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Caracterización de un mineral carbonáceo e identificación del efecto Preg-Robbing

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RESUMEN

El procesamiento de minerales refractarios por métodos convencionales resulta en recuperaciones pobres de oro, siendo una causa el efecto preg-robbing al presentarse la adsorción del complejo $Au(CN)_2^-$ en la superficie de materia carbonácea durante la lixiviación. Se hace necesario entonces caracterizar mineralógicamente e identificar la materia carbonácea para establecer la complejidad del mineral. Posteriormente se debe evaluar el grado del preg-robbing para diseñar el procesamiento y recuperar el máximo del metal precioso atrapado. Así, un mineral carbonáceo se caracterizó mediante DRX y por espectroscopía infrarroja, además de evaluar la capacidad de adsorción de $Au(CN)_2^-$ del mineral. Por DRX, se identificaron las especies calcita y cuarzo; por espectroscopía infrarroja, las bandas características de Ca-O, C-O, Si-O y la C=C asociada a materia carbonácea; de la capacidad de adsorción se determinó un valor $q=0.198$ mg $Au(CN)_2^-/g_{mineral}$, que corresponde al 70% de $Au(CN)_2^-$ adsorbido, por lo que el mineral se clasifica como preg-robbing.

Palabras clave: Mineral carbonáceo, efecto preg-robbing, $Au(CN)_2^-$, adsorción

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Carbonaceous Ore Characterization and the Identification of the Preg-Robbing Effect

ABSTRACT

Limited gold recovery from refractory ores by conventional methods is due to the preg-robbing effect. Adsorption of the $Au(CN)_2^-$ complex on the surface of carbonaceous matter during the gold leaching defines this. Mineralogical characterization is required to identify the carbonaceous matter and then establish the complexity of the ore. Subsequently, the preg-robbing degree must be evaluated to design the processing and gold recovery. Thus, a carbonaceous mineral was characterized by XRD and infrared spectroscopy (FTIR), evaluating its adsorption capacity of $Au(CN)_2^-$. XRD identified calcite and quartz species; the characteristic bands of Ca-O, C-O, Si-O, and C = C associated with carbonaceous matter, calcite, and quartz were identified by FTIR. A value q= 0.198 mg $Au(CN)_2^-$/g ore was obtained from the adsorption capacity, corresponding to 70% of $Au(CN)_2^-$ adsorbed, evidencing the preg-robbing effect.

Keywords: *Carbonaceous mineral, preg-robbing effect, Au(CN)2-, adsorption*

INTRODUCTION

Gold is a highly stable precious metal; it can be obtained from ores classified as non-refractory grinding or refractory ore. The Au recovery from mineral processing of refractory ores is difficult by conventional methods such as cyanidation [1]. The limited gold extraction from these ores is due to the preg-robbing effect, defined as the adsorption of the leached gold-cyanide complexes [2-4]. The preg-robbing effect depends on the nature of the refractory ores and, therefore, its characterization is essential. The preg-robbing ability of refractory ores has been related to the content of carbonaceous materials and the maturity of the organic carbon structure on a scale from amorphous to graphitic [4, 5]. This degree of maturity can be evaluated by characterization techniques such as X-ray diffraction (XRD) and infrared spectroscopy (FTIR), among others. Santiago et al. [5] reported that a carbonaceous mineral with a disordered structure presents a high degree of adsorption or a higher degree of preg-robbing based on XRD analysis. Afenya [2] reported the existence of amorphous and graphitic carbon and that it acquired different structures according to the degree of maturation. By infrared spectroscopy, the presence of functional groups such as $-CH_3$, $-CH_2$, -C=C-, -C=O, -COOH, and in some cases, impurities in the ore were identified by Si-O bonds related to quartz [2]. Ofori and coworkers [6] reported infrared characterization by comparing the spectra of an anthracite sample with and without biological treatment, seeking to reduce the preg-robbing degree, and the surface modification was analyzed. The main changes occurred in the band of 2929 cm^{-1}, corresponding to aliphatic hydrocarbons, and those of 2856 cm^{-1} and 1715 cm^{-1} corresponding to carbonyl groups C=O. Increasing these groups reduces the degree of aromaticity and thus the adsorption of complexes of $Au(CN)_2^-$.

