



Cu²⁺ REMOVAL FROM AQUEOUS SOLUTIONS WITH A CUBAN VOLCANIC GLASS MINERAL

Luis I Ortega-Hernández¹, Heydi M Fernández-Hechevarría¹, Rafael López-Cordero², Miguel A Autie-Pérez^{1,3*}, A Infantes-Molina³ and E Rodríguez-Castellón³

¹Departamento de Fundamentos Químicos-Biológicos (FQB), CUJAE, Cuba

²Centro de Investigaciones del Petróleo (CEINPET), MINBAS, La Habana, Cuba

³Departamento de Química Inorgánica, Cristalografía y Mineralogía, Andalucía Tech, Universidad de Málaga, Spain

ABSTRACT: A natural Cuban mineral from Sama Arriba mine (SAN) was used as an adsorbent for Cu²⁺ removal from aqueous solutions. SAN material was characterized by a variety of experimental techniques in order to know the chemical and phase composition as well as its textural properties. Characterization results indicated that the main phase present was calcite CaCO₃ that is partially transformed into malachite during Cu²⁺ adsorption process. Moreover, the textural properties indicated that the mineral presented some porosity mainly of macro porous nature. The experimental adsorption isotherms of Cu²⁺ ions were performed in batch-type adsorption systems and the experimental data linearized considering the Langmuir model with a very good correlation. The SAN capacity to remove Cu²⁺ from water solutions was higher than the data reported in the literature for other materials.

Key words: Cuban mineral, Water contamination, Cu²⁺ adsorption, Langmuir model, Batch adsorption system.

*Corresponding author: E Rodríguez-Castellón, ³Departamento de Química Inorgánica, Cristalografía y Mineralogía, Andalucía Tech, Universidad de Málaga, Spain E-mail: castellon@uma.es

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INTRODUCTION

Industrial and domestic activities produce great volumes of pollutant liquid wastes. These wastes should be treated in order to avoid their mixture with superficial and underground water and therefore the pollution of different aquatic systems. Among the great number of pollutants generated from refinery, mineral and metallurgic industries, heavy metals are particularly dangerous. Waste water containing heavy metals is a very dangerous environmental problem: non-biodegradability features; hazardous for animal and human health since they accumulate in living tissues causing many harmful effects; infer in the biochemical and biological oxidation processes; and cause serious problems in waste water treatment plant sludge's [1,2].

Several are the materials and processes found in the literature to face this serious environmental problem: active carbons adsorbents for Cr(VI) [3] and Cu(II) and Eu(III) removal [4]; algae for Cr³⁺ and Pb²⁺ removal [5]; polymers for Cd, Cu and Pb complexation [6]; and calcium alginate immobilized mycelia of *Polyporus squamosus* for the capture of Cr, Mn, Fe, Ni, Cu and Pb [7]. These materials and procedures are complex due to the high energy consumption required and even the necessity of using very specific reactants. The challenge is the development of cheaper processes that involve the usage of natural materials or modified-natural materials as is the case of algae for Cr³⁺ and Pb²⁺ removal [5].

Cuba possesses a great variety of natural resources as non-metallic deposits: zeolites, kaolinite, bentonite, palygorskite and volcanic glass. Among them, zeolites (as-received or modified) have been widely studied. The first scientific papers focused on these zeolites are from the 70's. These zeolites have been evaluated as molecular sieves [8], as filler of chromatographic columns [9], as solid adsorbent for atmospheric gases [10], as natural gas adsorbent [11], as catalyst for nitric oxide reduction [12,13], and recently to separate paraffin mixtures [14,15]. A very interesting area of application of these materials is water decontamination. In this sense Rodríguez and Rodríguez [16] studied in the lab-scale, Cu²⁺ and Ni²⁺ removal from mine drain by combining precipitation-neutralization processes with an ionic exchange one and using natural sodium clinoptilolite. A quasi total removal of these ions (99%) was achieved. Marquez *et al.* [17] used Cuban natural zeolites in water filtration for industrial and human consumption. These authors observed an improvement of water color and turbidity, pH control and Al³⁺, Fe²⁺ y Mn²⁺ removal at lower process costs. Chabalina and Ramírez [18] investigated Cu²⁺, Ni²⁺, Cd²⁺, Cr³⁺ and Zn²⁺ removal from galvanic garages by using Cuban zeolites with very interesting results in terms of selectivity and exchange capacity.

