


Alternative activated carbon method for recovery of gold from thiosulfate solutions
Método alternativo de carbón activado para la recuperación de oro a partir de soluciones de tiosulfato

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Abstract

The activated carbon adsorption (CIP) process used for the gold recovery stage has proven to be highly effective and efficient in being able to recover complexes formed from cyanide leaching solutions. However, the recovery of the gold-thiosulfate complex from leaching solutions has been difficult due to the low recoveries obtained in this process; This is due to the diameter of the complex ion formed from thiosulfate solutions. The present work seeks to carry out the adsorption of the gold-thiosulfate complex; carrying out a pre-treatment to activated carbon washing (AC-PW) it with sodium cyanide and sodium thiosulfate solution to impregnate the activated carbon with the cuprocyanide complex (AC-PW-Cu) to obtain the aurocyanide complex by ion exchange, in addition to obtaining the adsorption of the gold thiosulfate complex. Evaluating the impregnation of activated carbon with cuprocyanide complex, as well as contact with the gold-thiosulfate complex, in discontinuous assays. Using concentrations of 5 to 20 mg/L of gold, 0.2 mol/L of sodium thiosulfate and 12.5 g of activated carbon, obtaining results in adsorption assays of 97 to 99% recovery, expanding the possibilities of being able to recover the gold complex formed from leaching with sodium thiosulfate.

Keywords: activated carbon, adsorption, cuprocyanide, thiosulfate, gold.

Resumen

El proceso de adsorción en carbón activado (CIP) utilizado para la etapa de recuperación de oro ha demostrado ser altamente efectivo y eficiente para poder recuperar complejos formados a partir de soluciones de lixiviación con cianuro. Sin embargo, la recuperación del complejo oro-tiosulfato a partir de soluciones de lixiviación ha sido difícil debido a las bajas recuperaciones obtenidas en este proceso. Esto se debe al diámetro del ion complejo formado a partir de soluciones de tiosulfato. El presente trabajo busca llevar a cabo la adsorción del complejo oro-tiosulfato; realizando un pretratamiento de lavado al carbón activado (AC-PW) con cianuro de sodio y solución de tiosulfato de sodio para impregnar el carbón activado con el complejo cuprocianuro (AC-PW-Cu) para obtener el complejo aurocianuro por intercambio iónico, además de obtener la adsorción del complejo de tiosulfato de oro. Evaluando la impregnación de carbón activado con el complejo de cuprocianuro, así como el contacto con el complejo oro-tiosulfato, en ensayos discontinuos. Utilizando concentraciones de 5 a 20 mg/L de oro, 0.2 mol/L de tiosulfato de sodio y 12.5 g de carbón activado, obteniendo resultados en ensayos de adsorción de 97 a 99% de recuperación, ampliando las posibilidades de poder recuperar el complejo aurífero formado a partir de la lixiviación con tiosulfato de sodio.

Palabras clave: carbón activado, adsorción, cuprocianuro, tiosulfato, oro.

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1 Introduction

Sodium cyanide is widely used in the leaching of gold-containing ore. The resulting pregnant leach solution is typically subjected to gold recovery through processes such as Merrill-Crowe or carbon adsorption. However, due to environmental and regulatory restrictions, cyanide-based leaching is banned in several regions around the world. Therefore, it is growing interest in developing alternative lixiviants that not only demonstrate high gold dissolution efficiency but also offer a reduced environmental impact. Sodium thiosulfate has emerged as a promising alternative owing to its high selectivity for gold, lower affinity for base metals such as copper, and its relatively benign environmental profile (Gallagher *et al.*, 1990; Marsden & House, 2006; McDougall & Copperthwaite, 1980; Young *et al.*, 2012). Extensive studies have demonstrated its effectiveness even in the presence of cyanide-consuming minerals and preg-robbing carbonaceous materials (Abbruzzese *et al.*, 1995; Edwards *et al.*, 2013; Fleming & Nicol, 1984; Grosse *et al.*, 2003).

