

Copper Adsorption on Calcined Substrates from Three Granulometric Fractions Coming from Two Refractory Variable Charges Lithological Materials

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Abstract— The paper presents the adsorption of copper ions on calcined substrates with variable charge surfaces prepared with refractory lithological materials coming from localities near Mérida city, Mérida State, Venezuela, (Lagunillas and Los Guáimaras). The studies were performed on activated and non activated calcined substrates, prepared from three granulometric fractions: gross fraction (1200 μm – 425 μm), medium fraction (425 μm – 250 μm) and fine fraction (< 250 μm). The obtained isotherms were *L* type, showing strong affinity of Cu^{+2} ions for substrates surfaces, especially in case of activated substrate. This type of isotherm suggest specific adsorption with the formation of a directional covalent bonding between Cu^{+2} ion and the substrate surface formed by iron, aluminum, manganese and titanium amphoteric oxides. The linear fit using the Freundlich and Langmuir models show good linear correlations; however, differences between calculated and experimental values are higher when Freundlich model is applied. Adjustment to Langmuir model show better linear correlations and smaller differences and variability between calculated and experimental data so Langmuir model is more appropriated for experimental data interpretation

Keywords— Adsorption, calcined substrates, copper ion, lithological materials, three granulometric fractions.

I. INTRODUCTION

Adsorption properties of tropical soils of variable charges are very well described in the soil literature [1]. There are reviewed and discussed heavy metals adsorption mechanism by these is kind of soils. In a previous study [2], three granulometric fractions from three lithological materials of variable charges founds near Mérida city, Venezuela specifically Lagunillas, Los Guáimaras and El Vallecito, were described and characterized for further use in preparing adsorbents substrate for ionic adsorption.

The high content of metals that form amphoteric oxides with variable charges like iron, aluminum, titanium and manganese, and others amorphous silicates and aluminosilicates with variable charges surfaces allows their use for preparing adsorbing substrates for cation as well as for anions adsorption. As a consequence of this particular property, these materials can participate in cation and anion exchange and chemisorption reactions with transitional metals and oxyanions with alkaline or acid treatment of surface substrate [3]. Such kind of property make these lithological materials versatile for preparing calcined adsorbing substrates and it's applications in several ways in water treatment, water purification and softening owing their capacity for anion and cation exchange, heavy metals, oxyanions and organic matter removing by adsorption processes.

Studies on calcium adsorption on these kinds of substrate revealed that calcium participates in an exchange reaction getting nonspecific adsorption capacities ranging from 140 up to 200 $\text{mg kg}^{-1} \text{Ca}^{+2}$ for substrate prepared with Lagunillas material and from 143 up to 180 $\text{mg kg}^{-1} \text{Ca}^{+2}$ for substrate prepared with Los Guáimaras material [4]. In case of substrates prepared with Lagunillas and Los Guáimaras materials, the exchanging performance is improved significantly (500 % and 300 % respectively) by treating the substrate with 0.01 M NaCl solution, as a consequence of substrate regeneration by calcium displacement. The study of copper and zinc adsorption on this kind of substrate revealed that these transitional metals could participate in a specific chemisorption reaction which is *pH* dependent, especially copper ions [5]. It is reported adsorption of 21.5, 13.9 and 23.4 $\text{mg kg}^{-1} \text{Cu}^{+2}$ and 10.13, 16.92 and 15.29 $\text{mg kg}^{-1} \text{Zn}^{+2}$ for the substrates prepared with the El Vallecito, Los Guáimaras and Lagunillas materials respectively.

By the other hand, sulphate adsorption on this kind of substrate prepared with material from Lagunillas and Los Guáimaras showed an adsorption capacity of $2.26 \text{ g kg}^{-1} \text{ SO}_4^{2-}$ on substrate made with Lagunillas material and $1.75 \text{ g kg}^{-1} \text{ SO}_4^{2-}$ for the Los Guáimaras material [6]. After acidic treatment sulfate adsorption was improved only 9%. The phosphate adsorption on a similar adsorbent substrate prepared with soil from Michelena, Táchira State has been also studied [7]. Adsorption of $272 \text{ mg kg}^{-1} \text{ PO}_4^{3-}$ was measured on calcined substrate and $524 \text{ mg kg}^{-1} \text{ PO}_4^{3-}$ on activated substrate. The main goal of this paper is to investigate the nature of copper adsorption on these calcined substrates prepared with the three granulometric fractions from each material as an example of transitional metal adsorption on this kind of substrate.

II. MATERIALS AND METHODS

Separation of granulometric fractions was made with the respective ASTM:II Laboratory Test Sieve (Endecotts Ltd, England) and shake with automatic vibrator Octagon Digital CE during 15 min. All measurements were made on in three granulometric fractions: gross fraction ($1200 - 400 \mu\text{m}$), medium fraction ($400 - 200 \mu\text{m}$) and fine fraction ($< 200 \mu\text{m}$) of Lagunillas and Los Guáimaras materials, according to the nomenclature showed in Table I.

TABLE I
CODES OF ANALYZING SAMPLES

Material	Gross fraction	Medium fraction	Fine fraction
Lagunillas	LFG	LFM	LFF
Los Guáimaras	GFG	GFM	GFF

Preparation of calcined substrate or exchanger and thermal treatment are described in the literature [4, 5]. Figure 1 show a flux diagram for the substrate preparation process.

To activate negative charges the calcined substrate is treated with alkaline solution of 0.01 N NaOH during 12 h. After this time the substrate is washed with distilled water until neutral pH. Adsorption was studied using batch equilibration procedure treating 2 g of calcined substrate with 5, 10, 15, 20, 25, 30 and 40 mL of 0.001 M Cu^{+2} , by triplicate. Suspensions were shaken at $20 \pm 2 \text{ }^\circ\text{C}$ for 24 h in 100 mL glass beakers. Cu^{+2} equilibrium concentration was determined in aliquot of 5 mL supernatant by complexometric titration with a 0.001 M EDTA solution.