Nonetheless other non-metallic minerals, such volcanic glass, have not received much attention beyond its use in buildings and ceramics. A relatively recent work of Blanco-Flores *et al.* [19] have demonstrated that a Cuban volcanic glass coming from Ají de Calderas deposit showed very interesting results for removing Cu²⁺ ions from aqueous solutions. It seems reasonable the search of natural resources to be applied in heavy metals depletion from waste water due to their environmental toxicity. From an economic point of view, natural resources are much cheaper (mainly in the large scale application) than synthetic materials. However, it is important to note, that depending on the deposit the chemical composition varies and therefore before its use for an specific application it should be deeply characterize.

With these premises it has been considered interesting the use of a non-metallic natural mineral, volcanic glass, to remove Cu²⁺ from aqueous solutions, its characterization by a great variety of experimental techniques as well as the design of the process to reach such a goal.

MATERIALS AND METHODS

The studied material was a mineral material from Samá Arriba deposit (Cuba) in its natural state (SAN). It was grinded and sieved with a particle size ranged 0.1-0.25 mm. The chemical composition of SAN material was evaluated by means of inductively coupled plasma atomic emission spectroscopy (ICP-OES) by using a Spectroflame FTMO8 SPECTRO. X-ray diffraction (XRD) measurement was carried out in a Rigaku (Phillips X'pert) equipment at 30 kV y 20 mA (CuK α Radiation). Thermal analysis was performed in a TGA Q5000 V3. 10 Build 258 equipment in a temperature range rt- 900°C. IR-spectroscopy analysis was carried out by using a Varian Spectra 220 equipment by mixing SAN material with KBr. N₂ adsorption-desorption isotherms were collected in a Micromeritics ASAP 2020 V3.03 E. SAN porosity was studied by means of Hg-porosimetry in a Sortomatic Carlo Erba Model 1800.

The experiments for removing Cu²⁺ ions from aqueous solutions were carried out by dispersing the SAN material (1.00 g) in 50 ml of solution containing different concentrations of Cu²⁺, under stirring. Samples were collected, filtered and analyzed to determine the amount of Cu²⁺ adsorbed per unit of mass of SAN material Q_{ads} (specific adsorption, mol/g). The amount of Cu²⁺ extracted from the solutions was determined with an UV Visible spectrophotometer Shimadzu UV mini-1240. Previously, the equipment was calibrated with copper(II) chloride dihydrate solution (1M) (CuCl₂.2H₂O, from Merk in a concentration range 0.1-0.7 mol/L, and their respective absorbance measured (Abs) at a wavelength of 600 nm.. Q_{ads} was obtained from the calibration curve and the Equation (1):

$$\frac{(C_i - C_{ex}) \times V_{ex}}{m} = \frac{C_{ads}}{m} = Q_{ads} \quad (1)$$

where C_i is the initial concentration of Cu²⁺ in solution; C_{ex} is the Cu²⁺ equilibrium concentration in the solution extracted; V_{ex} is the volume extracted; C_{ads} is the amount of Cu²⁺ adsorbed by the solid; and m is the mass of adsorbent employed.

The equilibrium time was calculated by collecting samples each 10 minutes. The experimental results were plotted, Q_{ads} vs C_{eq} , C_{eq} is the concentration in the equilibrium. The obtained isotherm was fitted by following the Langmuir model (2):

$$\frac{C_{eq}}{Q_{ads}} = \frac{1}{K \times N_m} + \frac{C_{eq}}{N_m} \quad (2)$$

Where, N_m is the monolayer capacity (moles required to cover the surface with a compact monolayer equal to one molecule/ion thickness); K is the Langmuir constant, related to adsorbate-adsorbent interactions. The graphical representation of Eq (2) should be a straight line if the adsorption follows the Langmuir model. From the slope and the intercept, N_m and K can be calculated. Finally, the solid obtained from each experiment was collected, dried and analyzed by XRD:

RESULTS AND DISCUSSION

The chemical composition of the volcanic glass (in the oxide form) is included in Table 1. These data indicate that the mineral is a mixture of mainly CaO (42.2%), SiO₂ (17.7%) and Al₂O₃ (2.3%), and lower amounts of other oxides.

