Aurocyanide adsorption onto granular activated carbon impregnated with SDS anionic surfactant

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Abstract
The impregnation of granular activated carbon with the anionic surfactant sodium dodecylsulfate (SDS) was studied and the influence on aurocyanide adsorption was evaluated. Thermodynamic and kinetic parameters were also determined. The impregnation of activated carbon with SDS improves gold adsorption by 10%, showing a cleansing effect on the carbon surface which was displayed in a higher specific surface area. Specific pore volume and average pore diameter did not undergo important changes. Increasing the temperature decreases gold adsorption on modified carbon. The standard enthalpy of adsorption and the activation energy were calculated, getting values of \(-41.3\) kJ/mol and \(15.0\) kJ/mol, respectively.

Keywords Adsorption · Aurocyanide · Activated carbon · Impregnation · Surfactant · SDS

Introduction
Leaching with cyanide (cyanidation) is a common process for gold and silver extraction widely used in the mining industry. This process consists of two stages: extraction and recovery. In the extraction stage, the gold present in the ores is dissolved in an aqueous cyanide solution according to the following chemical reaction:

\[
4\text{Au}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Au(CN)}_2^-(aq) + 4\text{OH}^-(aq)
\]  

(1)

The formation of the \(\text{Au(CN)}_2^-\) ionic complex from Eq. (1) allows the transfer of the gold to the aqueous solution [1]. In the recovery stage, the ionic complex in the ore pulp or in the cyanide solution is recovered by adsorption on activated carbon [2–5], cementation with zinc [6, 7], and melting.

The most widely used technique for gold adsorption is the carbon in pulp (CIP) process, because it is profitable, stable, and reliable. In this process, the ionic gold complex is adsorbed on activated carbon directly from the cyanidated ore pulp, followed by the elution of the gold adsorbed on the activated carbon. The activated carbon commonly used in the mining industry is made from coconut shells, but other raw materials can also be used, such as residues from agriculture and from the food and petroleum industry. In general, the main requirements for the activated carbon for a gold adsorption process are high adsorption capacity, high adsorption rate, and good resistance to abrasion [8]. Various methods of modification had been adopted to enhance the adsorption capacity of the activated carbon. It includes physical, chemical, and biological modification [9–11].

Activated carbon surface modification with foreign materials like ionic surfactant and metal loading improved the adsorption of inorganic pollutant, which is present in water as ions. Surface-active-agent (usually referred to as surfactants) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic, or zwitterionic, and accompanied by counter ions in the last two cases. When the surfactants are dissolved in a solvent at low concentration, could be adsorbed (or located) at interfaces, thereby altering...
significantly the physical properties of those interfaces. A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. Thus, surfactants are classified as anionic, cationic, zwitterionic, and non-ionic. The concentration at which a surfactant starts aggregation in solution is known as its critical micelle concentration (CMC). Surface active agent at a temperature and electrolyte concentration has a characteristic CMC value. As a result, there is considerable interest in the determination of CMC because in practice, it is the lowest concentration of the surfactant offering the optimum benefits [12, 13].

The main evidence of the effect of modification of activated carbon with surfactants is in the field of treatment of liquid effluents containing heavy metals. It has been reported that this type of modification produces a change in the physicochemical properties of activated carbon that improves the adsorption of lead, cadmium, and chromium. Therefore, the modification of activated carbon using some chemicals is considered a promising and attractive development line in the search for new applications and/or improvements in the adsorbing capacity of activated carbon [14–17].

Based on the background above, studies have been made with the aim of determining the effect of modifying activated carbon with cationic surfactant, CTAB, finding improvements in the adsorption of the aurocyanide complex \( \text{Au(CN)}_2^- \), and determining important kinetics parameters [18–22].

Continuing the previous work, in the present paper, we study the impregnation of granular activated carbon with the SDS anionic surfactant and its effect on the adsorption of the aurocyanide complex, carrying out a kinetics analysis that can allow the determination of parameters of interest and clarify the mechanism of action of the anionic surfactant.

### Experimental

#### Materials

A commercial granular activated carbon (GAC) was used for the impregnation with anionic surfactant and the adsorption of gold in aqueous solution. This material was washed with deionized water, dried at 60 °C for 48 h, and stored in a desiccator until its use. The anionic surfactant was sodium dodecylsulfate, SDS (Table 1). The gold solutions were prepared by dissolving KAu(CN)_2 in deionized water, adjusting the pH with KOH. All the chemicals were of analytical grade.

