec Center of Expertise for Environmental Analysis (2006). The iron, sulphate and phosphate contents were determined according to the methods of Rodier et al. (2009).

2.3 Discolouration Test of the Effluent from the Slaughterhouse with Products Adsorbents

2.3.1 Determination of Stirring Time and the Amount of Adsorbents Effective for Effluent Treatment

In order to find the amount of adsorbents to be used and the stirring time for optimum discoloration of the effluent, a composite plan centred experiment was used. The matrix of experiments presented in Table 1 shows the number of experiments performed and the variety of factors taken into consideration in this work. Indeed, it was a question of introducing for each experiment in a beaker, the mass of the corresponding adsorbent in 100 ml of the diluted effluent (1/100 dilution factor). The mixture was stirred at 250 rpm using a test jar during the time corresponding to each experiment proposed by the matrix. Then the mixture was allowed to stand for about 20 minutes to promote decantation. In order to avoid the influence of the adsorbent microparticles on the turbidity, the mixture was precautionarily filtered using a wattman filter paper (0.45 µm). Each experiment was repeated three times. To assess the adsorption of the organic material (biological dye) on the adsorbent material, the turbidity of the effluent before adsorption and that of the effluent after adsorption were measured using a Hanna brand turbidimeter.

Table 1. Experimental matrix of the centred composite plane

	Coded Variables		**Real Variables**	
Tests	**A**	**B**	**A**	**B**
1	1	-1	103.9	0.46
2	0	0	65.0	1.10
3	0	-1.41421	65.0	0.20
4	0	0	65.0	1.10
5	-1	-1	26.1	0.46
6	1.414214	0	120.0	1.10
7	0	0	65.0	1.10
8	-1.414214	0	10.0	1.10
9	1	1	103.9	1.74
10	0	0	65.0	1.10
11	0	0	65.0	1.10
12	0	1.414214	65.0	2.00
13	-1	1	26.1	1.74

A = Stirring time (min) and B = mass of the adsorbent (g)

2.3.2 Influence of Adsorption on other Parameters of the Effluent

The experience matrix allowed to determine a couple of factors consisting of the stirring time (A) and the mass of each optimum adsorbent (B) to be used for a better discoloration of the effluent from the slaughterhouse. It is this pair of factors that has been used to perform effluent bleaching test. At the end of these experiments, some physico-chemical parameters were monitored on the treated effluent whose time-mass pair gave the lowest turbidity after adsorption. The physico-chemical parameters monitored on the effluent are pH, electrical conductivity, organic matter, Fe^{2+}, SO_4^{2-} and PO_4^{3-}.

3. Results

3.1 Characterization of the Adsorbents Produced

3.1.1 Scanning Electron Microscopy (SEM)

Figure 1 presents the results of the scanning electron microscopy (SEM) obtained from the two adsorbents produced at different scales (1mm, 50µm and 20µm) of observation.