According to the above, the characterization of the carbonaceous ores is essential to identify the organic carbon responsible for the preg-robbing effect. Therefore, the analysis focused on the use of techniques such as X-ray diffraction (XRD), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were carried out for the characterization of a carbonaceous ore. Additionally, adsorption experiments of $Au(CN)_2^-$ in the ore to quantify the preg-robbing degree were conducted.

METHODOLOGY

Carbonaceous ore characterization

Two simples, namely 100 and +100 of a carbonaceous ore from Queretaro State, México, were characterized. The results were compared before and after the sodium carbonate elimination in samples. The elimination of sodium carbonate is carried out by adding HCl as described in the following paragraphs (see reaction 1) and permits to quantify the inorganic carbon content $C_{inorganic}$ (due to calcium carbonate). X-ray diffraction characterization was used to detect the crystalline phases in ore and seek to evidence the carbon species in the samples. For this analysis, a D8 Advanced Davinci (Bruker) equipment with Cu-Kα radiation and Ni filter was utilized. Data were recorded in a range of 2θ of 10 to 90° with a step size of 0.02° and 0.6 sec. The morphology of the samples at different magnifications was evaluated by scanning electron microscopy (SEM) in JEOL JSM-6400 equipment. The elemental analysis was performed by Energy Dispersive X-ray spectroscopy. The infrared spectra were recorded in a range between 4000 and 400 cm^{-1} and resolution of 4 cm^{-1}, in a Tensor 27 spectrophotometer (Bruker). The samples were prepared by mixing with KBr and compacted before analysis. The functional groups associated with the compounds in samples were assigned in spectra.

For the inorganic carbon content, $C_{inorganic}$ (as calcium carbonate), 25 g of each sample were neutralized by adding concentrate HCl (Quimica Meyer, purity 37%) in excess according to the following reaction:

$$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow H_2O_{(l)} + CO_{2(g)} + CaCl_{2(ac)} \tag{1}$$

Subsequently, the solutions were filtered under vacuum, and the residual acid content was quantified by back-titration with NaOH 0.09 N using phenolphthalein as an indicator. The difference between the HCl initial and residual corresponds to the consumed HCl by reaction with calcium carbonate. The quantification of $C_{inorganic}$ was performed thrice for each sample.

Pre-robbing degree determination

The preg-robbing degree of the carbonaceous ore was evaluated by the $Au(CN)_2^-$ adsorption experiments. For this, a solution containing $KAu(CN)_2$ in 10 mg/L in NaOH at pH 11 was prepared. The adsorption was performed taking different carbonaceous ore masses (0.1, 1 y 6 g) and mixed with 50 mL of the solution containing $KAu(CN)_2$. The samples were undergone in orbital agitation at 160 rpm for 24 h at 25°C. Afterward, the samples were filtered under vacuum, and the quantification of Au in solution (initial and residual) was carried out by flame atomic absorption spectrometry (FAAS) in Perkin Elmer 3100 equipment. The adsorption capacity of carbonaceous ore (q_{Au}) was computed as follow:

$$q_{Au} = \frac{C_0 - C_f}{w} \tag{2}$$

Where C_0 and C_f are the initial and residual Au (as $Au(CN)_2^-$ complex) in mg/L, and w corresponds to the weight in grams of carbonaceous ore. The adsorption capacity of carbonaceous ore was obtained before and after the sodium carbonate elimination in samples, and the results were used to estimate the preg-robbing degree (%PR) by the expression:

$$\%PR = 100\ (1 - [Au]_{final}/[Au]_{initial}) \qquad (3)$$

Where %PR corresponds to the adsorbed gold in carbonaceous ore, [Au] is the gold concentration as $Au(CN)_2^-$ before and after the adsorption expressed in mg/L.

RESULTS

Carbonaceous ore characterization

Figure 1 includes the diffraction patterns for the samples untreated. There are two main phases, identified as quartz SiO_2 and calcite $CaCO_3$, without peaks that evidence an organic content. This result shows a $CaCO_3$ high content in samples; therefore, the amount of $C_{inorganic}$ (due to calcium carbonate) was quantified, and results are resumed in Table 1. As is notable, more than half of the content corresponds to calcium carbonate (>55%), and it is in agreement with the description of the ores as carbonaceous limestone reported for the Queretaro State [7].