Using thiosulfate leaching, the stability range for the gold-thiosulfate complex lies within a wide pH range of 8.5 to 10.5—much broader than that of the cyanide complex, which requires a pH of 10.5 to 11.5 for safety and efficiency. Operating below pH = 10 in cyanide systems risks the formation of toxic hydrogen cyanide gas and reduced leaching yield (Abbruzzese *et al.*, 1995; Fleming *et al.*, 2003; Jiang *et al.*, 2022).

Activated carbon remains one of the most effective media for the recovery of gold complexes from leach solutions due to its large surface area (1,005–1,565 m²/g), high mechanical strength, favorable adsorption kinetics, suitable particle size, and the potential for thermal reactivation (Andrade *et al.*, 2018; Marsden & House, 2006; Streat *et al.*, 1987; Zadra *et al.*, 1952). The carbon adsorption process has largely supplanted the Merrill-Crowe method in the recovery of gold from low-concentration leachates (Arima *et al.*, 2002; Fleming *et al.*, 2003; Xia *et al.*, 2022).

Desorption of gold from loaded carbon can be achieved via conventional elution techniques, typically involving elevated temperatures (>100 °C), pressures (~500 kPa), and a stripping solution containing 1.0% NaOH and 0.1% NaCN at a pH of 11–12 over a 48-hour cycle (Marsden & House, 2006). In contrast, for thiosulfate-loaded carbon, desorption requires different conditions—often involving ammonia or ammonium hydroxide combined with thiosulfate at temperatures exceeding 75 °C (Vargas *et al.*, 2006). Given the potential of sodium thiosulfate as a viable alternative for cyanide in gold leaching, recent studies have explored strategies to enhance the adsorption of the gold-thiosulfate complex onto activated carbon.

One effective approach involves pre-treatment or impregnation of carbon to improve its selectivity and adsorption capacity.

For instance, Young *et al.* (2012) impregnated activated carbon with potassium cuprocyanide (K₂CuCN) in alkaline media (pH = 9, using NaOH) under stirring at 300 rpm for one hour at 20 °C. By adjusting the Cu:Au molar ratio below 80%, they achieved over 99% adsorption of the gold-thiosulfate complex from a 20 mg/L solution. Similarly, Yu *et al.* (2015) impregnated activated carbon with CuCl₂, followed by thermal treatment at 900 °C and subsequent exposure to potassium ferrocyanide (K₄Fe(CN)₆) for four hours, yielding gold complex adsorption efficiencies above 98%. In another study, Hon *et al.* (2018) used silver nitrate for pre-treatment, obtaining 70% adsorption. Chen *et al.* (2020) demonstrated that nitrogen-rich activated carbon could achieve up to 95% recovery, while Escobar-Ledesma *et al.* (2020) used thioglycolic acid pretreatment, achieving 90% adsorption. Jiang *et al.* (2022) explored thiosemicarbazide-modified carbon, successfully adsorbing Au(S₂O₃)₂⁻³ from thiosulfate solutions while minimizing copper interference (de la Torre-Miranda *et al.*, 2023).

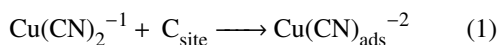
The present study aims to further enhance the adsorption of the gold-thiosulfate complex (Au(S₂O₃)₂⁻³) by employing a novel pre-treatment method involving sequential washing of activated carbon with sodium cyanide and sodium thiosulfate, followed by impregnation with the cuprocyanide complex. The purpose is to improve the ion exchange capacity for forming the aurocyanide complex while simultaneously increasing the adsorption efficiency of the gold-thiosulfate species and reducing non-specific adsorption of the cuprocyanide complex. Batch adsorption tests were conducted to evaluate the performance of the activated carbon treated under varying concentrations of cuprocyanide during impregnation and sodium thiosulfate in the leaching solution. This study contributes to the growing body of research supporting the industrial implementation of thiosulfate-based gold leaching and recovery systems, offering an environmentally safer and technically viable alternative to cyanide.