#### Table 1 Chemical properties of anionic surfactant used in this study

| Surfactant                  | Formula                        | MW (g mol\(^{-1}\)) |
|----------------------------|--------------------------------|---------------------|
| SDS (sodium dodecyl sulfate)| \( \text{CH}_3(\text{CH}_2)_1\text{OSO}_3\text{Na} \) | 288.38              |

#### Activated carbon impregnation

The unmodified dried granular activated carbon (GAC) was modified by impregnating it with the SDS surfactant. The contact ratio was 1 g of GAC per 100 mL of SDS solution at 0.5 CMC. Previously, the CMC of the SDS was determined by measuring the conductivity of the aqueous medium with different concentrations of the surfactant at ambient temperature. The solid/liquid system was stirred mechanically at 160 rpm at a controlled temperature of 25 ± 0.5 °C for 12 h. Once the impregnation was completed, the carbon was filtered, dried, and placed in a desiccator until its use. The modified activated carbon was designated as SDS-GAC.

#### Characterization of the activated carbon

To evaluate the surface morphology of the GAC and SDS-GAC samples, scanning electron microscopy (SEM-SE) analysis was performed on VEGAS3 TESCAN microscope. Elemental analysis was performed by the energy dispersive X-ray spectroscopy (EDS). Also, the specific surface area and pore volume of the samples were determined by a nitrogen gas adsorption analysis, using a Micromeritics ASAP 2010 instrument at −196 °C. Specific surface area was calculated by the BET (Brunauer–Emmett–Teller) Method.

#### Batch tests of gold adsorption

The gold adsorption tests were performed in a 500-mL glass reactor equipped with mechanical stirring. The reactor was placed in a thermostatic bath and the tests were run at a stirring speed of 300 rpm with 300 mL of the gold solution (11 mg/L) at a pH of 11. In all experiments, the solid/liquid ratio was 0.1 g of activated carbon per 100 mL of aqueous gold solution. The temperature was adjusted depending on the test, with 25 °C for the evaluation of the impregnation and 5, 25, 35, 50, and 80 °C for the evaluation of the effect of this variable with the SDS-GAC. Solution samples were taken periodically for the chemical analysis of the gold by atomic absorption spectroscopy (AAS). The percentage of gold adsorbed (\( R(\%) \)) onto the activated carbon was calculated using the following equation:

\[
R(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]
where $R$ is the percentage of adsorbed gold on activated carbon, $C_0$ is the initial gold concentration, and $C_t$ is the gold concentration (mg/L) at any time.

**Results and discussion**

**Determination of critical micelle concentration**

Figure 1 shows the conductivity versus SDS surfactant concentration graph, needed to determine the critical micelle concentration (CMC). The representation of the data is a curve whose slopes are different before and after the CMC. The straight line before the CMC has a slope of 70.3 and the one after the CMC has a slope of 32.2. These results verify the theory that points out that after the formation of micelles, the rate of increase of conductivity decreases as surfactant concentration increases.

To determine the CMC of the SDS surfactant, both straight lines were intercepted, giving as a result the concentration at which the micelles start forming, which is 8.23 mM. The precision of the method used is determined by the correlation coefficient of the curves ($R^2$), which is close to 1 for the curve before and after the CMC, 0.987 and 0.997, respectively. The value obtained from the CMC for the SDS surfactant is like those reported in the literature [23, 24].

**Characterization of the activated carbon**

Figure 2 shows the SEM (SE) images at 2000× of activated carbon samples. Figure 2a shows an irregular structure of neat activated carbon, with pores mostly around 20 µm, with no presence of small pores. Figure 2b shows an outer surface with pores of up to 40 µm, most of them covered with small pores.

Elemental analysis by energy-dispersive X-ray spectroscopy (EDS) shows the effect of impregnation in the surface composition of activated carbon. These results are presented in Fig. 3.

The spectra show mainly the change in composition of Na and S. The results revealed an increase in sodium from 0.260 to 1.61%; this is attributed to sodium is part of the chemical structure of the surfactant. Regarding sulfur, this element is not detected in the GAC but was determined to be present in 1.91% in SDS-GAC. Sulfur is part of the polar head of the surfactant. These variations confirm that the surfactant is adsorbed on the activated carbon surface.
Table 2 shows the results of the physisorption analysis (BET) and pore distribution and size of GAC and SDS-GAC. The SDS-GAC has a larger specific surface area of 807.8 m²/g compared to 772.6 m²/g for GAC, with a 4.6% area increase. The specific volume of the pores of SDS-GAC, of 0.39 cm³/g, does not undergo a significant change compared to 0.43 cm³/g corresponding to GAC. On the other hand, the average diameter of the pores shows the same behavior, and it is similar for both activated carbons, 1.92 nm and 1.93 nm for GAC and SDS-GAC, respectively.

### Table 2 Physical properties of studied adsorbents

| Property                | GAC  | SDS-GAC |
|-------------------------|------|---------|
| Specific surface area (m²/g) | 772.6 | 807.8  |
| Specific pore volume (cm³/g)   | 0.43  | 0.39   |
| Average pore diameter (nm)     | 1.92  | 1.93   |
activated carbon without impregnation is used, resulting in a 10% increase. The beneficial effect of the impregnation may be because the surfactant can act as a cleanser of the surface of the activated carbon, removing impurities that remained in the preparation stage of the activated carbon. This generates a larger number of active sites and therefore a greater specific area, allowing the adsorption of more gold in a given time.