Na ₂ O	MgO	Al ₂ O ₃	CaO	TiO ₂	Cr ₂ O ₃	MnO	Fe ₂ O ₃	SiO ₂
0.02	0.46	2.26	42.22	0.10	0.0023	0.16	1.07	17.71

Table 1: Chemical composition of SAN mineral (%).

The thermal analysis plotted in Figure 1 shows that the thermal decomposition starts at ca. 600°C. Between 600-750°C it is observed a sharp weight loss (35%) due to CO₂ release from CaCO₃ decomposition. This data indicates that the original mineral contains approximately 73.5% of CaCO₃, close to the values obtained from the elemental chemical analysis. It is also important to note that the weight loss is associated to an endothermic process characteristic of CaCO₃ decomposition (Figure 1).

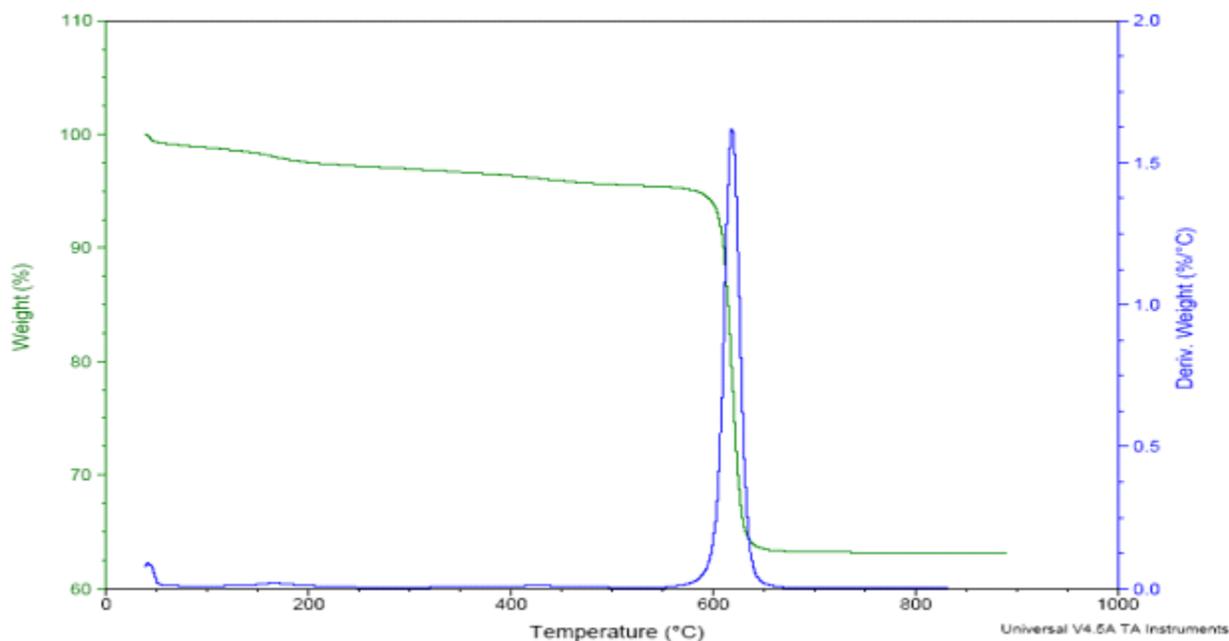


Figure 1: ATG curve for SAN material.

