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Comparative Analysis of Statistical Thickness Models for the Determination of the External Specific Surface and the Surface of the Micropores of Materials: The Case of a Clay Concrete Stabilized Using Sugar Cane Molasses

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Abstract

In this work, four empirical models of statistical thickness, namely the models of Harkins and Jura, Hasley, Carbon Black and Jaroniec, were compared in order to determine the textural properties (external surface and surface of micropores) of a clay concrete without molasses and clay concretes stabilized with 8%, 12% and 16% molasses. The results obtained show that Hasley's model can be used to obtain the external surfaces. However, it does not allow the surface of the micropores to be obtained, and is not suitable for the case of simple clay concrete (without molasses) and for clay concretes stabilized with molasses. The Carbon Black, Jaroniec and Harkins and Jura models can be used for clay concrete and stabilized clay concrete. However, the Carbon Black model is the most relevant for clay concrete and the Harkins and Jura model is for molasses-stabilized clay concrete. These last two models augur well for future research.

Keywords

Statistical Thickness Model, External Specific Surface, Microporous Surface, Clay Concrete, Molasses

1. Introduction

When characterizing a porous material for use in industry, specific surface area is a key property. However, textural properties are crucial for the very wide range of applications for which the material is used [1]. This is the case for clay soils stabilized with cane molasses for use in road construction. These specific elements are required for the physical adsorption of nitrogen and provide information on textural properties, in particular the total accessible surface area and porosity distribution.

For the record, the results given in the form of curves relating the quantities of nitrogen adsorbed as a function of the ratio between partial pressure and saturation vapour pressure for nitrogen, are called isotherms. Adsorption isotherms can also be used to calculate the external surface area and the microporous surface area using the t-plot method.

The external specific surface (or external area) represents the extent of a non-porous material as well as the surface developed by pores large enough to allow the formation of a multimolecular layer whose thickness t increases regularly with (P/P_0). Similarly, the BET method is generally used to characterize the specific surface area of porous materials. It can be used to obtain the external specific surface area σ_{ext} by including the presence of micropores whose surface is not accessible.

The t-plot method can be used to determine the external specific surface σ_{ext} by excluding the micropores, and gives a more representative surface in terms of accessibility, by considering the thickness of the multimolecular layer of adsorbed nitrogen [1].

Nevertheless, several statistical thickness models are given in the literature. Studies have already been carried out by NGOUALLAT *et al.* (2022), within the framework of microstructure analysis and the determination of isotherms and specific surfaces [2]. These studies show that the quantity of molasses in the materials does not modify the type IV nitrogen adsorption isotherm, which remains and a type H4 hysteresis loop in all the samples, which justifies the monolayer and multilayer absorption mechanism; these are therefore mesoporous materials [3].

From a microstructural point of view, we have also observed the presence of inter-aggregate pores (mesopores) in the various samples analyzed, which suggests an evolution of the open soil structure towards a dense granular matrix [4]. However, the aim of this study is to compare four statistical thickness models: the Carbon Black model, the Harkins and Jura model, the Hasley model and the Jaroniec *et al.* model, in the case of clayey concrete stabilized with sugarcane molasses, in order to find the optimum model that best simulates the phenomenon.

2. Materials and Methods

The t-plot statistical thickness models most commonly used to determine the textural properties of materials are: the Harkins and Jura model, the Carbon Black model, the Halsey model and the Jaroniec *et al.* model [5] [6]. Other models exist, and we present those used in this article.

2.1. Statistical Thickness: Harkins and Jura Model

The empirical value of the statistical thickness t is expressed in the form of the equation of Harkins *et al.* [1] [7] [8] [9] [10], valid for as long as (P/P_0) < 0.8:

$$\dagger\left(\dot{A}\right)=\sqrt{\frac{13.99}{0.034-\log\left(\frac{P}{P_0}\right)}} \tag{1}$$

2.2. Statistical Thickness: Carbon Black Model

The Magee proposes a calculation of the statistical thickness t for carbon black valid for 0.2 < (P/P_0) < 0.5 [1] [6] [11]:

$$t\left(\dot{A}\right)=0.88\left(\frac{P}{P_0}\right)^2+6.45\left(\frac{P}{P_0}\right)+2.98 \tag{2}$$

2.3. Statistical Thickness: Halsey Model

Halsey's statistical thickness is represented by the following equation [11] [12]:

$$t\left(\dot{A}\right)=3.54\left(\frac{-5}{\text{In}\frac{P}{P_0}}\right)^{\frac{1}{3}} \tag{3}$$

2.4. Statistical Thickness: Jaroniec *et al*. Model

Jaroniec's statistical thickness is given by the following equation [8]:

$$t\left(\dot{A}\right)=\left(\frac{60.65}{0.03071-\log\frac{P}{P_0}}\right)^{0.3968} \tag{4}$$

2.5. External Specific Surface of the Material

The external specific surface σ_{ext} is obtained by determining the slope (standard linear regression) from the graph of the quantity of nitrogen adsorbed per gram of sample (Qa) as a function of the statistical thickness t. The value of σ_{ext} is calculated using equation Halsey statistical thickness is represented by the following equation [11] Halsey statistical thickness is represented by the following equation [1] [13]:

$$\sigma_{ext}=P\times15.47 \tag{5}$$

With

P, the value of the slope of the curve va = f (t);

15.47: a constant related to the conversion of the volume of nitrogen and the units in m^2/g.