Differences between C_i and C_{eq} were assumed to be due to adsorption. Adsorption isotherms were obtained by plotting the amount of copper adsorbed (mmol g^{-1} substrate) against the equilibrium concentration (mmol) and fitted to the linear form of the Freundlich equation (1).

$$\log C_{ad} = \log K + \frac{1}{n} \log C_{eq} \quad (1)$$

$$C_{ad} = K \times C_{eq}^{1/n} \quad (2)$$

Constants K and $1/n$ are given by the graph from the intercept and the slope respectively. Values of K and $1/n$ are then introduced in equation (2) to determine value of calculated C_{ad} and then compared with experimental value. Adsorption data were also fitted to the linear form of Langmuir equation (3) and K_2 and K_1 are determined by the straight line from the slope and the intercept respectively. Values of K_1 and K_2 are then introduced in equation (4) to determine value of calculated $1/m$ and then compared with experimental value.

$$\frac{C_{eq}}{x/m} = \frac{1}{K_1 \times K_2} + \frac{C_{eq}}{K_2} \quad (3)$$

$$\frac{x}{m} = \frac{K_1 \times K_2 \times C_{eq}}{(1 + K_1 \times C_{eq})} \quad (4)$$

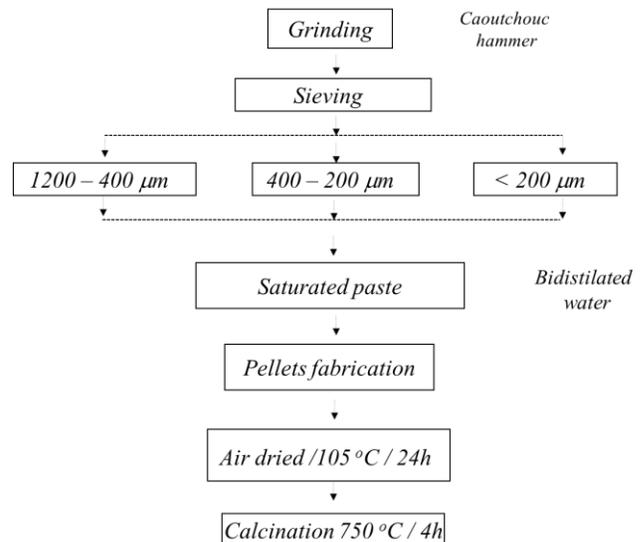


Figure 1. Flux diagram for the substrate preparation process.

III. RESULTS

A. Adsorption Studies on Adsorbent Substrate made with Lagunillas Material

1) *Isotherm graph*: Figure 2 shows the adsorption isotherms of Cu^{+2} on adsorbent substrates made with the three granulometric fractions from Lagunillas material, (LFG, LFM and LFF) activated with 0.10 N NaOH and non activated. The isotherm profiles show but doesn't confirm information about which kind of interaction between Cu^{+2} ions and substrate surface take place. However, the L type isotherm is indicative of great affinity between adsorbent and adsorbate and in general it tends to a saturation zone. The flat part of the curve suggests formation of a saturated monolayer of copper ions on the surface as is predicted by the Langmuir model and chemisorption occurs on a single layer.

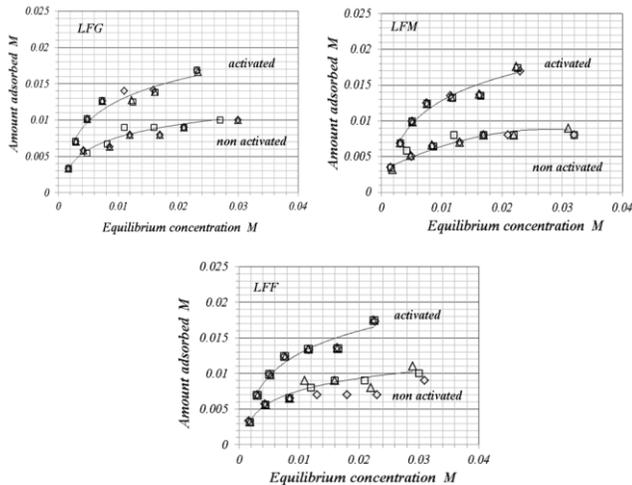


Figure 2. Copper adsorption isotherms on substrates made of the three granulometric fractions from Lagunillas material.

As it can be seen from the isotherm graph, copper adsorption is greater on activated material than in non activated material. It is due to the greater negative charges density created after oxides deprotonation with alkaline treatment. It is also seen from the isotherm graphs that there is no a defined influence of granulometric fraction on adsorption phenomena.

2) *Adjustment to Freundlich model*: Figure 3 show linear adjustments of adsorption data using the Freundlich model for activated and non activated adsorbent substrates made of the three granulometric fractions from Lagunillas material, activated and non activated.

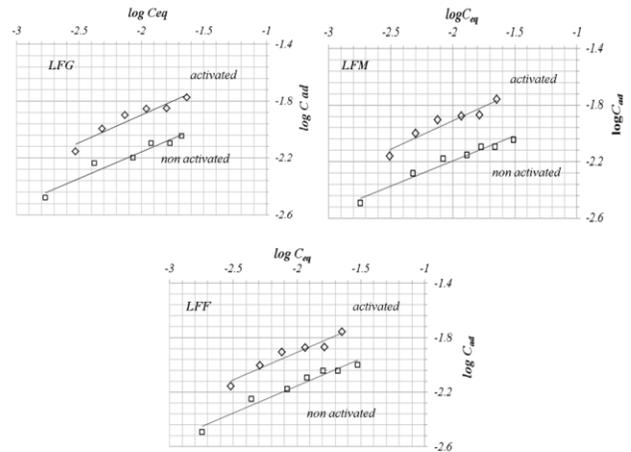


Figure 3. Fitting isotherms to the logarithmic form of the Freundlich equation for adsorbent substrates, prepared from the three granulometric fractions from Lagunillas material.