The IR spectrum of the mineral, represented in Figure 2, also shows the presence of carbonate in the form of CaCO_3 with characteristic bands at 1492, 1080, 866 and 706 cm^{-1} [20]. Moreover, it is observed

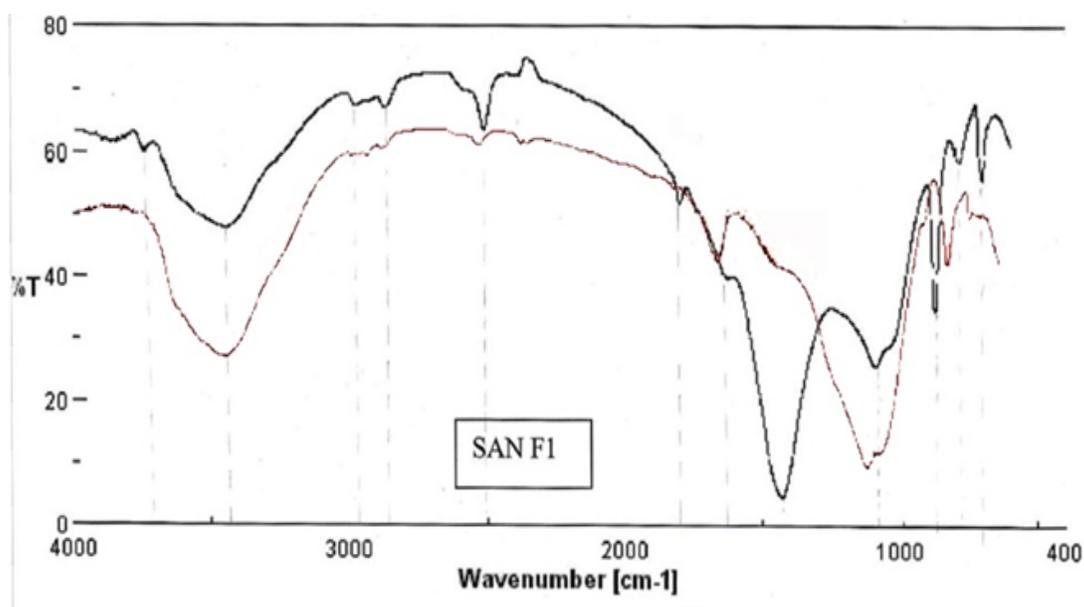


Figure 2: IR Spectrum of natural SAN (black) and SATQ (red).

a band at *ca.* 1100 cm^{-1} due to the presence of characteristic units of SiO_4^{2-} in accordance to the chemical analysis that showed Si as the second main component. Moreover and with the aim of verifying the presence of CaCO_3 , the mineral was treated with HCl solution and some bubbles were released due to CO_2 . After HCl treatment, it was obtained the IR spectrum of the resultant material. By comparing both spectra (Figure 2), the natural sample (SAN) in black and acid-treated (SATQ) in red, it is clearly observed how the band at 1492 cm^{-1} disappeared as a consequence of the CaCO_3 dissolution. It is also observed an increase in the intensity of the band at 1100 cm^{-1} ascribed to SiO_4^- due to the increment of the last as a result of CaCO_3 loss [21]. Both techniques indicate that a great proportion of CaCO_3 is present in the mineral.

The crystalline phases present in SAN mineral was determined by means of X-ray diffraction (XRD). The diffractogram included in Figure 3 corresponds to the SAN mineral and presents several diffraction lines. The main one located at $2\theta = 29.4^\circ$ is characteristic of CaCO_3 in the form of calcite, the natural form of CaCO_3 [22]. Moreover the reference patterns of such a compound (CaCO_3) was also included in Figure 3, where it is clearly observed that the diffraction pattern of SAN matches quite well with that of CaCO_3 reference material (ICSD #16710). Moreover it is observed a diffraction peak at $2\theta = 9.8^\circ$ characteristic of SiO_4^{2-} . Figure 3 also includes the XRD pattern of the sample after HCl treatment (SATQ). It is clearly observed the disappearance of the main peak at $2\theta = 29.4^\circ$ characteristic of CaCO_3 and the sharp increase of the peak at 9.8° , in accordance to IR results, i.e., increase of SiO_4^- bands at expenses of CaCO_3 ones.

The textural properties of this material were evaluated from the N_2 adsorption-desorption isotherm at -196°C and Hg porosimetry. The obtained isotherm is represented in Figure 4 A. It is of type II according to IUPAC classification, typical of porous solids presenting meso and macroporosity. By applying the BET equation to the experimental results, it is obtained a straight line as observed in Figure 4 B. The specific surface area obtained was $41.1 \text{ m}^2/\text{g}$.