If the statistical thickness is given in nm, a conversion factor is added, giving:

$$\sigma_{ext} = P \times 1.547 \quad (6)$$

2.6. Microporous Surface of the Material

The difference between the specific surface area value determined by the BET method and the external specific surface area obtained by the t method is used to determine the microporous surface area according to equation [1] [13]:

$$\sigma_{BET} - \sigma_{ext} = \sigma_{micropores} \quad (7)$$

2.7. Model Selection Criteria

Four criteria are used to compare and select models: the adjusted R^2 criterion, the Akaike information criterion (AIC), the Bayesian information criterion (BIC) and the Chi-square. The best model is the one with the lowest AIC, the lowest BIC, the highest R^2adj and the lowest Chi-square [14]. The values of the criteria were obtained using Origin pro software.

2.8. Physical Adsorption of Nitrogen

Nitrogen adsorption experiments on clay concretes were carried out using a Micro Active for ASAP 2460 Version 2.01 apparatus.

2.9. Geotechnical Characterization of Clay Soil

Table 1 gives the geotechnical characteristics of the clay soil.

2.10. Sugar Cane Molasses

The sugar cane molasses used comes from the "Société Agricole de Raffinage Industriel du Sucre (SARIS-Congo)", a sugar industry organized in the town of Nkayi, Republic of Congo. The molasses used has the following characteristics: the Brix value is 82.85%, which represents a sugar content of 82.85%. The corresponding polarity is 29.07% and the purity 35.09% [2].

2.11. Composition of Stabilized Clay Concretes

Table 2 shows the composition of stabilized and non-stabilized clay concretes.

Table 1. Geotechnical characterization of the clay soil used [15] [16].

	Particle size distribution				Atterberg limits			Compactibility		Methyleneblue
Materials	%fins (<80 µm)	Clay < 2 µm	Limon entre 2 µm and 63 µm	Sable entre 63 µm and 2 mm	W_L (%)	W_P (%)	I_P (%)	d (g/cm³)	W (%) (OPM)	VBS (g/100g)
Soil taken at 1 metre deep	88	54	34	12	42	21	21	1.68	15	0.34

Table 2. Quantity of materials used [2] [15].

Quantity of sugar cane molasses to be introduced into the mixer

Continued

Weight of dry soil sample	Water weight (%Water = 1.5 W_L)	0% molasses	8% molasses	12% molasses	16% molasses
88 g	54 g	34 g	12 g	42 g	21 g

Table 3. Experimental nitrogen adsorption ratio and statistical thicknesses for clay concrete without molasses.

Relative Pressure (P/P_0)	Harkins model Thickness (nm)	Carbon Black Thickness (nm)	Halsey model Thickness (nm)	Jaroniec model Thickness (nm)	Quantity Adsorbed (cm^3/g STP)
0.05194145	0.3262	0.33173965	0.4217	0.4573	7.19016053
0.08407268	0.3551	0.35284888	0.4474	0.4898	7.74184275
0.11996141	0.3827	0.37664149	0.4711	0.5199	8.2490695
0.15496155	0.4072	0.40006226	0.4918	0.5462	8.70265916
0.18999487	0.4304	0.42372332	0.5111	0.5708	9.14388884
0.22495869	0.4529	0.44755172	0.5297	0.5946	9.59146215
0.25993486	0.4754	0.4716038	0.548	0.6179	10.0480287
0.29498358	0.4979	0.49592175	0.5663	0.6413	10.5223821
0.33000122	0.5209	0.52043466	0.5848	0.6648	11.0162698
0.36461934	0.5443	0.54487883	0.6035	0.6885	11.5216408
0.3995725	0.5688	0.56977418	0.6229	0.7132	12.0428018
0.4345296	0.5944	0.5948874	0.6432	0.7387	12.5757069
0.46933312	0.6212	0.62010394	0.6643	0.7653	13.1181841

3. Results and Discussion

3.1. Samples without Cane Molasses

The experimental ratio of nitrogen absorption on clayey concrete, in particular the relative pressure (P/P_0) and the quantity of nitrogen adsorbed, is given in Table 3. The statistical thickness values according to the models obtained using: formula 1 for the Harkins and Jura model, formula 2 for the Carbon Black model, formula 3 for the Halsey model, formula 4 for the Jaroniec *et al.* model, are also presented in Table 3.

The shape of the curves in Figure 1 reveals capillary condensation in the pores that begins as the slope starts to increase, which justifies the presence of condensed water molecules in the mesopores, between the particles and grains in the clay concrete, which is obvious because clay concrete is water-based with an initial water content of 63% (Table 2).

Figure 2 shows the linear interpolation of the curves for the amount of nitrogen adsorbed per gram of sample.

Linear interpolation of the curves showing the quantities of nitrogen adsorbed as a function of statistical thickness (Figure 2), enabled us to obtain linear regression lines of the form $Q_{ads} = Pt + Q_0$ ($y = Q_{ads}$, $x = t$ (statistical thickness)). The slope P is used to calculate the external surface of the material (formula 6). The ordinate at the origin Q_0 is used to obtain the volume of the micropores.

However, in this study we are only interested in the surface area of the micropores. Table 4 gives the values of the model selection criteria clay concrete.