Table II show fitted equations, correlation coefficients and K values for all cases. From equations, $1/n$ values, which represent slope of the straight line, agree with those reported by literature between 0.3 and 0.5 and could be interpreted as a deviation from linearity of the model [8, 9].

From graph and correlation coefficients it can be seen relative good linearity in all cases (one single 9), even when K values are higher for activated substrates from the three granulometric fractions, results doesn't show evidence of granulometric fractions influence on the performance of adsorption phenomena. From respective K values, adsorption in non activated material range from 1.15 to 1.40 $\text{g kg}^{-1} \text{Cu}^{+2}$ substrate and on activated substrate range from 2.42 to 2.55 $\text{g kg}^{-1} \text{Cu}^{+2}$ substrate.

However, to prove adjustment to the model it is not enough to show good linearity according to the logarithmic form of Freundlich equation (1); it is necessary to show good correlation between experimental and calculated data from equation (2), and little difference between them. Figure 4 show correlations between experimental and calculated data and Table III show correlation coefficients, average difference and variation coefficients in all cases. In general, there is better linear correlation for activated substrate than for non activated substrate and little average difference, in %, between experimental and calculated value but there is great variability between individual differences. This could be owed to the irregular surface of substrate making active adsorbent sites not equivalent between them.

TABLE II
RESULTS FOR FREUNDLICH MODEL: FITTED EQUATION, CORRELATION COEFFICIENTS AND K VALUE, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LAGUNILLAS MATERIAL

Granulometric Fraction	Fitted equation	r	K (mmol/2g subst)
LFG non activated	$\log C_{ad} = -1.4093 + 0.3738 \log C_{eq}$	0.9746	0.0390
LFG activated	$\log C_{ad} = -1.1180 + 0.3898 \log C_{eq}$	0.9559	0.0762
LFM non activated	$\log C_{ad} = -1.4874 + 0.3540 \log C_{eq}$	0.9821	0.0326
LFM activated	$\log C_{ad} = -1.0976 + 0.4064 \log C_{eq}$	0.9546	0.0799
LFF non activated	$\log C_{ad} = -1.3560 + 0.3990 \log C_{eq}$	0.9800	0.0441
LFF activated	$\log C_{ad} = -1.0956 + 0.4066 \log C_{eq}$	0.9620	0.0802

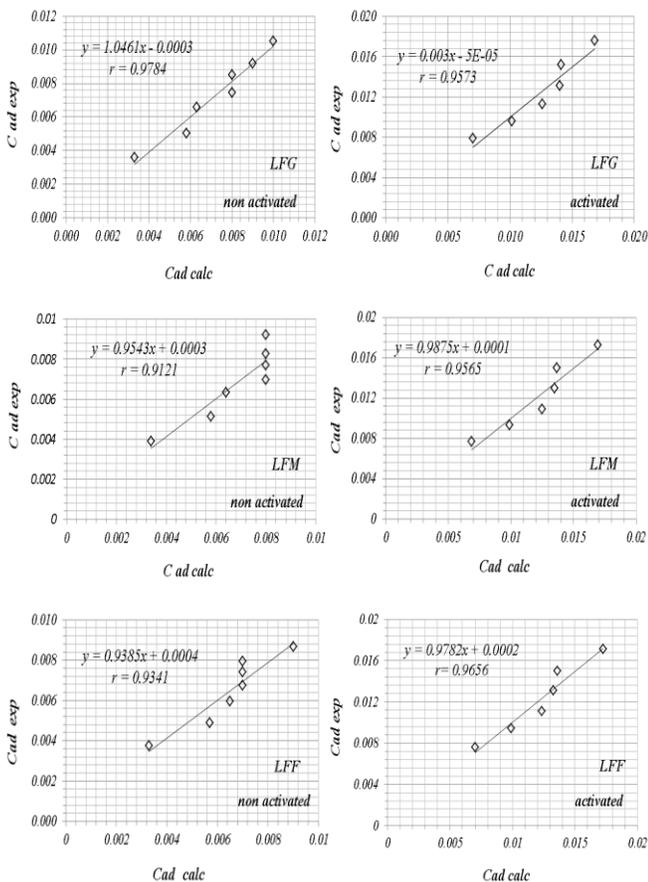


Figure 4. Correlations between calculated and experimental value of C_{ad} , for activated and non activated adsorbent substrates, prepared from the three granulometric fractions from Lagunillas material.

TABLE III
CORRELATION COEFFICIENTS, AVERAGE DIFFERENCE AND VARIATION COEFFICIENTS (%VC) FOR DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF C_{ad} FROM FREUNDLICH EQUATION, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LAGUNILLAS MATERIAL

	R^2	Average difference	% VC
LFG activated	0.9166	0.35 ± 9.10	-26.00
LFG non activated	0.9572	0.99 ± 7.95	8.01
LFM activated	0.9149	0.39 ± 10.43	-26.00
LFM non activated	0.8321	0.52 ± 11.20	-21.08
LFF activated	0.9324	0.30 ± 7.96	-26.00
LFF non activated	0.8725	0.48 ± 10.72	-22.34

3) *Adjustment to Langmuir model:* Figure 5 show adjustments to the Langmuir model and in Table IV it is shown fitted equations, linear correlations coefficients and values of constants K_1 and K_2 . Correlation coefficients show a better linearity than in the case of Freundlich model so Langmuir model describe in a better way copper adsorption on adsorbent substrate made of Lagunillas material. K_2 which defines straight line slope, is higher for activated substrates confirming what it was shown by the Freundlich model but these values neither show evidence about influence of granulometric fractions on adsorption phenomena, as K_2 value are almost constant in all cases.