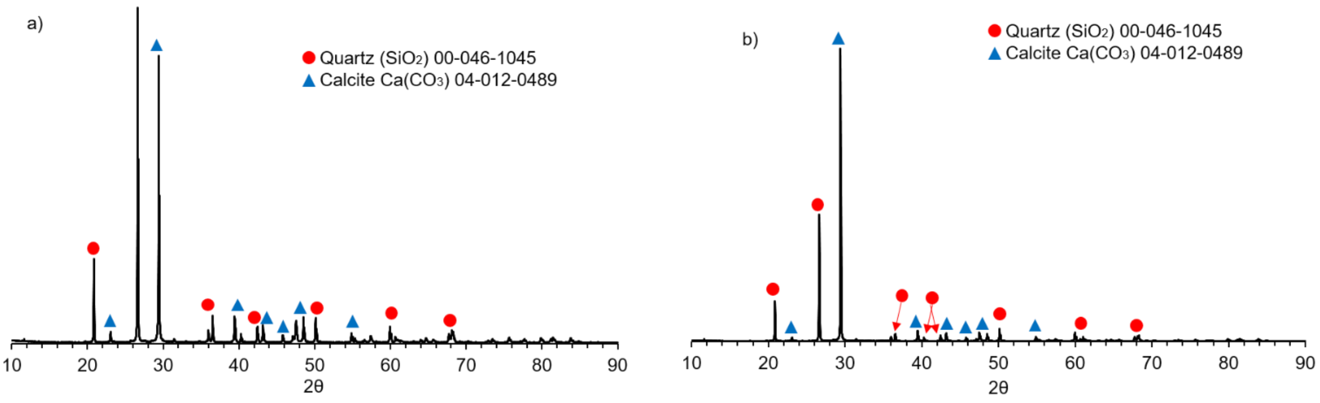

Figure 1. Diffraction patterns for carbonaceous ore. a) 100 and b) +100.

Table 1. Percentage of calcium carbonate in the carbonaceous ore.

Sample	$CaCO_3$ (%)	Average (%)	Standard deviation
100	55.97	55.58	2.21
	53.20		
	57.56		
+100	57.31	57.69	0.87
	57.07		
	58.69		

Figure 2 shows the diffraction patterns of the samples 100 and +100 after treatment to remove calcium carbonate. When the ore was treated with HCl, the diffractogram showed signals attributed to quartz, and the signals associated with $CaCO_3$ have not been observable due to the treatment. In addition, it was indexed low carbon intensity signals indicating the presence of carbonaceous matter. The XRD technique does not reveal the degree of disorder or amorphousness of the carbon since the quartz signals cover the other signals of lower intensity, as indicated by Santiago et al. [5].

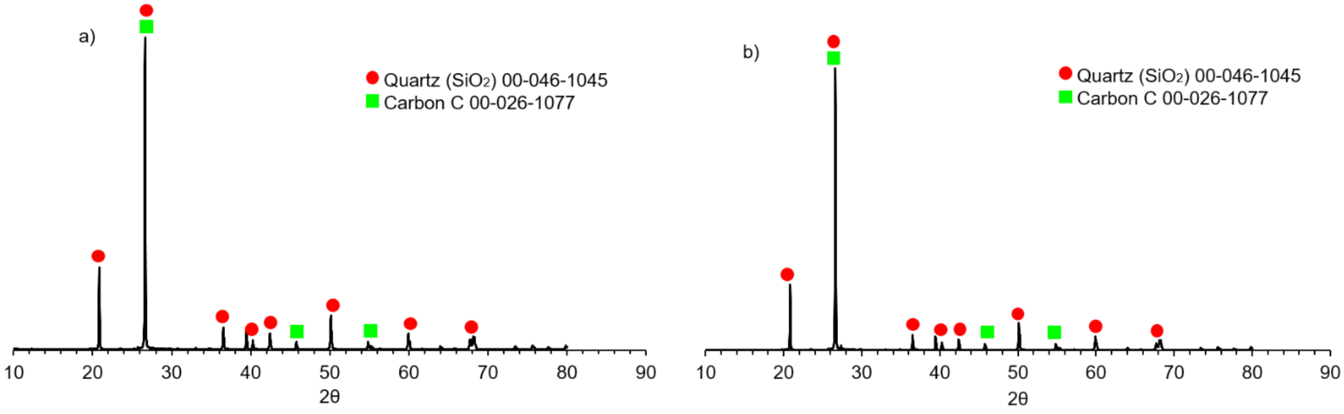

Figure 2. Diffraction patterns for samples a) 100 and b) +100, after removal of calcium carbonate.