**Effect of the temperature**

The results shown in Fig. 5 correspond to gold adsorption at a time of 420 min at temperatures of 5, 25, 35, 50, and 80 °C on SDS-GAC. Gold adsorption is inversely proportional to temperature, achieving more than 90% adsorption at a temperature of 5 °C and around 45% gold recovery at 80 °C. This behavior is proper of the aurocyanide adsorption process onto activated carbon and has been reported by various authors [2, 25–27]. Then, when using activated carbon impregnated with SDS surfactant, the effect of temperature is like what would have occurred when using an unmodified carbon.

This phenomenon is related to the solubility of the aurocyanide complex; as the temperature increases, the solubility of the gold complex is higher, since the solubility of the aurocyanide complex increases 14 times as the temperature of the aqueous solution increases. So, at a higher temperature, the gold complex has a greater tendency to remain in the aqueous solution than to be adsorbed by the activated carbon. This phenomenon also takes place when working with unmodified activated carbon, and it is one of the foundations for carrying out the desorption at a high temperature [28–30].

**Adsorption enthalpy**

The standard adsorption enthalpy, $\Delta H_{ads}^o$, was determined with the purpose of estimating the heat of adsorption and getting to know the nature of the process. The following equation was used, assuming an Arrhenius type behavior.

$$D = B \cdot \exp \left( \frac{\Delta H_{ads}^o}{R \cdot T} \right)$$

(3)

where $D$ is the distribution coefficient of the gold, which corresponds to the ratio between the gold load on the carbon at equilibrium ($q_e$) and the gold concentration in the aqueous solution at the equilibrium ($C_e$). $B$ is Arrhenius temperature independent factor, $T$ is the temperature in Kelvin, and $R$ is the universal gas constant. Equation (3) was linearized, and the graph of Fig. 6 was obtained.

Figure 6 yields a standard adsorption enthalpy of $-41.3$ kJ/mol, showing the exothermic nature of the adsorption process. For unmodified carbon and under similar experimental conditions, a standard adsorption enthalpy of $-24.97$ kJ/mol is obtained, showing that the SDS-GAC does not change the exothermic nature of the gold-cyanide complex adsorption onto activated carbon.

**Activation energy**

The activation energy was obtained using the Arrhenius equation:

$$k = A \cdot \exp \left( -\frac{E_{a}}{R \cdot T} \right)$$

(4)
where $A$ (min$^{-1}$) is a temperature-independent factor, $E_a$ (kJ/mol) is the activation energy, $R$ (8.314 J/mol K) is the universal gas constant, and $T$ (K) is the temperature.

The values of the adsorption kinetics constants, $k$, according to previous studies and for short adsorption times and low gold concentrations [31–33], were obtained assuming a first-order kinetic model, and are shown in Table 3.

The $\ln(k)$ values were graphed versus $1/T$, and the results are shown in Fig. 7. The activation energy of the gold adsorption process on SDS-GAC was calculated using the resultant slope of the linear relation of Fig. 7, whose value was 14.98 kJ/mol.

According to this value, the gold adsorption process on SDS-GAC is controlled kinetically for mass transfer, specifically diffusional control in the solution film that surrounds the carbon particles. Using the same procedure, the activation energy for unmodified carbon was determined, getting a value of 12.07 kJ/mol. So, this control mechanism is like the one for the adsorption of gold on unmodified activated carbon.

### Table 3 Adsorption kinetics constants at different temperatures

| Temperature (K) | $k \times 10^2$ (min$^{-1}$) |
|-----------------|-----------------------------|
| 278.15          | 2.26                        |
| 298.15          | 1.47                        |
| 308.15          | 0.80                        |
| 323.15          | 0.74                        |
| 353.15          | 0.60                        |

**Conclusion**

The adsorption of the complex ion Au(CN)$_2^-$ onto granular activated carbon impregnated with SDS anionic surfactant was studied. The impregnation process consisted of the surfactant adsorption on the surface of granular activated carbon, which caused surface cleaning and generation of active sites. This generated the increase in specific surface area. The adsorption experimental results of this work have shown that by using SDS-GAC, the gold adsorption percentage is 10% higher than when using GAC. Temperature has a negative effect on the adsorption of gold because with increasing temperature also increases the solubility of aurocyanide complex in aqueous medium. The negative value of standard enthalpy of adsorption $\Delta H^{\text{ads}} = -41.3$ kJ/mol revealed and confirmed the exothermic nature of this adsorption process. The adsorption activation energy, $E_a$, was equal to 14.98 kJ/mol. This low activation energy value indicates that the kinetics of gold adsorption on SDS-GAC is controlled by diffusion.

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