TABLE IV
RESULTS FOR LANGMUIR MODEL: FITTED EQUATION, CORRELATION COEFFICIENTS, AND K_1 AND K_2 VALUES, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LAGUNILLAS MATERIAL

Granulometric Fraction	Fitted equation	r	K_1	K_2
LFG non activated	$C_{eq}/(x/m) = 0.8343 + 172.60 C_{eq}$	0.9933	206.88	0.0058
LFG activated	$C_{eq}/(x/m) = 0.5243 + 103.01 C_{eq}$	0.9888	196.47	0.0097
LFM non activated	$C_{eq}/(x/m) = 0.4850 + 230.31 C_{eq}$	0.9977	474.86	0.0043
LFM activated	$C_{eq}/(x/m) = 0.5703 + 98.21 C_{eq}$	0.9868	172.20	0.0102
LFF non activated	$C_{eq}/(x/m) = 0.8012 + 219.73 C_{eq}$	0.9807	274.25	0.0046
LFF activated	$C_{eq}/(x/m) = 0.5711 + 97.56 C_{eq}$	0.9832	170.82	0.0103

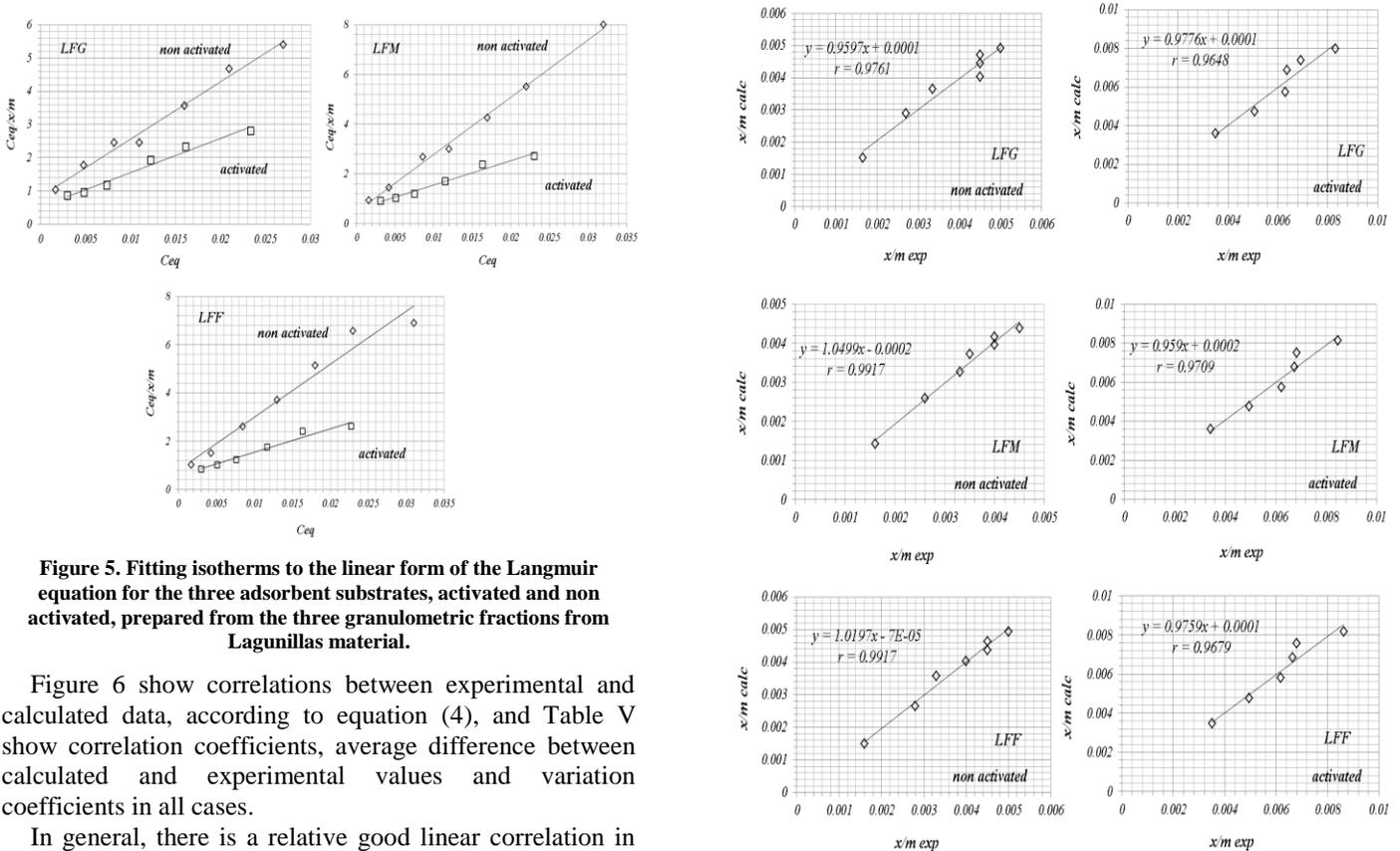


Figure 5. Fitting isotherms to the linear form of the Langmuir equation for the three adsorbent substrates, activated and non activated, prepared from the three granulometric fractions from Lagunillas material.

Figure 6 show correlations between experimental and calculated data, according to equation (4), and Table V show correlation coefficients, average difference between calculated and experimental values and variation coefficients in all cases.

In general, there is a relative good linear correlation in all cases, little average difference, in %, between experimental and calculated value and a smaller variation coefficient than in the cases of Freundlich adjustment, showing better accuracy of Langmuir equation.