The Hg porosimetry curve is depicted in Figure 5 and shows a sharp increase at low pressures, what is characteristic of interparticle filling. After the initial increase, it is observed a slope change (20-100 atm) due to the presence of macropores with diameters in the range, 750-150 nm. Later, the curve reached a plateau (between 100-800 atm). These data indicate that the number pores with diameters ranging from 150-20 nm is quite low (<10%) and the amount of pores with diameters 50-20 nm (mesopores) are much lower (<6%). The quantitative results are included in Table 2. From this table it is seen that from the total adsorbed volume, 95% corresponds to the adsorption in pores higher than 50 nm. From these results it can be inferred that the solid presented meso and mainly macroporosity according to IUPAC classification.

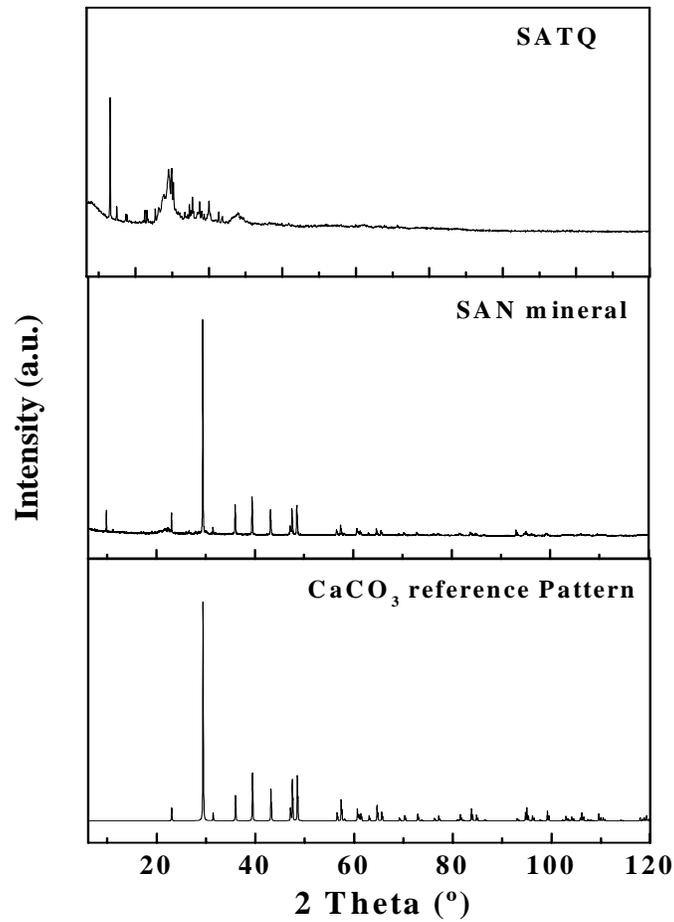


Figure 3: X-ray diffractogram of SAN and SATQ materials.

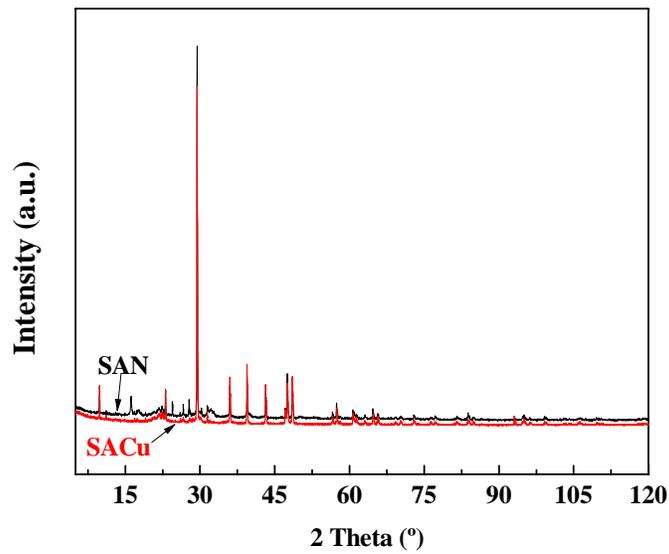


Figure 4: X-ray diffractogram of SACu (red) y SAN (black).