Figure 3 presents the FTIR spectra for samples 100 and +100, before and after treatment to $C_{inorganic}$. In the spectrum of untreated samples (blue line), the bands at 1421.61 cm^{-1} and 875.27 cm^{-1} correspond to the stretching vibrations of C-O bond related to calcium carbonate, while the band in 797.49 cm^{-1} was assigned to the Ca-O. The bands agree with those reported by Lachehab et al. [8].

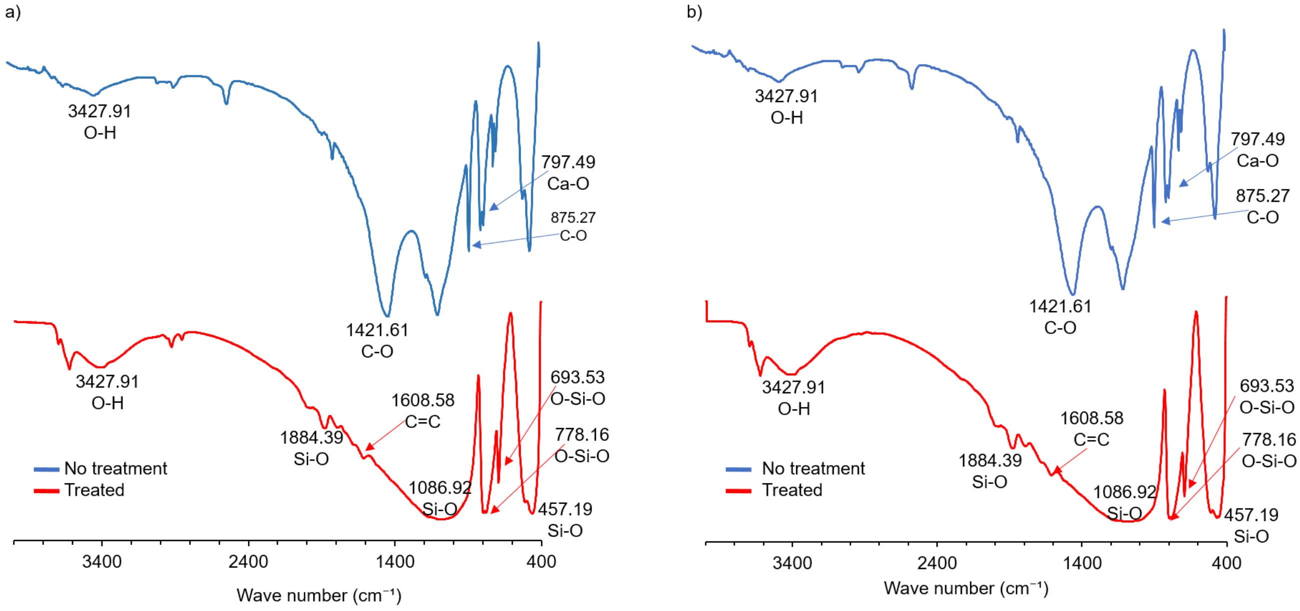

Figure 3. Infrared spectra of the samples a) 100 and b) +100, before (blue line) and after treatment (red line) to remove calcium carbonate.

On the other hand, when the samples were treated for $C_{inorganic}$ (red color), the spectra changed significantly, and only the bands assigned to the Si-O bond were kept. Additionally, a low-intensity band appears at 1608.58 cm^{-1} which corresponds to bonds C=C in aromatic compounds, indicating the carbonaceous organic matter presence [9]. For this assignment, it was taken into consideration that carbonaceous matter in ores was analyzed according to the degree of maturation [4, 5] and has been compared with the structure of the activated carbons and their derivatives due to their adsorption behavior [10]. The band at 3427.91 cm^{-1} was associated with the O-H of water molecules. This assignment agrees with that reported by several authors [8, 11].

Figures 4 and 5 show the micrographs, elemental analysis, and elemental distribution in samples 100 and +100 before and after treatment for $C_{inorganic}$.