Figure 6. Correlations between calculated and experimental value of C_{ad} , for the three adsorbent substrates, activated and non activated, prepared from the three granulometric fractions from Lagunillas material

TABLE V
 CORRELATION COEFFICIENTS, AVERAGE DIFFERENCE AND VARIATION COEFFICIENTS (%VC) FOR DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF x/M , FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LAGUNILLAS MATERIAL

	R^2	Average difference	% VC
LFG activated	0.9308	-0.82 ± 7.05	-8.62
LFG non activated	0.9528	-0.73 ± 7.71	-10.52
LFM activated	0.9427	-0.50 ± 6.45	-12.96
LFM non activated	0.9834	-1.24 ± 5.78	-4.68
LFF activated	0.9369	-0.75 ± 6.21	-8.28
LFF non activated	0.9834	-0.79 ± 5.13	-6.46

B. Adsorption Studies on Adsorbent Substrate made with Los Guáimaras Material

1) *Isotherm graph*: Figure 7 shows the adsorption isotherms of copper on adsorbent substrates made of the three granulometric fractions from Los Guáimaras material (GFG, GFM and GFF), activated with NaOH 0.10 N and non activated. Isotherms show similar characteristics as in the former case of substrate made of Lagunillas material but it seems to be a greater affinity between substrate surface and copper ions, especially for activated substrate, probably producing a specific adsorption or chemisorption of copper ions by the surface oxides. On the other hand, isotherms graphs are very similar in all cases for the adsorbent substrates made of the three granulometric fractions, showing no influence of granulometric fraction on the process of adsorption.

2) *Adjustment to Freundlich model*: Figure 8 show linear adjustments of adsorption data to the Freundlich model for all adsorbent substrates made of the three granulometric fractions from Los Guáimaras material, activated and non activated. Table VI show fitted equations, correlation coefficients and K values for all cases. The $1/n$ values agree with those reported by literature between 0.3 and 0.5. From graph and correlation coefficients it can be seen, as in the former cases, relative good linearity for all cases but K values are higher than in case of substrate prepared with Lagunillas material.

This K values are lightly smaller for activated than for non activated substrates prepared from gross and fine granulometric fractions but is two and a half times higher in activated substrate from medium granulometric fraction. A possible explanation could be the fact that Freundlich model is less accurate than Langmuir model and can't reproduce what is shown by isotherms.

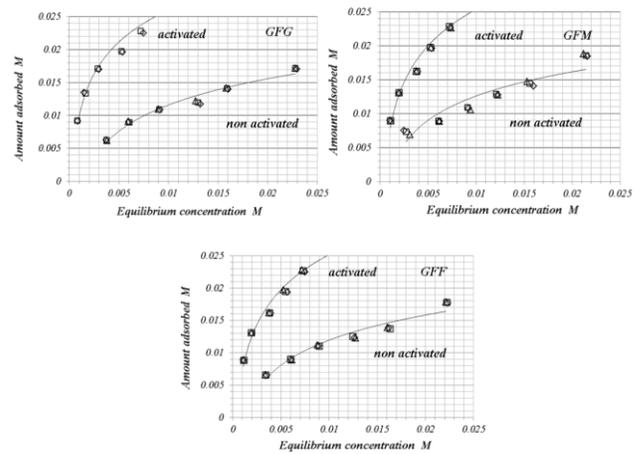


Figure 7. Copper adsorption isotherms on substrates prepared from the three granulometric fractions from Los Guáimaras material.

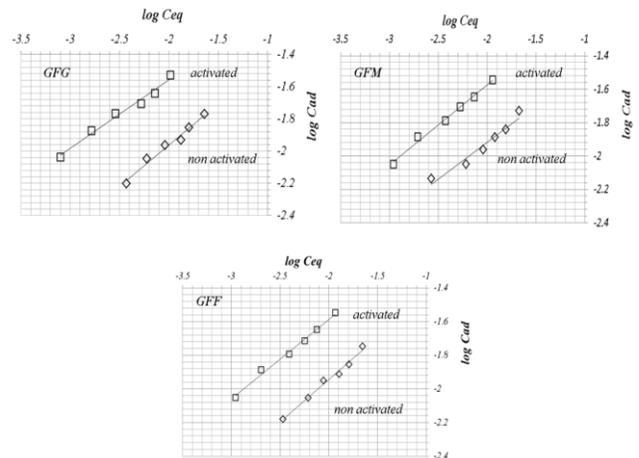


Figure 8. Fitting isotherms to the logarithmic form of the Freundlich equation for the three substrates from Los Guáimaras material.

Figure 9 show correlations between experimental and calculated data while Table VII show correlation coefficients, average difference and variation coefficients in all cases.

In general, there is better linear correlation for activated than for non activated substrate and little average difference, in %, between experimental and calculated

value but there is great variability between individual differences in the case of activated and non activated substrates made of medium granulometric fraction.

TABLE VI
RESULTS FOR FREUNDLICH MODEL: FITTED EQUATION, CORRELATION COEFFICIENTS AND K VALUE, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LOS GUÁIMAROS MATERIAL

Granulometric Fraction	Fitted equation	r	K (mmol/2g subst)
GFG non activated	$\log C_{ad} = -0.7118 + 0.4237 \log C_{eq}$	0.9917	0.1942
GFG activated	$\log C_{ad} = -0.9304 + 0.5152 \log C_{eq}$	0.9887	0.1174
GFM non activated	$\log C_{ad} = -1.0312 + 0.4441 \log C_{eq}$	0.9766	0.0931
GFM activated	$\log C_{ad} = -0.6188 + 0.4782 \log C_{eq}$	0.9957	0.2405
GFF non activated	$\log C_{ad} = -0.6418 + 0.4723 \log C_{eq}$	0.9956	0.1176
GFF activated	$\log C_{ad} = -0.9297 + 0.5070 \log C_{eq}$	0.9929	0.0802