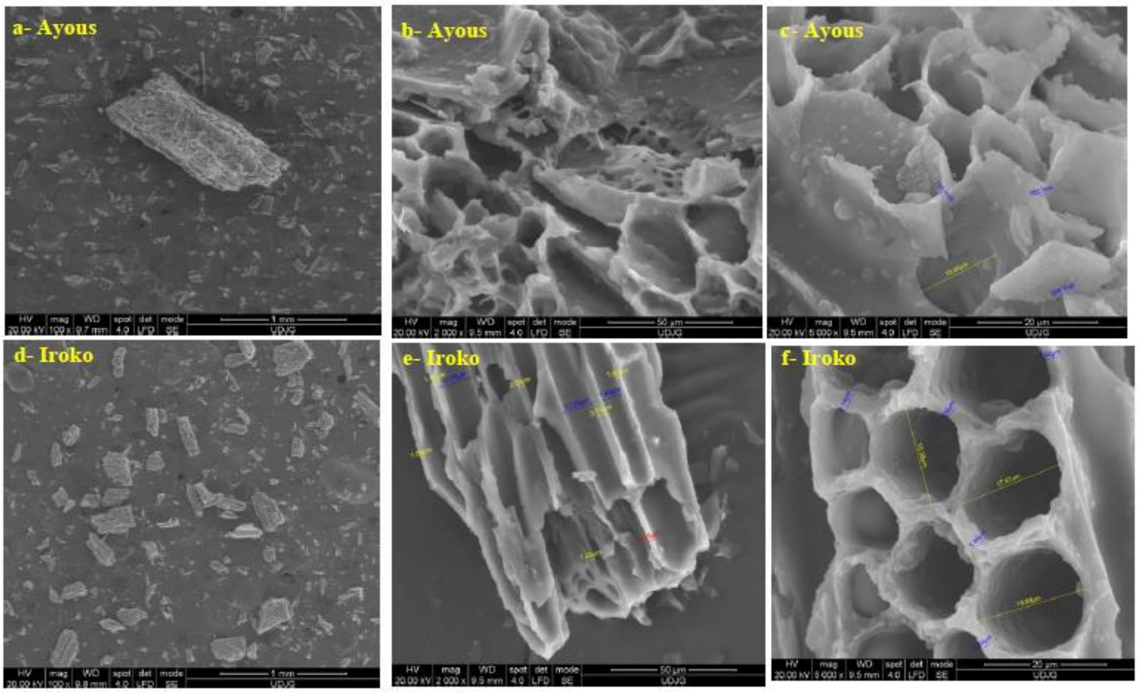

Figure 1. Scanning Electron Microscopy of Ayous adsorbent (a, b, c) and Iroko adsorbent (d, e, f)

The two adsorbents are of morphologically different structure with respect to each other. At the 1mm scale, the two adsorbents are characterized by irregular tapered shapes of various sizes. Ayous present more debris of small size with an impression of friability more accentuated than Iroko. Both are characterized by a varied porosity observable to 50 µm (**Fig**. 1b and 1e) and 20 µm (**Fig**. 1c and 1f). Indeed, Iroko has profound and regularly rounded pores with an average diameter size mostly close to 15 µm and 7 µm. The thickness of the separation strips between Iroko pores measure on average more than 2 µm, which makes this adsorbent less friable compared to Ayous. The porosity of Ayous is hollow and ballooned from the inside like a pod. The pores of Ayous have orifices with an average diameter ranging from about 13 µm to 2 µm in majority. The thickness of the separation between the pores of Ayous is evaluated at the nanometer (≈ 800 nm on average). It is the difference in structural shape of the pores observed in the two adsorbents that justifies the predisposition of Ayous to more friability and fragility compared to Iroko, as observed in Figure 1(a and d). The porous structures that characterize these two adsorbents are a satisfaction of production, but the structural forms hollow and ballooned at Ayous then rounded and deep at Iroko unfortunately do not allow to directly conclude on the effectiveness of one or the other for the discoloration of slaughterhouse effluents.

3.1.2 Fourier Transform Infra-Red Spectroscopy

The infra-red absorption spectra obtained on the two adsorbents produced are shown in Figure 2.