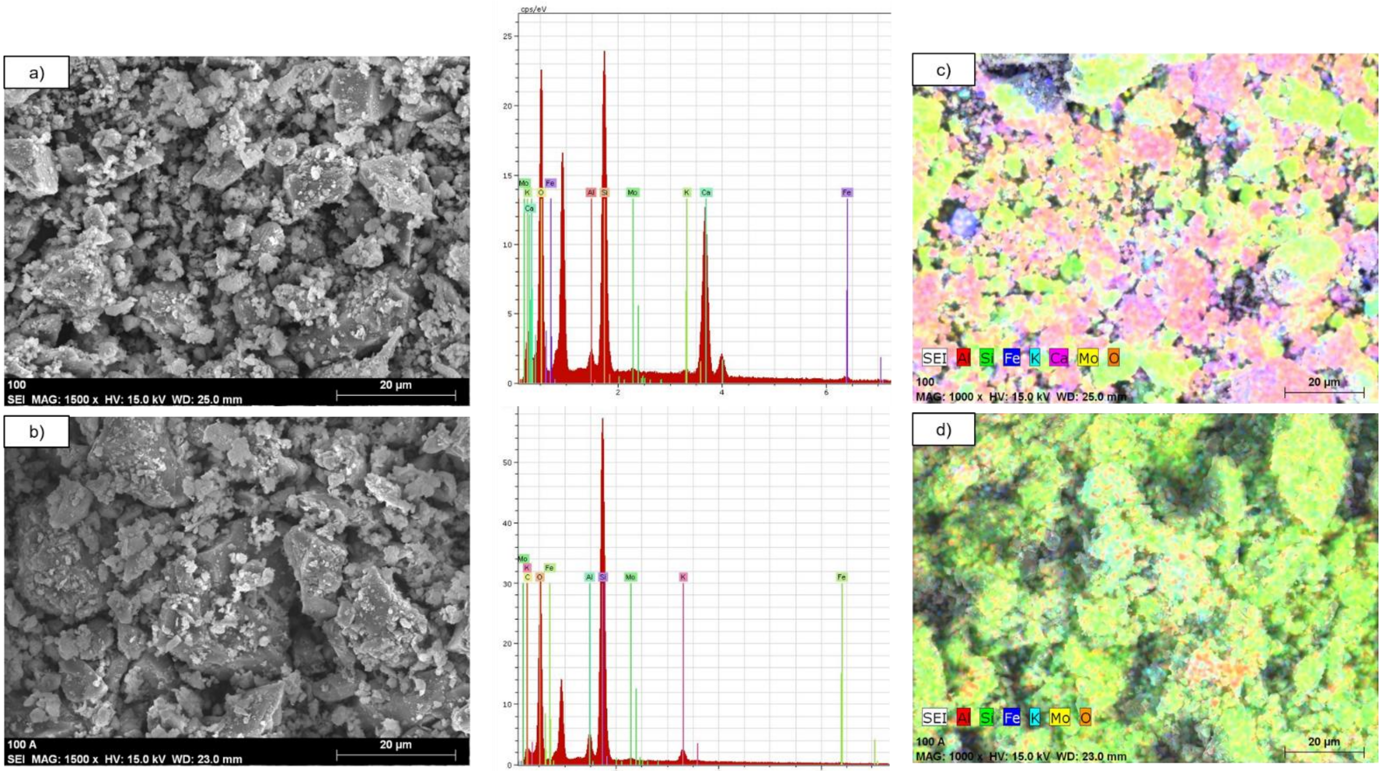

Figure 4. Analysis of sample 100 by SEM: a) Micrograph and EDS before treatment, b) Micrograph y EDS before treatment, c) mapping before treatment, and d) mapping after treatment.