2 Methodology

2.1 Activated carbon impregnated with cuprocyanide complex

To carry out the experimentation of the present investigation, Figure 1, commercial grade activated carbon mesh N° 6-8 was used (brand CALGON), washed with deionized water to remove all impurities and unclog pores. Laboratory grade reagents such as

sodium cyanide (Meyer) and standard copper were used to prepare the cuprocyanide complex (HYCEL), equation 1.



For the experimental work, a Batch system was used, to carry out the adsorption process, synthetic solutions of cuprocyanide complex were prepared at different concentrations of cuprocyanide complex (1, 5 and 10 mg/L). Once the solutions were prepared, the activated carbon was impregnated, according to equation 1, with the cuprocyanide complex solution (AC-Cu) through mechanical stirring at 300 rpm, for 30 minutes using 12.5 g of activated carbon. Once the carbon impregnation was completed, solid-liquid separation was carried out. Afterwards, the impregnated activated carbon was put in contact with the solution of the gold-thiosulfate complex through mechanical stirring at 300 rpm for 30 minutes. Solutions of the sodium gold-thiosulfate complex were prepared by varying the concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ (0.03, 0.06, 0.1 and 0.2 mol/L) and a gold concentration of 5 mg/L. The atomic absorption spectroscopy technique (PerkinElmer AAnalyst 400 AA) was used to determine the concentration of copper and gold in the solution; metallurgical balances were used to determine the concentration adsorbed on the activated carbon.

The exchange reaction is considered to occur on the surface of the activated carbon, as described by the chemical equation 2, (Young *et al.*, 2012):

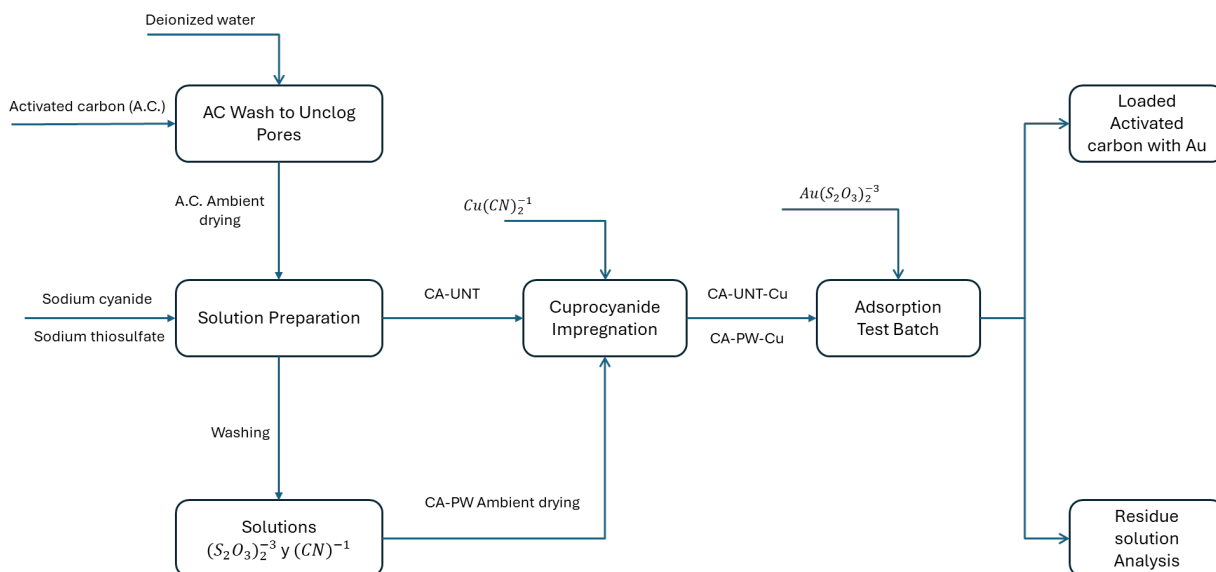
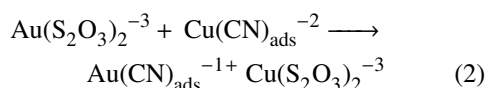


Figure 1. Flowchart for the adsorption of the thiosulfate gold complex.