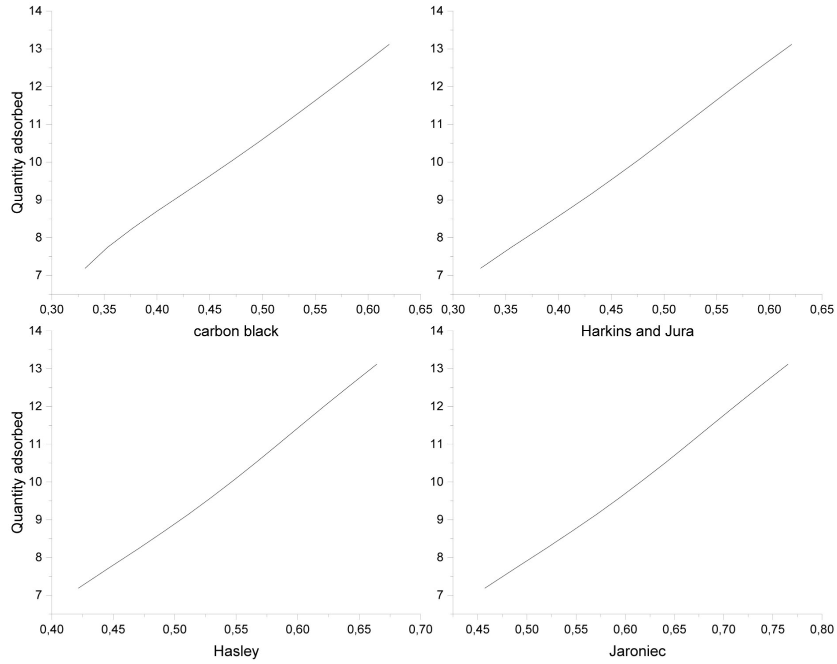

Figure 1. Quantity of nitrogen adsorbed per gram of sample for clay concrete without molasses as a function of statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

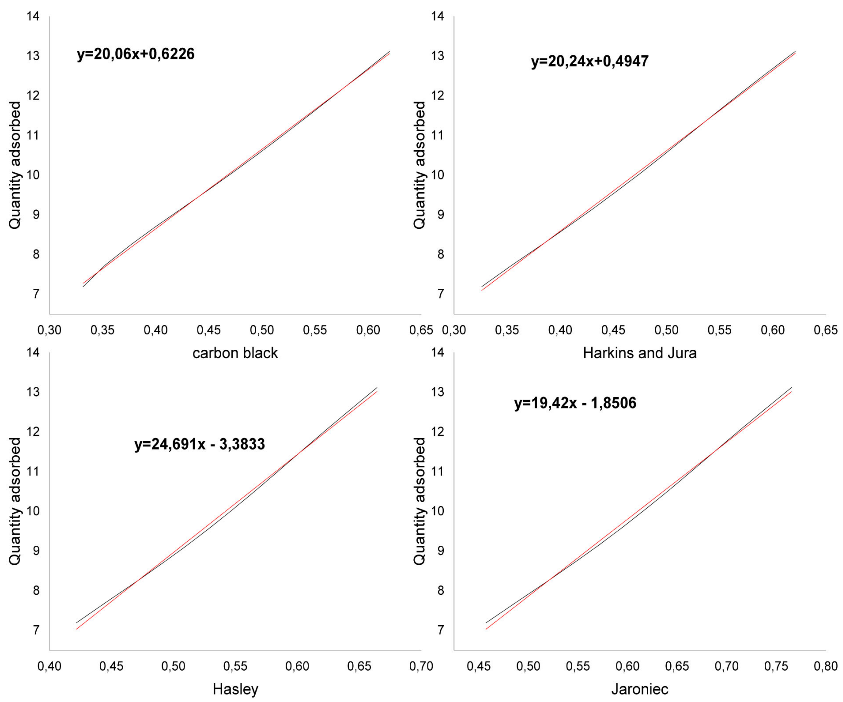

Figure 2. Linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample for clay concrete without molasses as a function of the statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

Table 4. Comparison of models using the AIC, BIC, chi-square and adjusted coefficient of determination criteria for clay concrete.

	Carbon black model	Harkins and Jura model	Halsey model	Jaroniec model
AIC	−69.619	−64.293	−71.6053	−64.3526
BIC	−70.591	−65.265	−72.5771	−65.3244
χ^2	0.00287	0.00432	0.00246	0.00430
R^2_{adj}	0.99919	0.99878	0.99931	0.99879

Table 5. Experimental ratio and statistical thicknesses for clay concrete stabilised at 8%.

Relative Pressure (P/P_0)	Carbon Black Thickness (nm)	Harkins model Thickness (nm)	Halsey model Thickness (nm)	Jaroniec model Thickness (nm)	Quantity Adsorbed (cm^3/g STP)
0.05320009	0.33256312	0.327	0.42285	0.45875	4.59337222
0.08428969	0.35299207	0.3553	0.44759	0.49003	5.03139846
0.12008606	0.37672456	0.3828	0.47124	0.52005	5.39794175
0.15508688	0.40014761	0.4073	0.49188	0.54631	5.69964509
0.1901536	0.42383101	0.4305	0.51124	0.57099	5.96632946
0.22523051	0.44773781	0.4531	0.52991	0.59480	6.22516461
0.26021708	0.47179875	0.4755	0.54821	0.61815	6.47345195
0.2951889	0.49606485	0.4981	0.56648	0.64144	6.71312166
0.32999108	0.52042693	0.5209	0.58486	0.66484	6.96127649
0.3647712	0.54498653	0.5444	0.60362	0.68868	7.21626715
0.39973281	0.56988886	0.5689	0.62307	0.71333	7.47654771
0.43471059	0.59501798	0.5945	0.64332	0.73890	7.75092887
0.46963921	0.62032666	0.6215	0.66454	0.76558	8.04449433

The Hasley model has the highest R^2_{adj} value, the lowest χ^2 value, the lowest BIC value and the lowest AIC value (**Table 4**), indicating that it is the best performing of the four models, followed by the carbon black model, then the Jaroniec model and finally the Harkins and Jura model.

3.2. Samples Stabilized with 8% Cane Molasses

Table 5 gives the ratio of nitrogen absorption on clay concrete stabilized at 8%, i.e. the relative pressure (P/P_0) and the corresponding quantity of adsorbed nitrogen. It also gives the statistical thickness values calculated according to the Carbon Black model, the Harkins and Jura model, the Halsey model and the Jaroniec model.