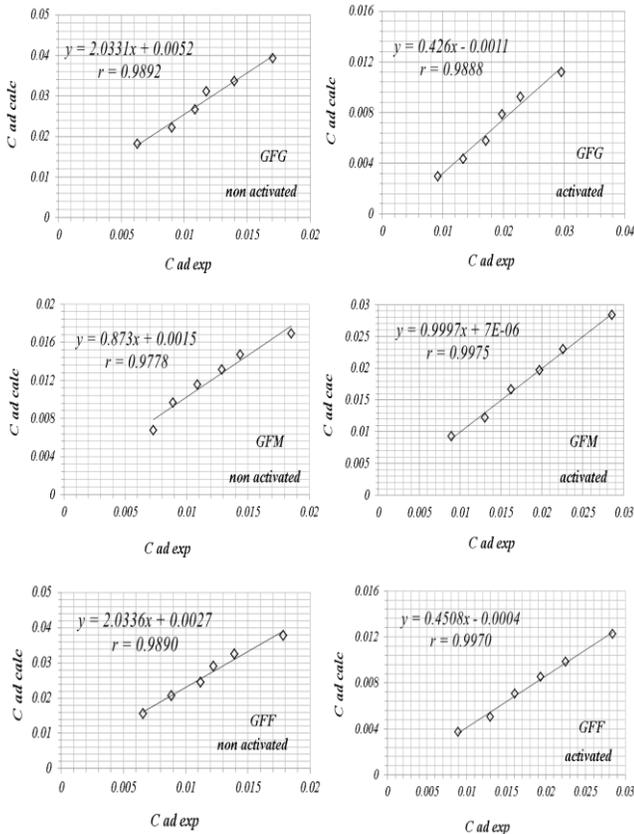


Figure 9. Correlations between calculated and experimental value of C_{ad} , for the three adsorbent substrates, activated and non activated, prepared from the three granulometric fractions from Los Guáimaras material.

TABLE VII
CORRELATION COEFFICIENTS, AVERAGE DIFFERENCE AND VARIATION COEFFICIENTS (%VC) FOR DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF C_{ad} FROM FREUNDLICH EQUATION, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LOS GUÁIMAROS MATERIAL

	R^2	Average difference	% VC
GFG activated	0.9777	14.22 ± 7.67	0.57
GFG non activated	0.9630	60.23 ± 3.11	0.05
GFM activated	0.9949	-0.045 ± 3.92	-85.60
GFM non activated	0.9560	-0.22 ± 7.33	-32.85
GFF activated	0.9940	-135.16 ± 11.83	-0.08
GFF non activated	0.9781	56.07 ± 2.12	0.04

3) *Adjustment to Langmuir model:* Figure 10 show adjustments to the Langmuir model and Table 8 show fitted equations, linear correlations coefficients and values of constants K_1 and K_2 . Correlation coefficients show a similar linearity as in the case of Freundlich model. K_2 which defines straight line slope is lightly higher for activated than for non activated substrates as it is expected. As in the case of substrate made of Lagunillas material, neither these values doesn't show evidence about influence of granulometric fractions on adsorption phenomena. Also, K_1 values are more than two times greater for activated substrate than non activated substrate.

TABLE VIII

RESULTS FOR LANGMUIR MODEL: FITTED EQUATION, CORRELATION COEFFICIENTS, AND K_1 AND K_2 VALUES, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LOS GUÁIMAROS MATERIAL

Granulometric Fraction	Fitted equation	r	K_1	K_2
GFG non activated	$C_{eq}/(x/m) = 0.9304 + 82.517 C_{eq}$	0.9764	88.69	0.0121
GFG activated	$C_{eq}/(x/m) = 0.1675 + 57.442 C_{eq}$	0.9736	342.94	0.0174
GFM non activated	$C_{eq}/(x/m) = 0.7877 + 80.685 C_{eq}$	0.9467	102.43	0.0124
GFM activated	$C_{eq}/(x/m) = 0.2211 + 54.131 C_{eq}$	0.9844	244.83	0.0185
GFF non activated	$C_{eq}/(x/m) = 0.8862 + 80.051 C_{eq}$	0.9696	90.33	0.0125
GFF activated	$C_{eq}/(x/m) = 0.2292 + 54.634 C_{eq}$	0.9792	238.36	0.0183

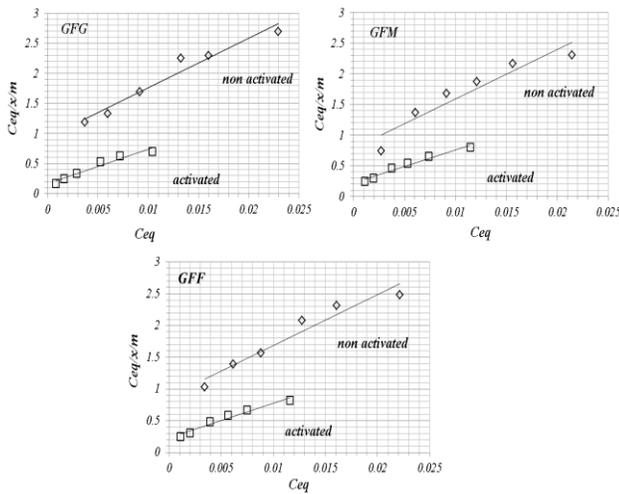


Figure 10. Fitting isotherms to the linear form of the Langmuir equation for the three substrates activated and non activated, prepared from Los Guáimaras material.

Figure 11 show correlations between experimental and calculated data, according to equation (4), and Table IX show correlation coefficients, average difference between calculated and experimental values and variation coefficients in all cases. In general, there is also a relative good linear correlation between calculated and experimental data; there are little average differences, in %, between these values and a smaller variation coefficient than in the cases of Freundlich adjustment, showing once again better accuracy of Langmuir equation.