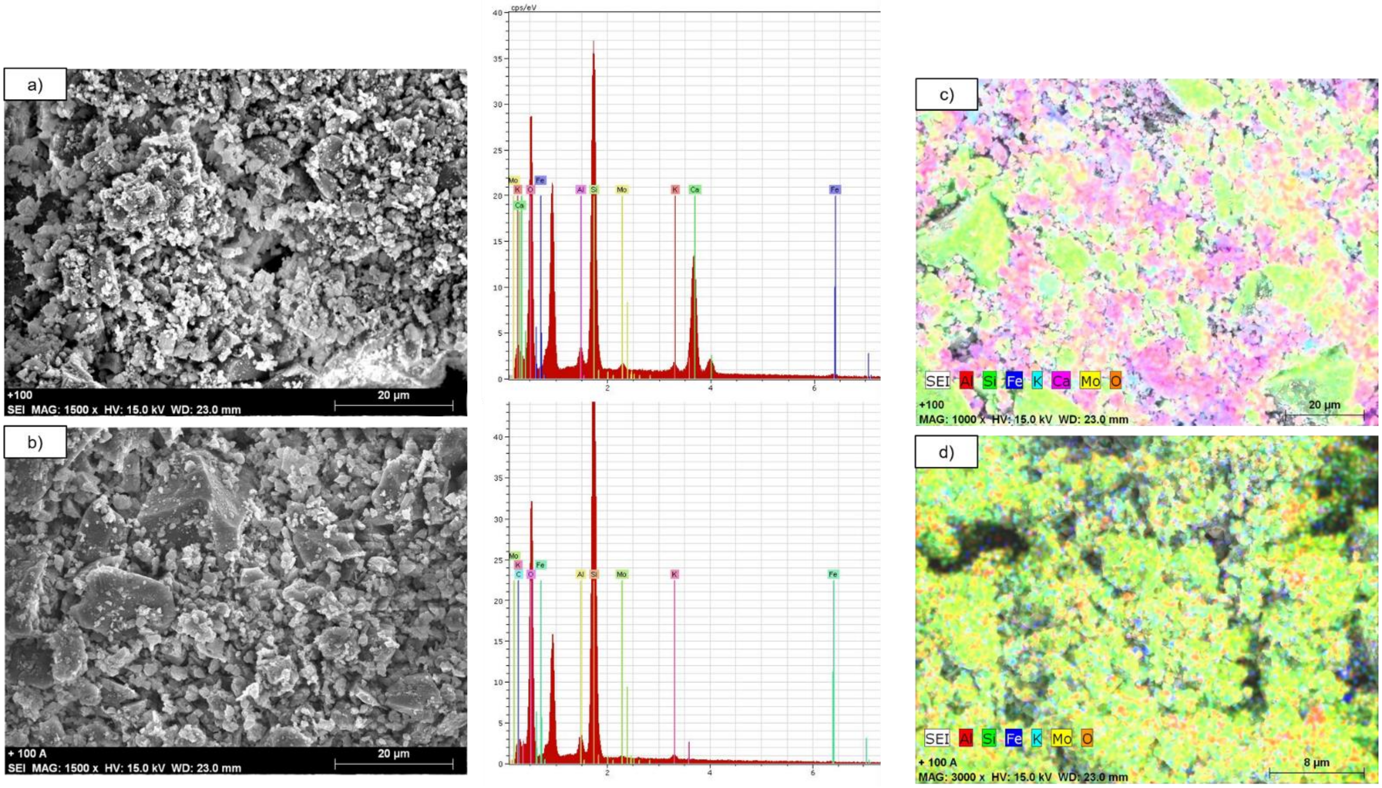

Figure 5. ***Analysis of sample +100 by SEM: a) Micrograph and EDS before treatment, b) Micrograph y EDS before treatment, c) mapping before treatment, and d) mapping after treatment.***

For the case of sample 100, particles with varied shapes and sizes are observed (Figure 4a). Elemental analysis reveals the presence of calcium and silicon; this result was congruent with those obtained by XRD. On the other hand, in the sample with treatment (Figure 4b) the calcium is not observed in the EDS analysis, demonstrating that the inorganic carbon treatment removed it. For the sample +100 (Figure 5a), the micrographs show the same behavior observed in the previous figure; however, it is notable the absence of a white layer when the inorganic carbon treatment was carried out; this can be related to the calcium carbonate.

The elemental distribution observed was heterogeneous and the main elements were silicon (green) and calcium (pink) (Figure 4c y 5c), while the iron (blue) was located in some areas of the sample. On the other hand, in the treated samples (Figure 4d y 5d), the element with the highest proportion was silicon (green), and in some zones, it is possible to observe a small amount of aluminum.