The shape of the curves (**Figure 3**) reveals multilayer adsorption on a surface with low porosity, which can be explained by the occupation of the pores by sugarcane molasses. We observe a straightening of the curves (linearization) compared with the curves obtained for non-stabilized clay concrete. This corresponds to the absence of capillary condensation in the mesopores between the particles and the grains. In fact, the presence of molasses, mainly made up of sucrose, glucose and fructose [2], which are molecules rich in hydroxyl groups (OH) in the mesopores of the material, favours the establishment of hydrogen bonds with the water molecules. The latter are then integrated into the molasses macromolecules in the material's mesopores. The linearization of these curves will become clearer as the molasses content of the clay concrete increases.

The linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample (**Figure 3**) is given in **Figure 4**.

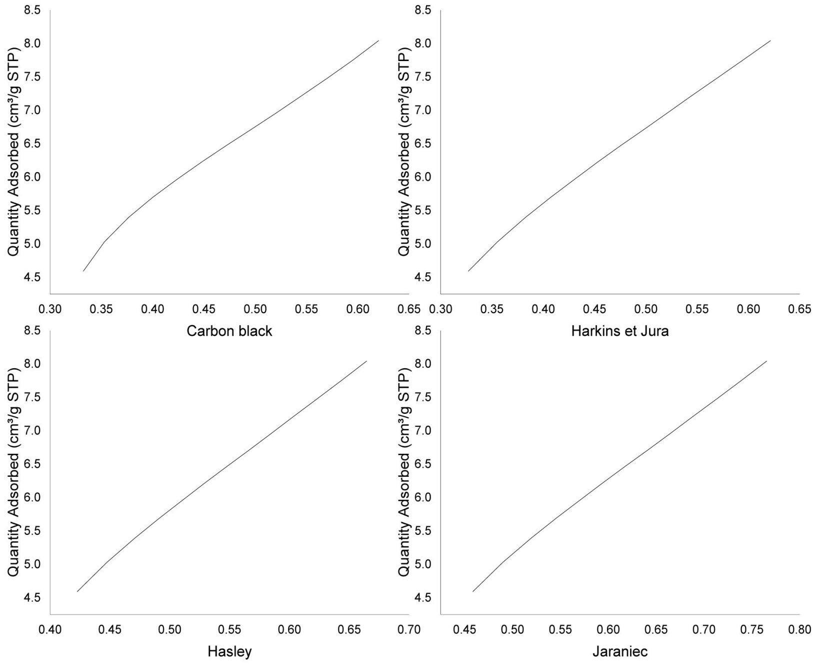

Figure 3. Amount of nitrogen adsorbed per gram of sample for clay concrete stabilised at 8% as a function of statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

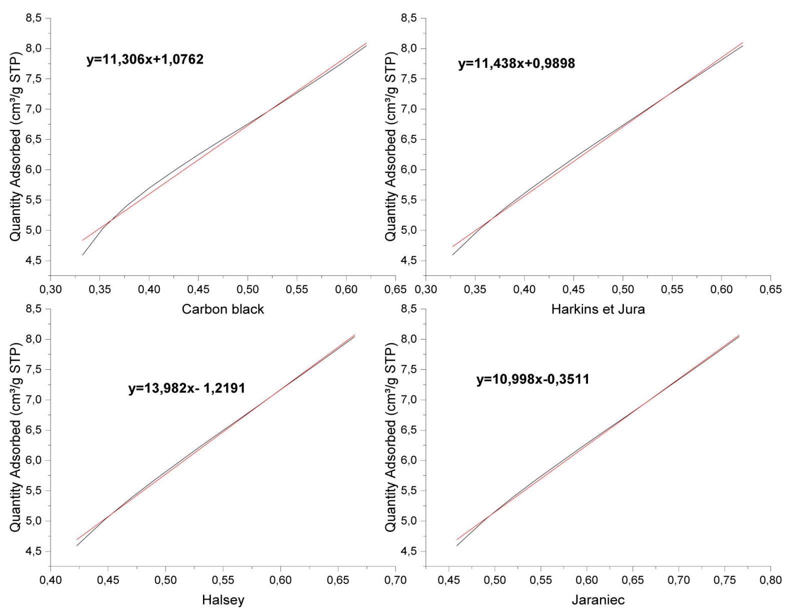

Figure 4. Linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample for clay concrete stabilized with 8% molasses as a function of the statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

Table 6. Comparison of the models using the AIC, BIC, chi-square and adjusted coefficient of determination criteria for clay concrete stabilized at 8%.

	Carbon black model	**Harkins and Jura model**	**Halsey model**	**Jaroniec model**
AIC	−57.6751	−75.2636	−70.3224	−74.7588
BIC	−58.647	−76.2354	−71.2942	−75.7306
χ^2	0.00718	0.00186	0.00271	0.00193
R^2_{adj}	0.99367	0.99836	0.99761	0.99830

Table 7. Experimental ratio and statistical thicknesses for 12% stabilized clay concrete.

Relative Pressure (P/P_0)	Carbon Black Thickness (nm)	Harkins model Thickness (nm)	Halsey model Thickness (nm)	Jaroniec model Thickness (nm)	Quantity Adsorbed (cm^3/g STP)
0.05308813	0.33248986	0.3269	0.4227	0.4586	3.85650881
0.08420541	0.35293646	0.3552	0.4475	0.4899	4.26261562
0.12003265	0.37668895	0.3828	0.4712	0.52	4.61493035
0.15507332	0.40013849	0.4073	0.4918	0.5463	4.903023
0.19012508	0.42381166	0.4305	0.5112	0.5709	5.16448421
0.2251296	0.44766872	0.4531	0.5298	0.5947	5.41336961
0.26024665	0.47181918	0.4755	0.5482	0.6181	5.65290921
0.29515384	0.49604042	0.4981	0.5664	0.6414	5.89922444
0.3301429	0.52053367	0.5211	0.5849	0.6649	6.14393856
0.36470392	0.54493882	0.5444	0.6035	0.6886	6.38946297
0.3998042	0.56993992	0.5689	0.6231	0.7133	6.64502022
0.43476824	0.59505958	0.5945	0.6433	0.7389	6.90238246
0.46970311	0.62037315	0.6215	0.6645	0.7656	7.18295549

Table 6 gives the values of the model selection criteria for clay concrete stabilized with 8% molasses.