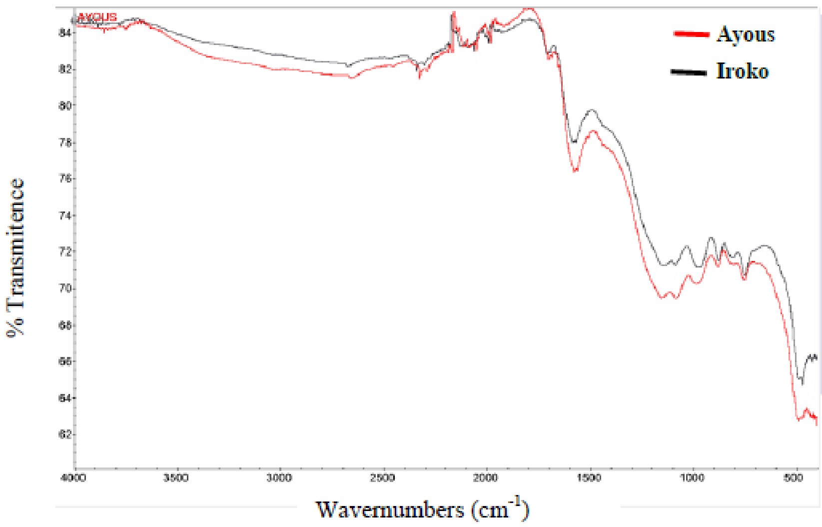

Figure 2. IR absorption spectra obtained

The IR absorption spectrum of Ayous reveals two elongation vibrations. The first is a band observed at 1080 cm^{-1} probably corresponding to the **C-C** bond. The second is a thin band observed at 1576 cm^{-1} indicating the existence of the **C=C** bond. A deformation vibration characterized by a thin band between 730 and 770 cm^{-1} brings out the monosubstituted aromatic $\mathbf{C_{tri}}$**-H** bond. As for the IR absorption spectrum of Iroko, it reveals the existence of five elongation vibrations and one deformation vibration. The first elongation is a band of medium intensity between 500 and 600 cm^{-1}, corresponding to the **C-I** bond. The second which appears between 700 and 800 cm^{-1} is an elongation vibration corresponding to the **C-Cl** bond. The other elongation vibrations are observed between 1000 and 1040 cm^{-1} (**C-F** bond), between 1050-1450 cm^{-1} (**C-O** and **C-C** bond) with a wide band and precisely at 1559 cm^{-1} indicating the presence of the bond **C=C**. The deformation vibration is a band of high intensity, corresponding to the aromatic $\mathbf{C_{tri}}$**-H** bond in 1,2,2 trisubstituted observed between 860-900 cm^{-1}. The Iroko adsorbent has the particularity to possess carbon-allogeneic bonds (**C-I**, **C-F**, **C-Cl**), which constitutes its main difference from Ayous adsorbent that does not have this kind of bonds.

3.1.3 Iodine and Methylene Blue Index

The iodine and methylene blue index values of the adsorbents produced are summarized in Table 2. They give informations on the micro and macroporosity of the adsorbents. These indices obtained vary according to the type of material used, that is to say according to the basic chemical structure of the sawdust species. The results of this Table 2 reveal that Ayous has produced the most microporous and macroporous adsorbent compared to Iroko substrate.

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Table 2. The porosities and surface function of the adsorbents produced and characteristics of adsorption isotherms

	Porosities			**Characteristics of adsorption isotherms**			
Adsorbents	**I_{iodine} (mg/g)**	**I_{MB} (mg/g)**	**D_{MB} (%)**	**R^2**	**Q_{max}**	**K_L**	**S_{MB} (m^2/g)**
Ayous	757.6 ±7.6	9.52 ±0.05	95.25 ±0.06	0.965	21.10	2.410	69.6
Iroko	630.7 ±8.8	8.16 ±0.03	81.60 ±0.20	0.992	4.48	1.531	14.8

	Different surface functions of the two adsorbents produced					
	pH	**Carboxylic groups (meq/g)**	**Lactone groups (meq/g)**	**Phenolic groups (meq/g)**	**Total acidity (meq/g)**	**Basic groups (meq/g)**
Ayous	4.62 ±0.01	0.000	0.003	0.162	0.164	0.000
Iroko	4.05 ±0.01	0.000	0.009	0.141	0.150	0.000

I_{iodine} = iodine Index; I_{MB} = Methylene Blue Index; D_{MB} = Despondency of MB; R^2 = correlation coefficient; K_L = Langmuir constant; Q_{max} = maximum adsorption capacity; S_{MB} = specific surface of the adsorbents obtained by the adsorption of the BM

3.1.4 Mass Effect Adsorbents and Methylene Blue Adsorption Isotherm

The effect of the mass of the two adsorbents produced on the adsorption of methylene blue is shown in Figure 3.