2.2 Activated carbon impregnated with cuprocyanide complex and treated with sodium thiosulphate and sodium cyanide solution

To obtain better adsorption of the gold-thiosulfate complex, 12.5 g of the activated carbon was treated with sodium thiosulfate solution 0.2 mol/L, for 30 minutes, then with sodium cyanide solution 150 mg/L, for 30 minutes. Afterwards, the activated carbon passed through the impregnation with cuprocyanide complex at 10 mg/L, using a gold-thiosulfate complex solution of 5 mg/L for 30 minutes.

2.3 Adsorption isotherms

The adsorption isotherm is a model that is represented with a curve, in which the experimental data are sought to fit this curve to obtain the theory that describes the adsorption phenomenon. Freundlich's Isothermal Model, Ec. 3, describes the formation of a heterogeneous multilayer surface on the surface of the adsorbent, (Foo & Hameed, 2010; Pinzón-Bedoya & Vera Villamizar, 2009; Tejada-Tovar *et al.*, 2020):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Where K_F is the Freundlich constant, n is the intensity of the adsorption, which is the adsorption capacity at equilibrium (mg/g) and C_e is the concentration at equilibrium (mg/L). Eq. 4 expresses its linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The Langmuir Isotherm Model describes the formation of a homogeneous uniform layer on the surface of the solid, which is expressed:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (5)$$

Where q_e is the adsorption capacity at equilibrium (mg/g), Q_0 is the maximum adsorption capacity, monolayer (mg/g), K_L is Langmuir's constant that defines the affinity of the adsorbate for the adsorbent and C_e is the concentration at equilibrium (mg/L), K_L also associated with the adsorption energy (L/mg). Its expressed linear form is as follows:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{K_L Q_0 C_e} \quad (6)$$

Maintaining the amount of activated carbon, washing solutions, impregnation concentration, thiosulfate concentration, temperature, time and varying the gold concentrations in the adsorption batch tests, the experimental data are evaluated.

3 Results and discussion

3.1 Adsorption of the gold-thiosulfate complex without impregnating the activated carbon

Figure 2 shows the gold-thiosulfate complex adsorption in relation with the activated carbon used. It can be observed that the adsorption of the gold-thiosulfate complex is increased by having a higher quantity of activated carbon, the best adsorption was obtained with 12 g of activated carbon at 50%.

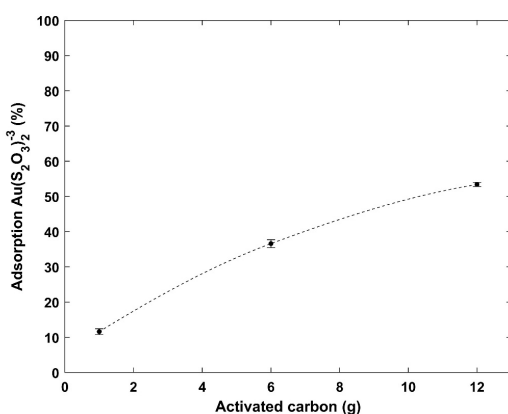


Figure 2. Adsorption of the gold-thiosulfate complex (%) in function to the untreated activated carbon without impregnating (g) at 300 rpm, [Na₂S₂O₃] = 0.03 M, [Au] = 5 mg/L, volume 100 mL, t=30 min., during 30 min of contact.