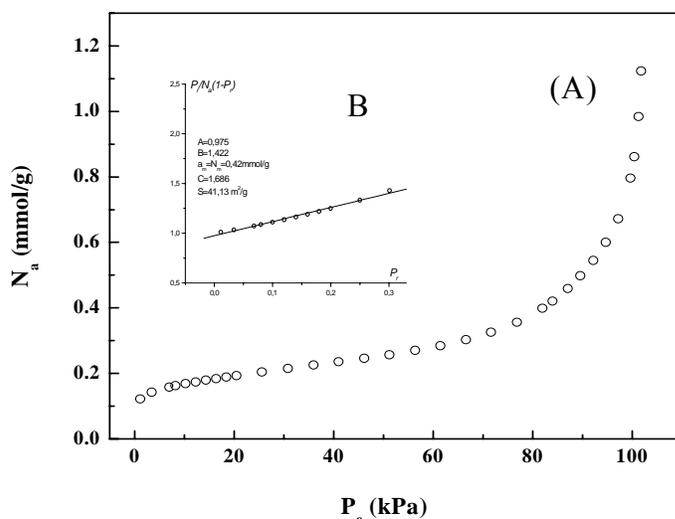


Figure 5: N_2 adsorption isotherm at 77 K (A) and BET plot (B).

Table 2: Total volumen (V_T), volumen of pores with a diameter <50 nm ($V<50$ nm), and volumen of pores with a diameter >50 nm ($V>50$ nm) from HG porosimetry data.

Mineral	V_T (cm ³ /g)	$V<50$ nm (cm ³ /g)	$V>50$ nm (cm ³ /g)
SAN	0.208	0.011	0.197

The characterization results indicate that the main phase present in SAN natural material is $CaCO_3$ presenting some porosity and therefore could be a good material to remove Cu^{2+} ions from aqueous solutions.

The kinetic experiment of Cu^{2+} adsorption, i.e., quantity adsorbed vs time, are showed in Figure 6A. It is observed an initial linear increase up to 30 min, then the amount adsorbed hardly increased, reaching a plateau, i.e., the material did not adsorb more. From these experimental data, it was selected 30 minutes as the required time to reach the equilibrium under these experimental conditions. The experimental adsorption isotherm is depicted in Figure 6 where the Q_{ads} is represented vs C_{eq} for Cu^{2+} in SAN mineral. It is showed the same feature, which is: a sharp increase in the amount adsorbed; and the reach of a plateau. The plateau is reached for $C_{eq}>0.007$ mol/L with an associate value of $Q_{ads} \approx 0.007$ mol/g. The adsorbed curve is typical of monolayer adsorption and therefore, if these data are fixed by following the Langmuir model it is obtained a straight line ($R>0.999$) as observed in Figure 7. From this fit the monolayer adsorption capacity (N_a) was determined, with a value of $7.5 \cdot 10^{-3}$ mol/g. This value is much higher than those found in the literature for other materials such as perlite [23]; kaolinite [24] and oxidized anthracite [25] (See Table 3). Therefore, this natural mineral seems to be a good candidate to remove Cu^{2+} from water solutions.

Table 3: Cu^{2+} adsorption capacity of SAN and other adsorbent materials found in the literature.

Material	N_a (μ mol/g)
Tuff	4.17
Sepiolite	606
Activate carbon	70
Rise Shell	61.4
Volcanic glass	4530
Kaolinite	21.4
Perlite	15.9
Oxidized antracite	1450
SAN	7500

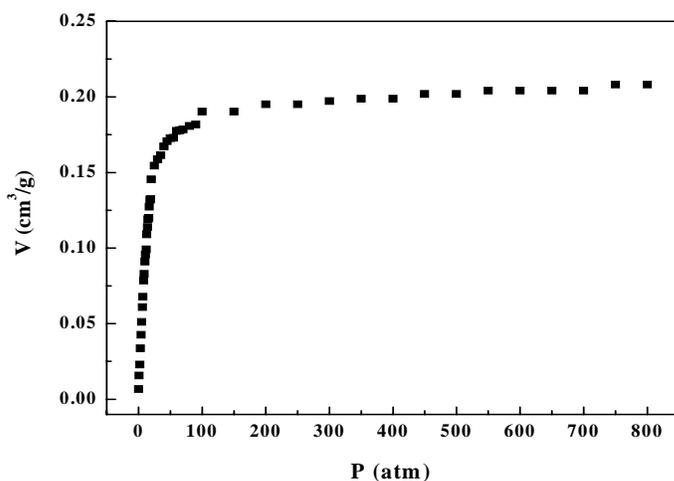


Figure 6: Hg volume introduced as a function of the pressure for SAN material.