The Harkins and Jura model has the highest R^2_{adj} value, the lowest χ^2 value, the lowest BIC value and the lowest AIC value (**Table 6**), indicating that it is the best performing of the four models, followed by the Jaroniec model, then the Halsey model and finally the Carbon black model.

3.3. Samples Stabilized with 12% Cane Molasses

Table 7 gives the experimental ratio of nitrogen absorption on clay concrete stabilized at 12%: the relative pressure (P/P_0) and the quantity of nitrogen adsorbed. The statistical thickness values according to the models are calculated using formulae 1, 2, 3 and 4 (page 3).

The shape of the curves (**Figure 5**) shows a linearization with respect to the curve at 0% and 8%, which corresponds to multilayer adsorption on a surface with low porosity, which can be justified by the occupation of the pores by sugarcane molasses.

The linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample (**Figure 5**) is shown in **Figure 6**.

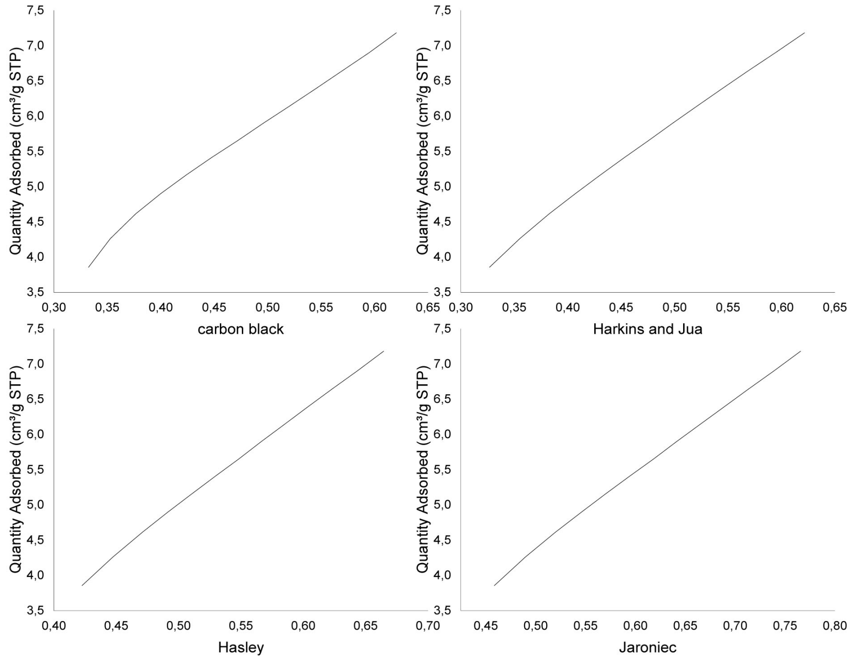

Figure 5. Amount of nitrogen adsorbed per gram of sample for clay concrete stabilized at 12% as a function of statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

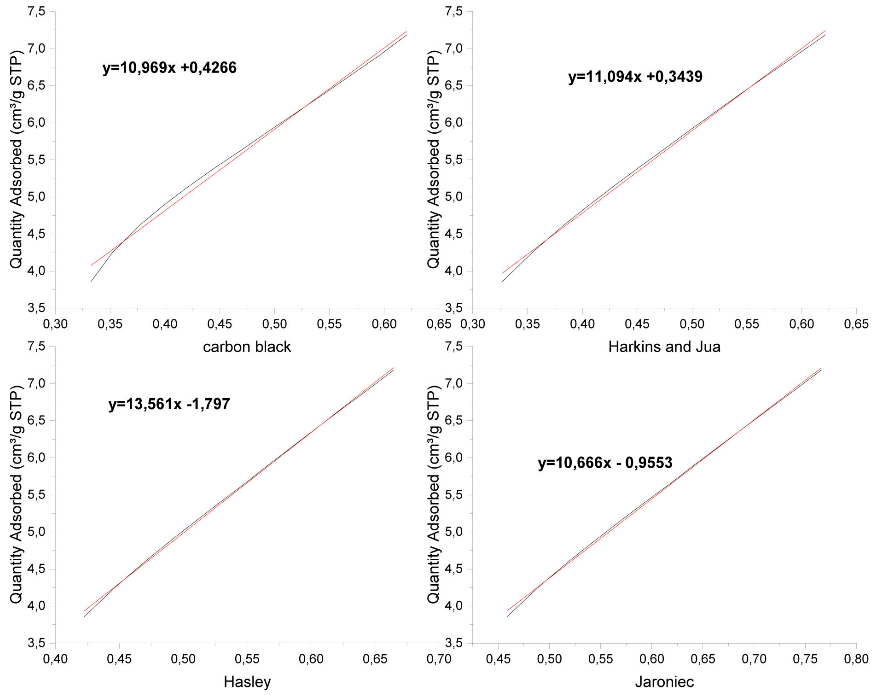

Figure 6. Linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample for clay concrete stabilized with 12% molasses as a function of the statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

Table 8 gives the values of the model selection criteria for 12% stabilized concrete.