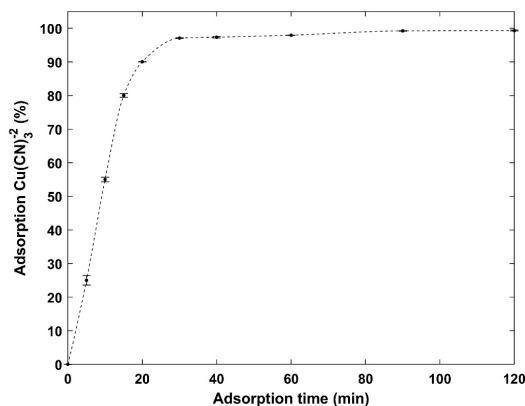


Figure 3. Adsorption of cuprocyanide complex (%) as a function of the time, in 12.5 g of activated carbon [Cu] = 10 mg/L, [CN] = 150 mg/L, volume of 100 mL and room temperature.

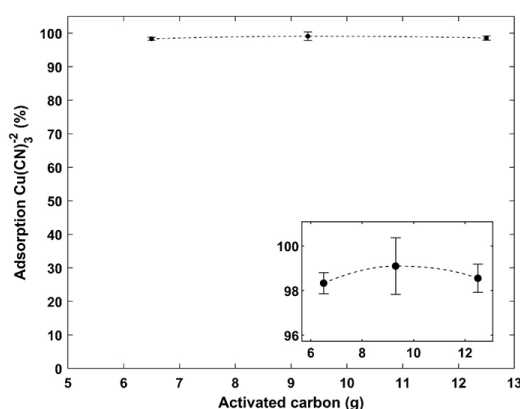


Figure 4. Adsorption of cuprocyanide complex (%) as a function of activated carbon (g), [Cu] = 10 mg/L, [CN] = 150 mg/L, 300 rpm, volume 100 mL, room temperature and t=30 min.

3.2 Cuprocyanide complex impregnation of activated carbon

To determine the contact time of the cuprocyanide complex with the activated carbon, placed in contact at different times, as shown in Figure 3, 30 minutes onwards the adsorption curve of cuprocyanide complex remains, that is, the adsorption percentage does not increase after 30 minutes.

Figure 4 shows the adsorption of cuprocyanide complex in relation to the activated carbon used during this investigation. The adsorption of the cuprocyanide complex remains above 98%.

Figure 5 shows the adsorption of the gold-thiosulfate complex as a function of the concentration of sodium thiosulfate in the leaching solution, using different concentrations of the cuprocyanide complex adsorbed during the impregnation of the activated carbon (AC-Cu). The adsorption of the gold-thiosulfate complex reached percentages above 90%

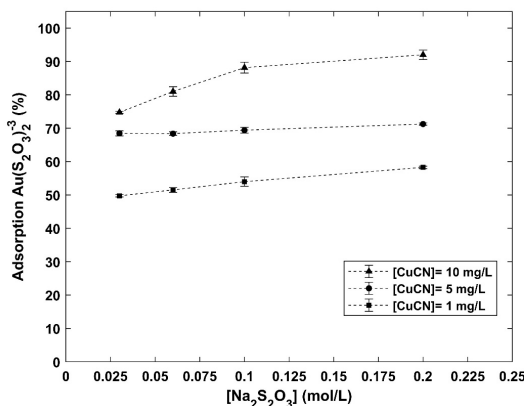


Figure 5. Adsorption of the gold-thiosulfate complex (%) as a function of sodium thiosulfate concentration (mol/L), at different concentrations of CuCN, [Au] = 5 mg/L, 12.5 g activated carbon, 300 rpm, volume of 100 mL and room temperature.

when using 0.2 mol/L of sodium thiosulfate and 10 mg/L of the cuprocyanide complex to impregnate the activated carbon.