Preg-robbing grade in ore

Figure 6 displays the adsorption capacity results reported as %PR for the samples 100 and +100 with and without treatment. This value indicates the percentage of gold in the form of $Au(CN)_2^-$ that was adsorbed by the mineral [4], and it was calculated by equation 3 for different masses of the carbonaceous ore. An increase in the ore mass promotes an augment in the %PR, suggesting that the adsorption was related to the carbonaceous ore. The same trend was observed in both graphs. For the case of sample 100 without treatment, the %PR was 33.7% (6 g ore), while with treatment, the maximum percentage was 69.7% (1 g ore). The results indicate that gold adsorption occurs less when carbonates are present than when the predominant phase is SiO_2. This can be attributed to two phenomena. The first one is due to particle size; since the ore presents a smaller particle size after treatment, a greater surface area was disposed, favoring the contact with the solution, and therefore the adsorption increases. The second is due to the presence of organic C, which content is higher in the treated samples than untreated, increasing the gold adsorption. Further experiments are required to quantify $C_{organic}$ in the samples and relate the result obtained to better evidence this behavior. Table 2 summarizes the adsorption capacity values (q_{Au}) for both samples with and without treatment. It was observed that the adsorption capacity similarly increased with the mineral mass to that observed in the preg-robbing degree and was maximized when the ore was treated (without calcium carbonate). According to Dunne et al. [12], the absorption capacity allows to classify the preg-robbing grade in the ore. Thus, for an adsorption capacity <0.001 mg Au/g of ore, the ore has a slight preg-robbing degree, while for adsorption capacity >0.5 mg Au/g ore, a strong preg-robbing degree is observed [10, 12]. Based on the adsorption capacity and %PR, the results suggest a moderate preg-robbing behavior.

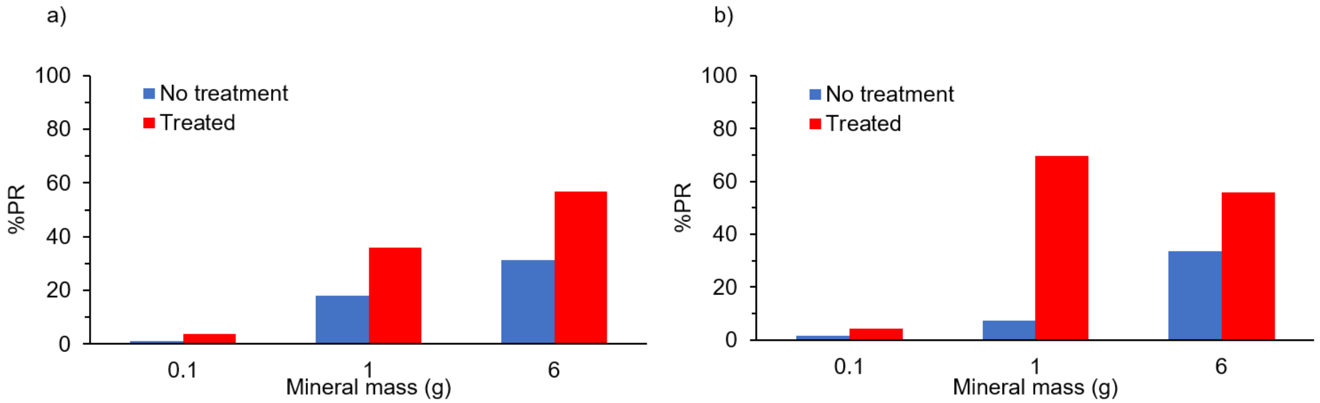

Figure 6. Preg-robbing degree (% PR) as a function of ore mass for sample: a) 100 and b) +100, before and after inorganic carbon treatment.

Table 2. Adsorption capacity (q_{Au}) for both samples with and without inorganic carbon treatment.

Sample	**Ore mass (g)**	**q_{Au} (mg $Au(CN)_2^-$/g ore)**	**Ore mass (g)**	**q_{Au} (mg $Au(CN)_2^-$/g ore)**
100 +	0.158	0.041	0.103	0.188
100 +	1.009	0.096	1.006	0.198
100 +	6.061	0.028	6.089	0.052
100	0.170	0.057	0.119	0.190
100	1.006	0.038	1.017	0.379
100	6.072	0.030	6.078	0.051

CONCLUSIONS

The characterization of carbonaceous ore by XRD disclosed that two main phases predominate, calcite ($CaCO_3$) which contributes more than 50% of the sample, and quartz (SiO_2). After calcium carbonate removal, the signals indicate the presence of quartz, and the carbonaceous matter was identified. The last was also assigned in FTIR spectra, where bands associated with C=C in aromatic compounds, mainly in the samples without calcium carbonate. From adsorption experiments, it was shown that the ore is responsible for the adsorption of the complex $Au(CN)_2^-$ and it depends on the ore's mass, indicating a moderate preg-robbing degree.

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