The Harkins and Jura model has the highest R^2adj value, the lowest χ^2 value, the lowest BIC value and the lowest AIC value (**Table 8**), indicating that it is the best performing of the four models, followed by the Jaroniec model, then the Halsey model and finally the Carbon black model.

3.4. Samples Stabilized with 16% Cane Molasses

The experimental ratio of nitrogen absorption on clay concrete stabilized at 16% and the statistical thickness values calculated using the model formulae (page 3) are shown in **Table 9**.

The curves in **Figure 7** are more linear than at 8% and 12% and at 0%, which corresponds to multilayer adsorption on a surface with low porosity, which may be justified by the prior occupation of the pores by sugarcane molasses. The adjusted correlation coefficients obtained for the Harkins and Jura model: 0.99836 (**Table 6**) for clay concrete stabilized at 8%, 0.99825 (**Table 8**) for clay concrete stabilized at 12%, 0.99936 (**Table 10**) for clay concrete stabilized at 16%, show an increase in linearization (**Figure 8**) with molasses content, which can be explained by the absence of condensation in the pores, as the molasses molecules occupy these pores.

Table 8. Comparison of the models using the AIC, BIC, chi-square criteria and the adjusted coefficient of determination for clay concrete stabilized at 12%.

	Carbon black model	Harkins and Jura model	Halsey model	Jaroniec model
AIC	−58.8134	−75.1589	−69.8529	−74.5081
BIC	−59.7852	−76.1307	−70.8247	−75.4799
χ^2	0.00658	0.00187	0.00281	0.00197
R^2_{adj}	0.99384	0.99825	0.99736	0.99816

Table 9. Experimental ratio and statistical thicknesses for clay concrete stabilized at 16%.

Relative Pressure (P/P_0)	Carbon Black Thickness (nm)	Harkins model Thickness (nm)	Halsey model Thickness (nm)	Jaroniec model Thickness (nm)	Quantity Adsorbed (cm^3/g STP)
0.08358735	0.35252868	0.3826	0.4471	0.4894	5.5790847
0.11981833	0.37654619	0.4071	0.4711	0.5198	5.97101725
0.15476076	0.39992837	0.4303	0.4916	0.5461	6.33384039
0.18983993	0.4236182	0.4529	0.5111	0.5707	6.67888037
0.22495839	0.44755151	0.4754	0.5297	0.5946	7.01800274
0.26008118	0.471705	0.4981	0.5481	0.6181	7.36323975
0.29522146	0.49608755	0.5212	0.5665	0.6414	7.70545417
0.33038712	0.52070539	0.5444	0.5851	0.6649	8.05151052
0.36470714	0.5449411	0.5689	0.6035	0.6886	8.41160545
0.39977152	0.56991655	0.5945	0.6231	0.7133	8.77957005
0.43469854	0.59500928	0.6215	0.6433	0.7388	9.16679767
0.46969561	0.62036769	0.6501	0.6645	0.7656	9.56917314

The linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample is shown in **Figure 8**.

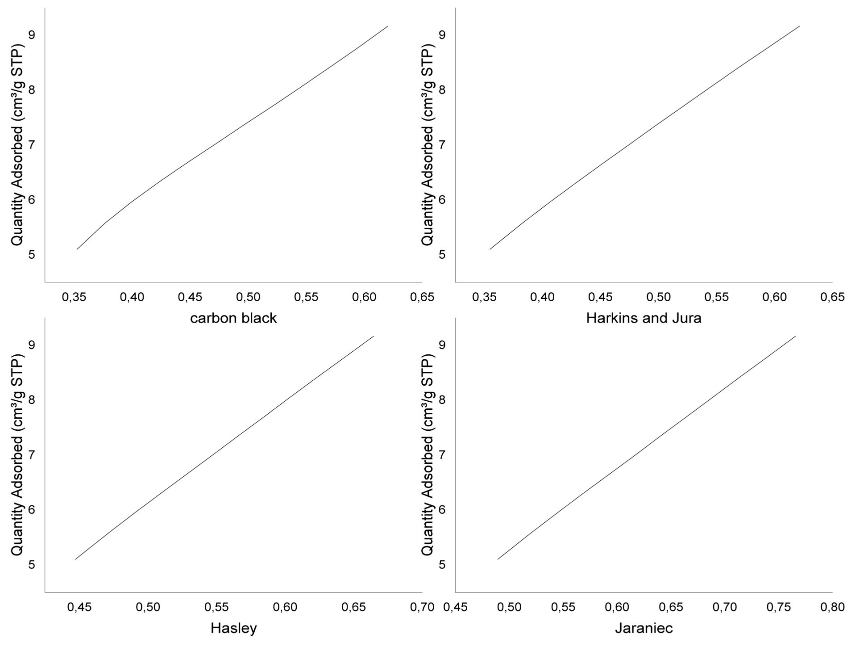

Figure 7. Amount of nitrogen adsorbed per gram of sample for clay concrete stabilized at 16% as a function of statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