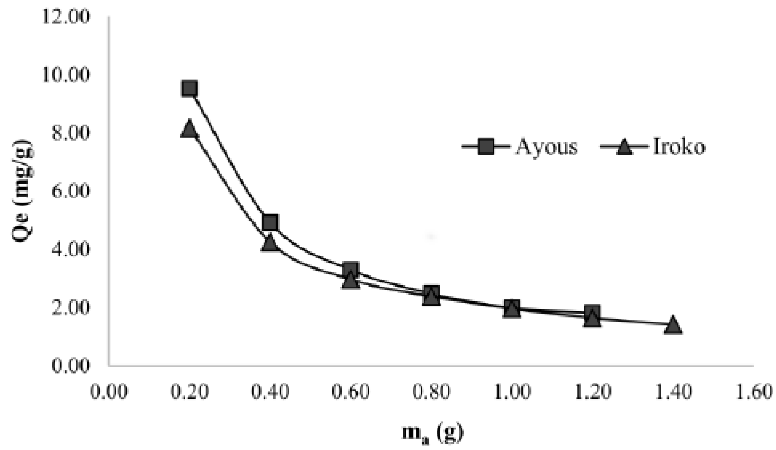

Figure 3. Effect of mass of the various adsorbents on the adsorption of methylene blue

Initial concentration of MB = 20 mg/L; stirring time = 1h30min; **Qe** = adsorbed quantity; $\mathbf{m_a}$ = mass of the adsorbent

It appears that the residual concentration of methylene blue (MB) decreases with an increase of the mass of adsorbents. After stirring for 1h30 min, the minimum effective masses of adsorbents selected for maximum adsorption of MB are 0.8 g and 1.4 g respectively for Ayous and Iroko. The Ayous species appears to be the most effective. This is consistent logically with the results obtained on the MB indices where the Ayous species had more meso and macropores than the Iroko species.

The adsorption isotherms of BM on the Ayous and Iroko adsorbents are shown in Figure 4 (a and c). According to this Figure, the adsorption capacity of the adsorbents increases with the increase of the MB concentration until a saturation which reflects the occupation of all the adsorption sites available on the adsorbents. The exploitation of the linear transform of the Langmuir equation (Figure 4 (b and d)) is allowed to determine the maximum adsorption capacity of MB (Q_{max}) of each adsorbent produced. The different parameters that result are summarized in Table 2.

3.2 Treatment Test of the Slaughterhouse Effluent

3.2.1 Optimal Conditions for the Adsorption Test

The general characteristics of the slaughterhouse effluent before the adsorption treatment are showed in Table 3. The objective of the adsorption test carried out in this work is to discolour the effluent from the slaughterhouse. And as it is mentioned above, turbidity is the best parameter to assess the discoloration level of the effluent. The stirring time in minutes (min) and the mass of the adsorbent (in g) are the factors that were optimized during these adsorption tests.

Table 3. Physico-chemical parameters of slaughterhouse effluent before and after treatment by adsorption

Slaughterhouse effluent		**pH**	**E Cond (µS/cm)**	**Turb (NTU)**	**OM (%)**	**PO_4^{2-} (mg/L)**	**SO_4^{2-} (mg/L)**	**Fe^{2+} (mg/L)**
	Before Treatment	7.73 ±0.05	6200 ±104	5368 ±204	4.15 ±0.18	354 ±7	4389 ±27	248 ±4
Ayous	After treatment	6.70 ±0.06	1700 ±80	122 ±12	1.76 ±0.11	237 ±13	985 ±24	100 ±1
Iroko	After treatment	7.11 ±0.08	1800 ±54	314 ±55	2.78 ±0.16	261 ±14	1023 ±29	111 ±2

OM = Organic Matter; Turb = Turbidity; E Cond = Electrical Conductivity

The results produced by the experimental design used for the determination of stirring time and the mass of Ayous and Iroko adsorbents effective for better discolouration are respectively summarized in Table 4. Equations (1) and (2) represent the mathematical models resulting from the experimental design carried out on the discoloration tests using adsorbents respectively based on Ayous and Iroko. They reveal that the quadratic combinations of stirring time (A^2) and mass of the adsorbent (B^2) have a significant negative effect on the discoloration of the effluent. The stirring time seems to have more negative than positive effect on the reduction of the turbidity of the effluent in the presence of Iroko adsorbent. Which is quite the opposite with Ayous adsorbent. But it is important to verify that these different influences of the stirring time and adsorbent mass factors are acceptable through the validation of the mathematical models expressed by equations (1) and 2.