3.2.1 Sodium thiosulfate and sodium cyanide pre-wash activated carbon impregnation

The sodium thiosulfate and sodium cyanide were used to prewash activated carbon (AC-PW). To compare the effect of this treatment, untreated activated carbon was used (AC-UNT) and both samples were impregnated with cuprocyanide complex solutions. The cuprocyanide complex adsorption (%) in relation to the activated carbon used (g) for untreated (AC-UNT) and prewashed activated carbon (AC-PW) is shown in Figure 6, where the adsorption is greater than 98% for AC-UNT and less than 30% for AC-PW.

The adsorption of the gold-thiosulfate complex was greater than 90% when prewashed and impregnated activated carbon (AC-PW-Cu) was used. Increasing AC-PW-Cu it was obtained higher the adsorption rate. Figure 7 shows the adsorption % in relation to the AC-PW-Cu used.

3.2.2 Cu concentration reduction in the cuprocyanide complex impregnation solutions

The copper concentration does not affect the adsorption rate of the gold-thiosulfate complex. When 5 or 10 mg/L were used the adsorption was greater than 98% for both concentrations. Table 1 shows the results obtained when copper concentration varied in the impregnation solution, 12.5 g of AC-PW and a 5 mg/L gold-thiosulfate complex concentration were used.

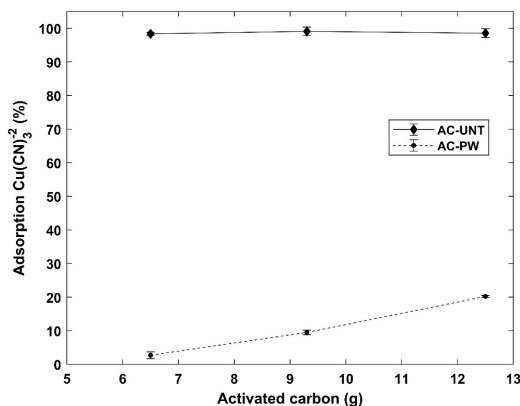


Figure 6. Cuprocyanide complex adsorption (%) with activated carbon (g) treated with [Na₂S₂O₃] = 0.2 mol/L, [CN] = 150 mg/L, 300 rpm, volume 100 mL, and impregnation time = 30 minutes, with [Cu] = 10 mg/L.

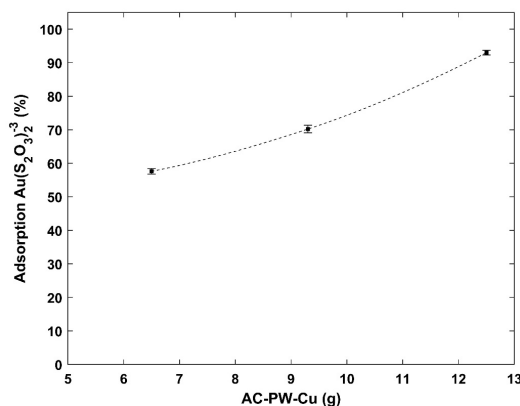


Figure 7. Adsorption of the gold-thiosulfate complex (%) as a function of activated carbon prewashed and impregnated (g) with cuprocyanide complex, [Na₂S₂O₃] = 0.2 mol/L, [Au] = 5 mg/L, volume of 100 mL, for 30 minutes.

Table 1. Cuprocyanide complex concentration in impregnation tests using AC-PW.

[Cu] (mg/L)	Cu _{ads} (%)	Au _{ads} (%)
0	0	60.0
5	23	99.4
10	63	99.4

The adsorption of the gold-thiosulfate complex is related to the gold concentration; the adsorption rate does not decrease significantly to the gold concentrations used in this research. The adsorption rate of washed and impregnated activated carbon (AC-PW-Cu) the gold concentration in the sodium thiosulfate was varied and shown in Figure 8.