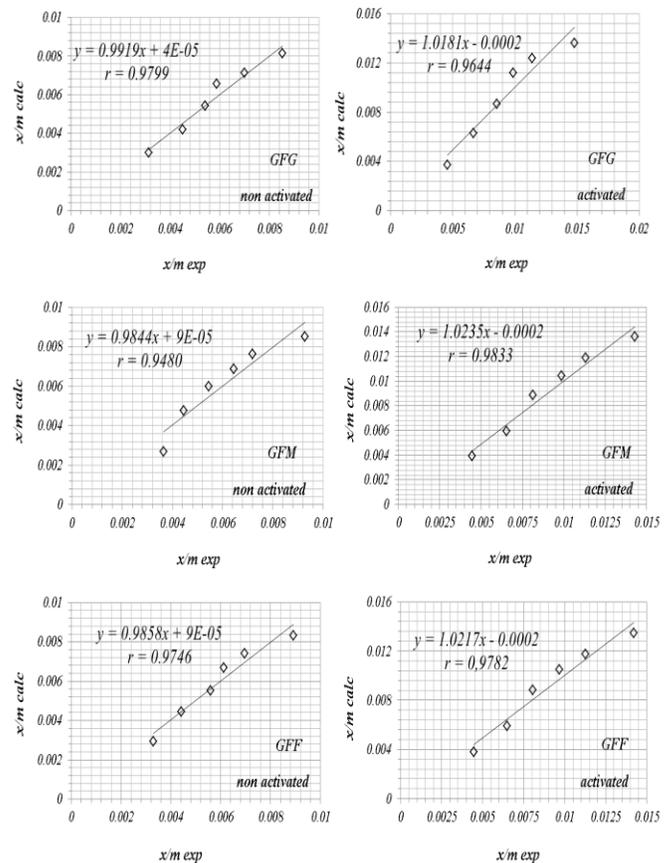


Figure 11. Correlations between calculated and experimental value of C_{ad} , for the three adsorbent substrates, activated and non activated, prepared from the three granulometric fractions from Los Guáimaras material.

TABLE IX
CORRELATION COEFFICIENTS, AVERAGE DIFFERENCE AND VARIATION COEFFICIENTS (% VC) FOR DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF X/M, FOR ACTIVATED AND NON ACTIVATED ADSORBENT SUBSTRATES, PREPARED FROM LOS GUÁIMAROS MATERIAL

	R ²	Average difference	% VC
GFG activated	0.9301	-2.81 ± 12.56	-4.46
GFG non activated	0.9602	-0.66 ± 6.27	-9.48
GFM activated	0.9688	-1.49 ± 8.99	-6.03
GFM non activated	0.9383	-2.97 ± 17.38	-5.85
GFF activated	0.9568	-1.85 ± 10.33	-5.69
GFF non activated	0.9499	-0.93 ± 7.83	-8.40

C. FT-IR Studies

To identify copper ion bond with substrate surfaces it was studied the of IR spectra (lower frequency zone) of crude materials (blue line) and calcined substrate (red and black lines) made of granulometric fraction up to 2000 μm (2 mm) particles diameter, from Lagunillas and Los Guáimaros materials. Figure 12 shows lower frequency region (1000 – 400 cm⁻¹) FT-IR spectra from Lagunillas material (Figure 12a) and Los Guáimaros material (Figure 12b).

The lower frequency region FT-IR spectra from crude Lagunillas material (blue line) show a broad band associated with Si – O vibration from quartz structure at 1031.52 cm⁻¹, Si – Si valence vibration from quartz at 754.19 and 693.77 cm⁻¹ and Si – O – M and M – O – H valence vibration at 535.63 and 471.39 cm⁻¹ respectively. These spectra also match with that exposed by Tang, [9, 10] for smectite type clay but all these bands could also be associated with amorphous silica and /or primary minerals [11]. In the lower frequency region FT-IR spectra from calcined material (red and black lines) also shows a strong band at 1040 cm⁻¹ corresponding to the Si - O valence vibrations, Si – Si valence vibration from quartz at 777.58 cm⁻¹ and Si – O – M and M – O – H valence vibrations from the smectite type clay at 558.44 cm⁻¹ and 483,66 cm⁻¹ (substrate calcined without copper) and 557.25 cm⁻¹ and 483.84 cm⁻¹ (substrate calcined with copper). Spectra from crude material and activated calcined substrate with and without copper are quiet similar so there is no evidence of copper bonding with oxides surface.

The lower frequency region of FT-IR spectra from crude Los Guáimaros material (blue line) shows characteristic bands for quartz (Si-O valence vibration 1101.87, 1033.42, 1008.12 and 913 cm⁻¹, Si – Si valence vibration 798.01, 779.08 and 694.70 cm⁻¹ and Si – O – Si distortion 431.00 and 470.12 cm⁻¹) and kaolinite (Si – O valence vibration 1008.12, 1033.42 and 1101.87 cm⁻¹, clay structural Al-Al-OH distortion at 913 cm⁻¹ and Si – O – M and M – O – H vibration 536.68, 470.12 and 430.98, cm⁻¹).