Table 4. Influences of the adsorbent mass (Ayous) and stirring time on the turbidity of the effluent of the slaughterhouse according to the experimental design

			Ayous		Iroko	
Test	Stirring time (min)	Mass of the adsorbent (g)	Turbidity before adsorption (NTU)	Turbidity after adsorption (NTU)	Turbidity before adsorption (NTU)	Turbidity after adsorption (NTU)
1	65	2	5270	1415 ±205	4095	594 ±89
2	65	0,2	5270	122 ±12	4095	354 ±105
3	65	1,1	5270	1995 ±35	4095	693 ±23
4	65	1,1	5270	1710 ±14	4095	625 ±66
5	65	1,1	5270	1070 ±14	4095	771 ±113
6	65	1,1	5270	1263 ±68	4095	357 ±37
7	65	1,1	5270	1645 ±134	4095	463 ±87
8	103.9	0,46	5270	608 ±79	4095	314 ±55
9	103.9	1,74	5270	1415 ±233	4095	823 ±132
10	26.1	1,74	5270	1735 ±148	4095	645 ±58
11	26.1	0,46	5270	714 ±112	4095	302 ±72
12	120	1,1	5270	995 ±130	4095	671 ±91
13	10	1,1	5270	1095 ±134	4095	425 ±158

$$Y = 1537 - 71 A + 457 B - 193 A^2 - 331 B^2 - 53 A*B \quad (1)$$

$$Y = 581.8 + 67.2 A + 148.9 B – 14.4 A^2 – 51.4 B^2 + 41.5 A*B \quad (2)$$

With Y= response (turbidity) ; A= stirring time ; B = mass of the adsorbent

In this regard, Table 5 presents the validation parameters of these mathematical adsorption models of the slaughterhouse effluent on the two adsorbents.

Table 5. Model Validation Indicator

Validation indicator	Ayous values	Iroko values	Acceptable values
R^2	80.42 %	61.34 %	80 %
Bias factor (Bf)	1.04	1.02	[0.75 - 1.25]
Accuracy factor (Af)	1.20	1.20	[0.75 - 1.25]
AAMD	0.20	0.19	[0 - 0.3]

AAMD = Absolute Analysis of Mean Deviation

It appears that only the correlation coefficient (R^2) obtained with the Ayous adsorbent is greater than 80%. On this basis, only the mathematical model of adsorption on Ayous can be validated according to Joglekar and May (1987). Because these authors consider that a model can be validated if it explains at least 80% of the variability of the response (R^2 adjusted). However, the values of the other validation indicators (bias factor, accuracy factor and AAMD) are positive for both adsorbents because they are in the range of acceptable values. Indeed, Dalgaard and Jorgensen (1998) estimate that a model is validated if the accuracy and bias factors are between 0.75 and 1.25. Baş and Boyaci (2007) consider that a model is valid if the AADM is between 0 and 0.3. On these bases, the mathematical models of the adsorption of the slaughterhouse effluent on the two adsorbents explain for more than 80% the variability of the turbidity decrease.

3.2.2 Optimum Values of the Factors for the Efficient Discolouration of the Effluent

For better discolouration by adsorption of the effluent from the slaughterhouse, the factor couples (agitation time - adsorbent mass) retained at the end of the experimental design can be judged on Table 4. It emerges that with 0.2 g of Ayous adsorbent, it is possible that after 65 minutes of stirring in a reactor, to reduce to nearly 97% the turbidity of 100 ml of a slaughterhouse effluent. Likewise, after 1h44 min of stirring, it is also possible to reduce by nearly 93% the turbidity of 100 ml of slaughterhouse effluent with 0.46 g of adsorbent product based on Iroko. Of the two adsorbents, Ayous demonstrates a better adsorption efficiency, because it allows to eliminate a maximum of turbidity in a very short time (65 min) with a small amount of adsorbent (0.2 g). This would mean that on a large scale, 90% the turbidity of 50 L of a slaughterhouse effluent could be reduce in 1 hour of stirring, by carrying out an adsorption with 100 g of our adsorbent produced from sawdust of Ayous. Beyond the effectiveness of these two adsorbents on turbidity, it was interesting to assess their influence on other parameters of the slaughterhouse effluent.