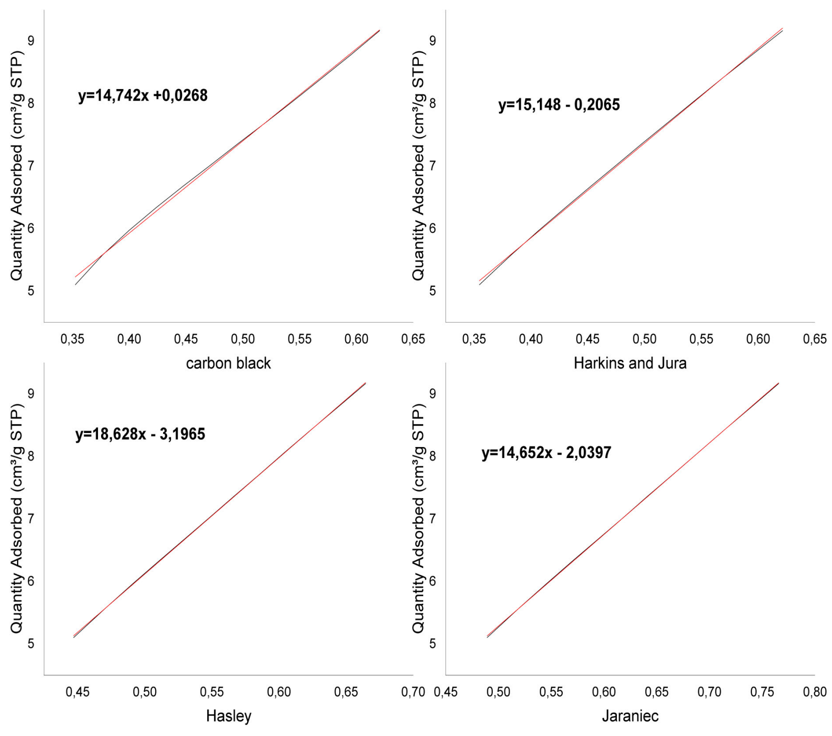

Figure 8. Linear interpolation of the curves for the quantity of nitrogen adsorbed per gram of sample for clay concrete stabilized with 16% molasses as a function of the statistical thickness t (carbon black, Halsey, Harkins and Jura, Jaroniec).

Table 10 gives the values of the model selection criteria for 16% stabilized concrete.

The Harkins and Jura model has the highest R^2_{adj} value, the lowest χ^2 value, the lowest BIC value and the lowest AIC value (**Table 10**), indicating that it is the best performing of the four models, followed by the Jaroniec model, then the Halsey model and finally the Carbon black model.

Table 11 gives the values of slope and external specific surface as a function of the statistical thickness models.

Table 12 gives the BET specific surface area and micropore surface area values for stabilized and non-stabilized concretes according to the models used.

The results obtained show that the Halsey model performs best for non-stabilized clay soil. However, the external specific surface area values obtained by this model are higher than the BET specific surface area values, so it is not possible to obtain the micropore surface area by this model. Thus, the Carbon Black model becomes the most relevant for non-stabilized clayey concrete, followed by the Jaroniec model, and finally by the Harkins and Jura model.

Table 10. Comparison of models using the AIC, BIC, chi-square and adjusted coefficient of determination criteria for clay stabilized at 16%.

	Carbon black model	**Harkins and Jura model**	**Halsey model**	**Jaroniec model**
AIC	−64.8245	−75.2547	−67.5963	−74.3025
BIC	−66.36987	−76.8000	−69.1416	−75.8477
χ^2	0.00255	0.00107	0.00203	0.00116
R^2_{adj}	0.99847	0.99936	0.99879	0.99931

Table 11. Slope and external specific surface values as a function of statistical thickness models.

	Carbon black		Halsey model		Harkins model		Jaroniec *et al.*	
	P (cm³ /g·nm)	σ_{ext} (m² /g)	P (cm³ /g·nm)	σ_{ext} (m² /g)	P (cm³ /g·nm)	σ_{ext} (m² /g)	P (cm³ /g·nm)	σ_{ext} (m² /g)
0% molasses	20.06	31.03	24.69	38.19	20.24	31.31	19.42	30.04
8% molasses	11.31	17.49	13.98	21.63	11.44	17.69	10.99	17.01
12% molasses	10.96	16.96	13.56	20.97	11.09	17.16	10.66	16.50
16% molasses	14 .75	23.21	18.63	28.82	15.1	23.26	14.65	22.66

Table 12. BET specific surface area and micropore surface area according to the models used.

	σ(BET) (m²/g) [2] [3]	Carbon black $\sigma_{micropore}$ (m²/g)	Halsey Model $\sigma_{micropore}$ (m²/g)	Harkins Model $\sigma_{micropore}$ (m²/g)	Jaroniec *et al.* $\sigma_{micropore}$ (m²/g)
0% molasses	32.84	1.81	1.53	-	2.8
8% molasses	21.04	3.55	3.35	-	4.03
12% molasses	18.61	1.65	1.45	-	2.11
16% molasses	23.56	0.35	0.3	-	0.9

The results obtained for stabilized clay concretes show that the Harkins and Jura model is the most relevant, followed by the Jaroniec model and, finally, the Carbon Black model. The Halsey model does not provide micropore surfaces for the same reason as mentioned above.

This change compared to unsterilized clayey concrete leads us to believe that stabilization using molasses brings about modifications to the external surface of clayey concrete by occupying the pores [4]. Ngouallat Mfoutou (2020) reports that 53.10^8 molasses molecules occupy the accessible surface of clay concrete [3].

The change in the shape of the curve from the curved form for clay concrete without molasses to the more linear form for stabilized clay concretes also expresses the change in texture of clay concrete from a porous material to a less and less porous material.

According to Tchemmou and Gherbi (2018), the t-plot method can be used to determine the external surface of microporous materials of the zeolite type [7]. For Magee (1995) cited Moulin (2018) [1], the Carbon black model is designed for the specific case of carbon blacks. Nevertheless, the results obtained show that the Carbon black model is also relevant for the case of clay concretes. Ngouallat (2022) used the Carbon Black statistical thickness model to obtain the textural properties of clay concretes stabilized with molasses [2].

According to Jeffrey Kevin (2008), the Carbon black statistical thickness model can also be used to determine the external surface of cetyltrimethyl ammonium bromide [3].