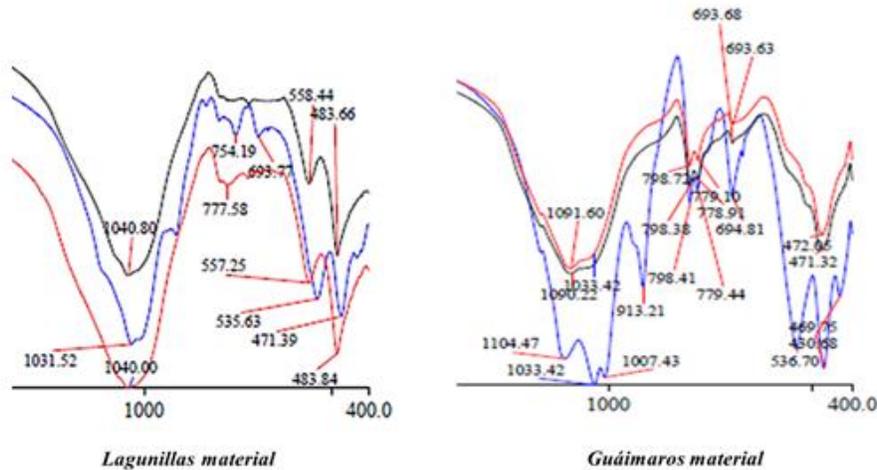


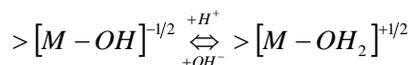
Figure 12. FT-IR spectra of crude materials (blue line) and calcined substrate (red and black lines) made of granulometric fraction up to 2.000 mm particles diameter, from Lagunillas and Los Guáimaros materials.

These bands overlap or mixing each other owing their proximity making difficult the spectra interpretation [12]. Quartz was already detected by the XRD analysis. These spectra also coincide with that exposed by Tang for kaolinite type clay [9, 10].

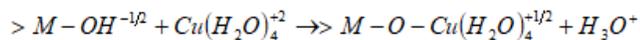
The lower frequency region of FT-IR spectra from calcined material (red and black lines) show changes in characteristic band associated with Si – O vibration, it appears like a single broad band around 1000 cm^{-1} , sharp band at 694.91 cm^{-1} from Si – Si valence vibration from quartz disappear and Si – O – M and M – O – H vibration valence vibration mentioned above for crude material spectra also disappear. Instead a single sharp band at 472.05 cm^{-1} (for calcined substrate with copper) and 471.32 cm^{-1} (for calcined substrate without copper) appear. Obviously these two bands are the same and doesn't show any covalence between copper and substrate surface, just calcination process changed structure.

IV. DISCUSSION

The isotherm profiles, as it was pointed out before, show but doesn't confirm information about the interaction between Cu^{+2} ions and calcined substrate surface, however L type isotherm is indicative of great affinity between copper ions and calcined substrate surfaces. In general, adsorption phenomenon is enhanced on activated surfaces with alkaline treatment just because alkaline treatment creates and homogenizes negative charge densities on adsorbent substrate surface according to reaction [3, 13]:



The flat part of the curve suggests formation of a saturated monolayer of copper ions on the surface as is predicted by the Langmuir model and chemisorption should occur on a single layer. This type of isotherms points to the formation of a covalent bonding between copper ions and the substrate surface that is formed by amphoteric metallic oxides as iron, aluminum, titanium and manganese oxides with variable surface charges. This fact is indicative of chemisorption, probably, according to theoretic model giving by the reaction through which an inner sphere complex is formed [3, 14, 15].



Isotherm profiles matches with those obtained by Jiang and collaborators for the Cu (II) adsorption on goethite and $\gamma - \text{Al}_2\text{O}_3$ [14], confirming specific adsorption or chemisorption between Cu (II) ions and oxide surface. Similar mechanism was proposed for the adsorption of Cu (II) ions on TiO_2 surfaces [16].

Adsorption capacities (K values) in almost all cases are higher for activated substrates than for non activated substrates showing that oxides deprotonation reaction take place. Similitudes between isotherms shape show that there is no evidence of the influence of granulometric fractions on the adsorption phenomena so bulk material should present similar chemical behavior. In general, fitted data by Freundlich and Langmuir models show acceptable linear correlations, especially for activated adsorbent substrates however, differences and variability between calculated and experimental data are higher when Freundlich model is applied. Adjustment to Langmuir model show better linear correlations and smaller differences and variability between calculated and experimental data so Langmuir model is more appropriated for experimental data interpretation. In fact both models pursue to explain the same type of isotherm but Freundlich is an empirical model and Langmuir was developed on valuable theoretical considerations. Variability of data can be explained because normally, it could be thought that solid surface should appear as a homogeneous and regular structure however, this type of surface exist only as a theoretic element. Actually, adsorbent substrate surfaces are irregular with defects according to topologic point of view. Also Langmuir assume that surface have a certain positions for adsorption, which are all equivalents and only one molecule or ion can occupy one single place. However, in the cases of these calcined adsorbent substrates, this assumption is not really true because not all adsorbent positions are equivalents just because of roughness and homogeneity of calcined substrate surfaces.

Spectroscopic IR study show presence of quartz and silica but doesn't show evidence of bonding between copper ions and calcined surface nevertheless, according to adsorption behavior, the interaction between copper ion and calcined substrate should have a covalent nature and it is better defined when calcined substrate reacts in acid media

V. CONCLUSION

In searching for new natural materials suitable to ionic adsorption and ionic exchange for different technological applications, the two lithological materials studied has shown to be appropriate for the preparation of ionic adsorbent substrates and their application in copper retention from aqueous solutions. These lithological materials have chemical and thermal properties that make them appropriate for the preparation of these calcined adsorbent substrate and applied them for different proposes. One application could be the treatment of heavy metal contaminated waters. Results have shown great affinity between metal ion and adsorbent calcined surface, characterized by an L type isotherm, associated to chemisorption reaction between adsorbate and adsorbent so any heavy metal as copper should behave in a similar way. Activation reaction also shows the creation of new negative charges that can participate in the adsorption phenomena, improving the efficiency of calcined adsorbent substrate for ionic retention. This is because different amphoteric metallic oxides deprotonates in alkaline medium increasing negative charge density on calcined adsorbent surface.

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