3.2.3 Influence of Adsorption on Physico-chemical Parameters of Effluent

After adsorption on the two adsorbents produced, the pH of the effluent decreases slightly while the electrical conductivity of the effluent significantly decreased (Table 3). The removal rate of iron contained in the effluent of the slaughterhouse by adsorption varies between 60% (Ayous) and 55% (Iroko). These two adsorbents produced allowed the removal of sulphate and phosphate with average reduction rates of 77.15% and 29.9% respectively. They also allowed the reduction of the organic matter (OM) of the slaughterhouse effluent by adsorption by almost 57.5 % with Ayous on one hand and 32.9 % with Iroko on the other hand.

4. Discussion

4.1 Adsorbents Products

The production yield is an important quantitative characteristic for the adsorbents. As part of this work, it is 58% of the initial substrate. It reflects the loss of mass during pyrolysis. The acid surface functions of the two adsorbents produced shown in Table 2, are mainly due to the fact that they have undergone activation with phosphoric acid. The pH values obtained in this work are comparable to the pH values obtained by Daoud and Benturki (2014) on activated carbon produced from jujube kernels. The main acid groups encountered on the surface of these adsorbents produced are lactone and phenolic groups. Which obviously agrees with the results obtained on the IR absorption spectra of the two adsorbents (figure 2a and 2b). Indeed, the **C-O** bonds observed between 1050 and 1450 cm^{-1} indicate the presence of phenol (Abdelaziz and Hulterberg, 2017), esters and lactones groups (Kibami *et al.*, 2017). Phenolic groups are the most abundant on the surface of these two adsorbents produced. This predisposes them to effective adsorption of cationic pollutants such as metals. In fact, the more acidic sites are rich in oxygenated groups, the more they will promote the adsorption of dyes and cationic elements (Khattri and Singh, 1999). These results differ slightly from the results of Bamba *et al.*, (2009), which curiously obtained activated carbons having not only the acid and basic functions, but their acidities were made of carboxylic acid and lactone functions. This difference would certainly be due to the nature of the substrates used in our various works.

4.2 Porosity of Adsorbents

Micro and macroporisity of adsorbents increase with the moisture content of the substrate. This is what explains the higher levels of micro and macro pores at Ayous compared to Iroko. This shows the ability of Ayous to fix more micro, meso and macro-molecules (dissolved or not) than adsorbent produced with Iroko. It is besides established that a adsorbent rich in meso and macroporosity will be effective for the adsorption of dye molecules such as Indigo Carmine, methylene blue and red S-Max contained in an effluent (Enaime *et al.*, 2017; Kra *et al.*, 2015; Daoud and Benturki, 2007; Gueye and Brunschwig, 2011). This assertion is confirmed by the despondency rates obtained following the adsorption tests carried out with the Ayous and Iroko-based adsorbents, on an effluent stained with methylene blue at a concentration of 150 mg/L (Table 2). But globally, the two adsorbents produced are more microporous than macro and meso-porous. This is due to the temperature used during the pyrolysis of the substrates. Indeed, it has been shown that at temperatures above 500 ℃, the probability of obtaining more macro and meso-pores is important while the micropores are the majority when the pyrolysis is at temperatures less than or equal to 500 ℃ (Gueye and Brunschwig, 2011; Kra *et al.*, 2015; Olivares-Marin *et al.*, 2006).

The iodine values obtained in this work are higher than those obtained by *Avom et al.*, (2002) on the production of active carbons based on palm diet rounds with a maximum value of 111 mg/g. They are also higher than those obtained by Enaime *et al.*, (2017) on the production of activated carbons from olive wastes whose maximum value is 435 mg/g, and by Soleimani and Kaghazchi (2014) on the production of adsorbents at base of several agricultural substrates with a maximum value of 450 mg/g under activation conditions close to ours. The difference between these results and those of the authors cited above can first be justified by the nature of the substrates used. It can also be justified by the difference of temperatures used in the different works.