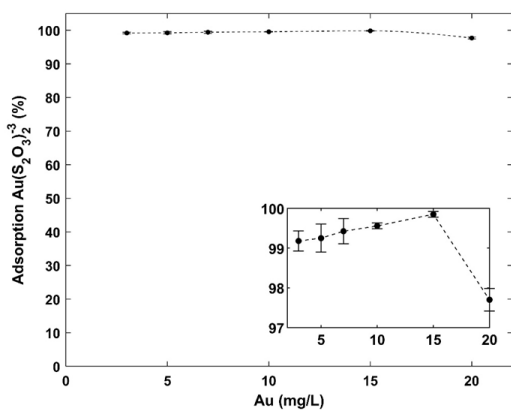


Figure 8. Adsorption of the gold-thiosulfate complex (%) with activated carbon (g) prewashed and impregnated with cuprocyanide complex, 12.5 g of activated carbon, $[\text{Na}_2\text{S}_2\text{O}_3] = 0.2 \text{ mol / L}$, volume of 100 mL, $t=30 \text{ min}$.

3.2.3 Adsorption isotherms

Applying the Freundlich and Langmuir models to the results of the tests expressed in Figure 8, the graphs are obtained in which there is a better fit to the Freundlich model compared to the Langmuir model (Figure 9). The parameters of the models are shown in Table 2. This confirms that the model that best fits the experimental data is the Freundlich isotherm model, which describes the formation of heterogeneous multilayers on the surface of the solid.

Table 2. Parameters for Langmuir and Freundlich models.

Freundlich			Langmuir		
K_F (mg/g)(dm ³ /g) ⁿ	n ads ints	R^2	Q_o mg/g	K_L L/mg	R^2
0.2171	1.7699	0.9616	0.1509	7.6848	0.9742

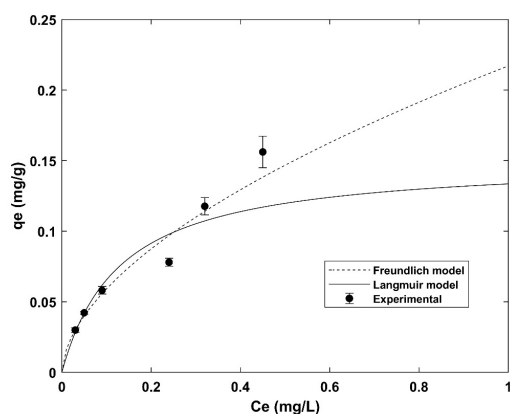


Figure 9. Isotherms models.

Conclusions

In this study, an alternative for the adsorption of gold from thiosulfate solutions was investigated. According to the type of exchange reactions in the copper-thiosulfate and aurocyanide complexes, the activated carbon must first be impregnated with cuprocyanide complex for the adsorption of the gold-thiosulfate complex.

The best conditions for the adsorption of the gold thiosulfate complex in activated carbon were obtained by impregnating the carbon with a concentration of 10 mg/L of cuprocyanide complex (AC-Cu) and 0.2 mol/L of sodium thiosulfate. Under these conditions, the adsorption of gold thiosulfate was greater than 98%. It was shown that the experimental results fit the Freundlich model, which describes that the adsorption phenomenon occurs by chemisorption, forming a chemical bond between the surface of the activated carbon and the gold-thiosulfate.

Activated charcoal treated with sodium cyanide and sodium thiosulfate prior to impregnation (AC-PW) with cuprocyanide results in less adsorption of $\text{Cu}(\text{CN})_3^{-2}$ than the results obtained; however, it does not affect the adsorption of the gold-thiosulfate complex. Whereas activated carbon, when impregnated with a lower concentration of $\text{Cu}(\text{CN})_3^{-2}$, has the possibility of adsorbing Au in thiosulfate solution as a aurocyanide, due to the exchange reaction that occurs between the gold-thiosulfate complex.

The use of thiosulfate in leaching, unlike cyanide, would have the advantage of storing cyanide in vessels that would provide greater safety to the environment and to personal handling.

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