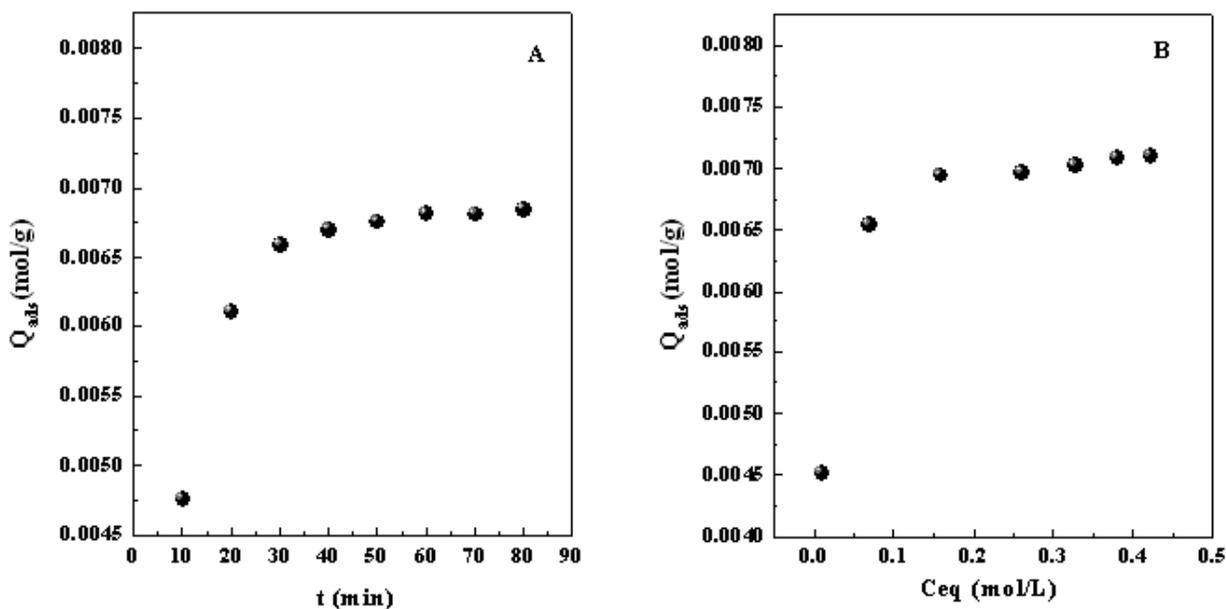


Figure 7: Cu²⁺ kinetic adsorption on SAN (A); and experimental adsorption isotherm of Cu²⁺ on SAN (B).

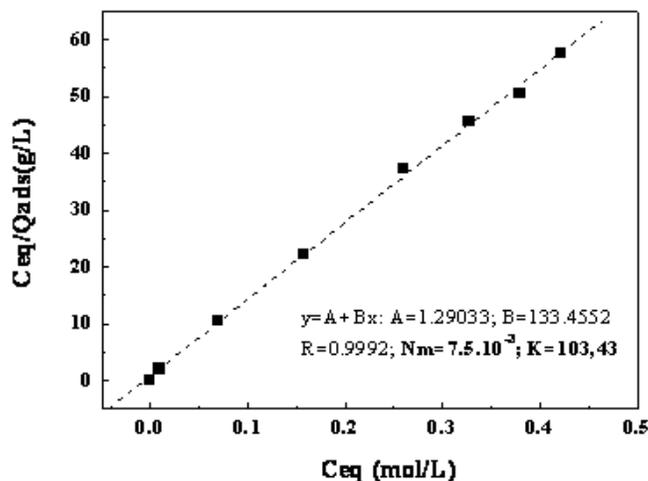


Figure 8: Experimental adsorption isotherm of Cu²⁺ in Langmuir coordinates for SAN mineral.