4.3 Mass Effect Adsorbents and Methylene Blue Adsorption Isotherm

It appears that the Langmuir model describes the adsorption of methylene blue (organic pollutant model) on both adsorbents with correlation coefficients close to unity (Khattri adn Singh, 1999; Benaïssa, 2007). This means that the adsorption of MB on these two adsorbents is carried out in monolayer (Avom *et al.*, 2001). So, each site of these adsorbents can only fix a single molecule of MB. Moreover, the superposition of MB molecules and the interaction between them on the surface of adsorbents cannot be possible (Yang *et al.*, 2016). The difference in points observed on MB adsorption isotherms (nine points for Ayous and four points for Iroko), is explained by the maximum adsorption capacity of each of the two adsorbents produced. Indeed, with a surface area (S_{BM}) of 69.6 m^2/g, the adsorbent produced with Ayous can adsorb up to 21.1 mg/g of MB. Yet the adsorbent product based on Iroko sees its adsorption sites saturate after fixing only 4.48 mg/g of MB. The S_{MB} obtained on the two adsorbents produced are lower than those obtained by Gueye and Brunschwig (2011) who has obtained larger specific surfaces area on activated carbon based on coconut, peanut shell and wood of eucalyptus assessed at 875 m ²/g, and by Kifuani *et al.* (2018) on agricultural waste of ***Cucumeropsis mannii*** assessed at 251.87 m ²/g.

4.4 Discolouration Test and Influence of Adsortion on other Parameters of Effluent

The decrease in the pH of the effluent after adsorption treatment on the two adsorbents produced is certainly due to the acidity of the surface of these adsorbents. However, regardless of the observed variation, these values remain within the normal pH range (between 6 and 9) of effluent discharges into the wild according to MINEPDED in Cameroon. The significant decrease of the electrical conductivity is due to the adsorption of the conductive cationic ions present in the effluent for an example Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+}, Mn^{2+}, Cr^{2+}. In this context, the Ayous adsorbent was the most effective of the two. The strong performance of the Ayous adsorbent on the adsorption of the micropollutants represented by the conductive ions, is explained by the fact that it has a higher micropore rate compared to that produced with Iroko.

The high adsorption rate of sulphates compared to that of phosphates is firstly due to the high concentration of sulphate that characterizes the slaughterhouse effluent from Ngaoundéré. Indeed, the adsorption rate of a pollutant also increases on an adsorbent with the concentration of the pollutant contained in the solution (Faisal *et al.*, 2014; Asmaa *et al.*, 2010). It is secondly due to the high solubility of phosphates than sulphates. Moreover, the more soluble a compound is the less it is adsorbed and vice versa. Adsorption decreases as solubility increases (Garcia-Araya *et al.*, 2003; Singh and Yenkie, 2006).

Turbidity is the most important physical parameter in this work. It represents the opacity of a cloudy medium that can be caused by the presence of fine matters suspended (MS), such as clays, silts, silica grains, and microorganisms (Rejsek, 2002; Rodier *et al.*, 2009). But in this work turbidity is mainly characterized by bovine red blood cells which constitute here the major part of the organic matter (OM) of the slaughterhouse effluent. The best efficiency presented by the Ayous adsorbent on the reduction of the OM is certainly due to its richness in macropores and its large surface area compared to that based on Iroko, because it is established that the best adsorbent is one that has among others a large specific surface area (Bhatnagar and Minocha, 2006). Furthermore, the OM of the slaughterhouse effluent is mainly constituted more or less soluble microparticles from the digestive tract of the animal and protein molecules of bovine red blood cells. It mainly represents the macromolecular fraction which is fixed on the macropores of the adsorbents during the treatment.

5. Conclusion

The objective of this work was to carry out a slaughterhouse effluent treatment test using the principle of adsorption on adsorbent material produced from two species of sawdust. At the end of this work, it suitable to notice that the two adsorbents produced effectively reduce the sulphated anions and the metal cations responsible for the high electrical conductivity of the effluent such as Fe^{2+}. They also allowed to satisfactorily reduce the organic matter of this effluent. The Ayous adsorbent showed a better ability to eliminate these pollutants contained in the effluent compared to Iroko. It reduces 97% of the turbidity of 100 ml of this slaughterhouse effluent in 65 minutes of agitation with only 0.2 g of adsorbent. In the rest of this work, it will be interesting to know whether among the sawdust species available in Africa in general and in Cameroon in particular, there are some that are more suitable for the production of adsorbent materials effective for the slaughterhouse effluent treatment as Ayous and Iroko. It would also be interesting to study the effect of combining the principles of "adsorption and biological treatment" on the effectiveness of treatment of the effluent from the slaughterhouse.

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