The carbon black and Halsey equations (Eq. 2 and 3) are applicable to carbon black and related materials [15].

According to Yijing Zheng (2008), the t-plot method (Halsey model, Harkin and Jura model, Carbon black model) used for the physical characterization of common adsorbents may not be applicable to carbon nanotubes [5].

The Harkins and Jura equation has been developed for well-selected alumina samples; however, it is applicable to other materials, including graphitized carbon blacks [17].

The most commonly applied thickness curves are those of Harkin-Jura and Halsey (Webb and Orr, 1997) [6]. Utpalendu Kuila and Manika Prasad (2011), have used Halsey thickness curves to estimate micropore volume and "open area", mesopore area, macropore area and external area (i.e. total area excluding micropore area) in natural clay minerals and shales [18].

4. Conclusion

The gist of this study has been to compare statistical thickness models for the determination of textural properties for the case of clay concrete and for stabilized clay concretes. The results showed that:

- Halsey's model can be used to obtain external surfaces. However, it does not allow the surface of the micropores to be obtained. It is not suitable for clay concrete and for clay concretes stabilized with molasses.

- The Carbon Black model, the Jaroniec model and the Harkins and Jura model can be used for clay concrete and for stabilized clay concrete.
- The Carbon Black model is the most relevant for clay concrete.
- The Harkins and Jura model is the most appropriate for molasses-stabilized clay concrete.

Conflicts of Interest

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

References

[1] Moulin, L. (2018) Vapothermolyse des pneus usagés. Valorisation du noir de carbone récupéré, relation procédé-produit. Doctoral Thesis, Université de Toulouse, France.

[2] Ngouallat, M.N. (2023) Étude des mécanismes internes lies à la stabilisation des sols fins argileux à l'aide de la mélasse de canne à sucre. Thèse de Doctorat, Université Marien-Ngouabi, Brazzaville.

[3] Ngouallat, M.N., Malanda, N., NzabaMadila, E.E. and Louzolo-Kimbembe, P. (2022) Adsorption Isotherm of BET Nitrogen of ConcreteswithConsolidated Soil by Sugar Cane Molasses. *Journal of Materials Science and Engineering B*, **12**, 78-96. https://doi.org/10.17265/2161-6221/2022.7-9.002

[4] Malanda, N., Mfoutou, N., Madila, E. and Louzolo-Kimbembe, P. (2022) Microstructure of Fine Clay Soils Stabilized with Sugarcane Molasses. *Open Journal of Civil Engineering*, **12**, 247-269.

[5] Zheng, Y.J. (2008) Evaluation of a New Method to Estimate the Micropore Volume and External Surface Areaof Single-walled Carbon Nanotubes. Master's Thesis, University of Tennessee, Knoxville. https://trace.tennessee.edu/utk_gradthes/3673 https://doi.org/10.4236/ojce.2022.122015

[6] Webb, P.A. and Orr, C. (1997) Analytical Methods in Fine Particle Technology. Micromeritics Instrument Corporation, Norcross, GA, USA.

[7] Siham, T. and Amina, G. (2018) Développement des zéolithes à porosité hiérarchisée: adsorbants pour la dépollution en solution aqueuse. Mémoire de Master, Université Mouloud Mammeride Tizi-Ouzou, Algérie.

[8] Kevin, J. (2008) Characterization of Powders and Porous Materials with Pharmaceutical Excipient Case Studies. Micromeritics Instrument Corporation, Norcross, GA, USA.

[9] Boukabous, H. (2017) Étude de l'élimination d'un colorant en présence de catalyseurs à base de TiO_2 supporté sur un silico-aluminophosphate microporeux. Université Abdelhamid Ibn Badis, Mostaganem.

[10] Emeline, R. (2013) Purification, recuit et désassemblage d'échantillons de nanotubes de carbone: propriétés structurales et caractérisations de surface. Thèse de doctorat, Université de Lorraine, France.

[11] ASTM (2014) Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption. https://www.astm.org/d6556-21.html

[12] Ghania, H. (2018) Cours des Phénomènes de surface et catalyse hétérogène. Université Hassiba Benbouali de Chlef, Ouled Fares.

[13] Shi, K.H., Santiso, E.E. and Gubbins, K.E. (2021) Current Advances in Characteri-

zation of Nano-Porous Materials: Pore Size Distribution and Surface Area. In: Moreno-Piraján, J.C., Giraldo-Gutierrez, L. and Gómez-Granados, F., eds., *Porous Materials. Engineering Materials*. Springer, Cham. https://doi.org/10.1007/978-3-030-65991-2_12

[14] Bertrand, F. and Maumy, M. (2008) Choix du modèle. IRMA, Université Louis Pasteur, Strasbourg, France.

[15] Ngouallat, M.N., Malanda, N. and Louzolo-Kimbembe, P. (2020) Analyse macroscopique des effets de la mélasse de canne à sucre sur le sol fin argileux. *Revue RAMReS—Sciences Appliquées et de l'Ingénieur*, **2**, 24-31.

[16] Malanda, N., Louzolo-Kimbembe, P. and Tamba-Nsemi, Y.D. (2017) Etude des caractéristiques mécaniques d'une brique en terre stabilisée à l'aide de la mélasse de canne à sucre. *Revue du CAMES—Sciences Appliquées et de l'ingénieur Cames*, **2**, 1-9.

[17] Magee, R.W. (1995) Evaluation of the External Surface Area of Carbon Black by Nitrogen Adsorption. *Rubber Chemistry and Technology*, **68**, 590-600.

[18] Kuila, U. and Prasad, M. (2011) Specific Surface Area and Pore-Size Distribution in Clays and Shales. *Geophysical Prospecting*, **61**, 341-362. https://doi.org/10.2118/146869-MS