In order to complete the study and from the monolayer adsorption capacity obtained, $N_a=7.5 \cdot 10^{-3}$ mol/g, it was possible to calculate the masses of SAN necessary to reduce the Cu^{2+} concentration in water solution of 10 mmol/L, in 20, 40, 60 and 80% at laboratory level as a function of water volume as compiled in Figure 9. The presented data show that the use of this natural mineral (SAN) is an easy way of Cu^{2+} removal.

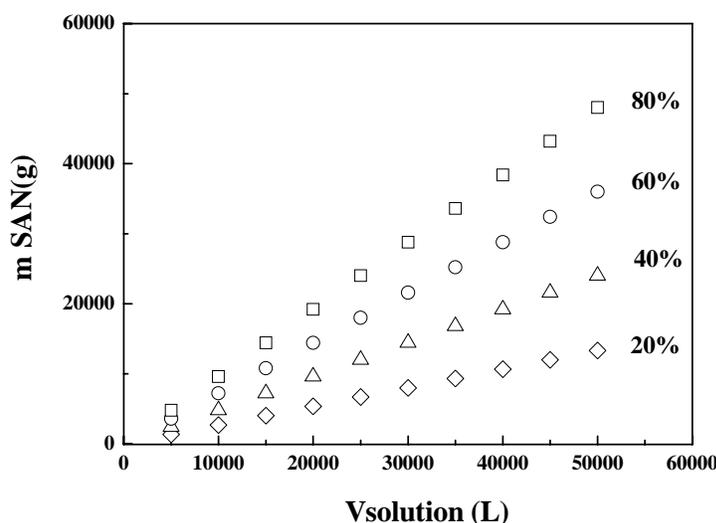


Figure 9: Amount of SAN mineral required eliminating Cu^{2+} ions in solutions containing different concentrations of these ions (%).

The characterization of SAN material after the adsorption process thereby XRD (Figure 10) shows that both diffractograms are similar, presenting the same characteristic peaks of calcium carbonate but now part of Ca^{2+} is substituted by Cu^{2+} . Moreover, the obtained material after reaction changed of color, from light yellow to green, also suggesting the presence of malachite (CuCO_3).

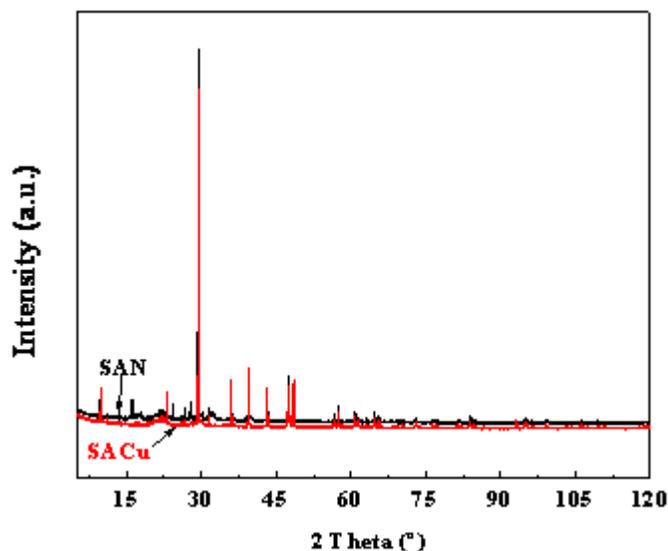


Figure 10: X-ray diffractograms of SAN material before (black) and after (red) Cu adsorption.

CONCLUSION

The mineral SAN was evaluated in the removal of Cu^{2+} ions from aqueous solutions. Several characterization techniques indicated that CaCO_3 was the main component and this material presented porosity in the range of meso-macropores. The kinetic study revealed that total elimination of Cu^{2+} was achieved in 30 minutes and therefore this material could be used in short cycle times.

The adsorption took place through the exchange of Ca^{2+} by Cu^{2+} , that is, calcite is partially transformed into malachite. It should be highlighted that the SAN mineral presented an adsorption capacity of Cu^{2+} greater than those found in the literature for other materials. Therefore it can be considered a good candidate to be used as an adsorbent of this ion in commercial scale not only for its good adsorption properties but also because it is quite cheap.

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