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Adsorption of Gold from Copper–Tartrate–ThiosulfateSolutions with Ion-Exchange Resins

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Abstract: The adsorption behavior of gold from copper–tartrate–thiosulfate solutions with ion-exchange resins was studied in this paper. Experimental parameters include resin dosage, pH, temperature, copper, tartrate, and thiosulfate concentration. A moderate increase in resin dosage, pH, temperature, and tartrate concentration is beneficial for gold adsorption, but an excessive tartrate concentration or higher temperature depresses the adsorption process. Increasing copper and thiosulfate concentrations may competitively occupy the active sites on the resin surface, leading to a reduction in the gold adsorption capacity. The XPS and FT-IR analyses indicate that copper and gold on the resin after adsorption mainly exist in the form of Cu^{+} and Au^{+}, and sulfur mainly exists in the form of SO_4^{2-} and $S_2O_3^{2-}$. This implies that the use of resin for gold recovery from thiosulfate leachate may face critical challenges because there is inevitably a higher content of copper and thiosulfate.

Keywords: gold; thiosulfate; tartrate; resin; adsorption

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1. Introduction

Cyanidation has been used in the gold mining industry for hundreds of years due to its mature process, relatively low cost, and considerable leaching efficiency. The carbon-in-pulp or carbon-in-leach (CIP/CIL) as the premier process for gold extraction greatly promotes the commercial application of gold recovery from cyanide solutions [1]. However, gold cyanidation has faced critical challenges since the day of its birth because cyanide is extremely toxic and easily causes ecological and health problems [2,3]. With the growing awareness and concern about public security and environmental protection, non-cyanide gold leaching techniques have attracted increasing attention [4,5].

Thiosulfate is one of the most promising substitutes that shows some encouraging performance in dealing with carbonaceous or copper-bearing gold ores, while the cyanide process is undesirable to treat these minerals [6,7]. Moreover, thiosulfate is nontoxic and cost-effective and shows good selectivity toward gold. Without a catalyst, gold dissolution in thiosulfate solutions is very slow [8]. Copper and ammonia generally act as the leaching catalyst to accelerate the gold dissolution process. Copper ions serve as the oxidant, while ammonia works as a stabilizer to prevent copper precipitation in alkaline media. Ammonia can also act as the complexing agent with aurous ions, accelerating the gold dissolution process [9–11]. It was reported that gold dissolution in copper–ammonia–thiosulfate solutions can be described as an electrochemical process [12]. In the anodic area, metallic gold is oxidized to aurous ions and then complexes with thiosulfate ions to form the $Au(S_2O_3)_2^{3-}$ complex. Meanwhile, the $Cu(NH_3)_4^{2+}$ complex in the cathodic area will be reduced to the $Cu(S_2O_3)_3^{5-}$ complex. Dissolved oxygen plays a critical role in maintaining the conversion between the Cu(II)/Cu(I) redox couple. However, the use of ammonia greatly restricts the commercial application of thiosulfate because ammonia is unstable

and easy to volatilize, which may be poisonous to the working environment and life safety. The threshold limiting value (TLV) for ammonia gas in air is 14 mg/m^3 according to the standard of MAK 2017, which is classified as similar to that of HCN (15 mg/m^3) [13]. Therefore, non-ammonia thiosulfate-based solutions are considered much greener and more feasible for gold extraction from ores or concentrates [14,15].

The introduction of tartrate or citrate in copper–thiosulfate solution shows some encouraging performance in dealing with carbonaceous or sulfide gold minerals [16–18]. The capability of gold leaching in copper–tartrate–thiosulfate solutions is comparable to that of cyanidation or copper–ammonia–thiosulfate leaching systems, while the consumption of thiosulfate can be significantly reduced. However, a critical issue that should be considered is the lack of an economical and sustainable gold recovery technique from copper–tartrate–thiosulfate solutions. It is worth noting that resin adsorption is considered the most promising method among the various gold recovery techniques, including carbon adsorption, solvent extraction, electrowinning, and precipitation [19,20]. Adsorption of gold using ion-exchange resins shows a fast adsorption speed and high gold loading capacity, requires low requirements for the clarity of solutions, and can regenerate at ambient temperature [21,22]. Dong et al. (2017) summarized the resin adsorption technique for gold recovery from pregnant thiosulfate solutions and proposed that the current research about gold recovery using ion exchange resins from pregnant thiosulfate solutions is in its infancy and a large number of further work is needed to make the recovery technique more efficient, economical and environmentally friendly [19]. To weaken or eliminate the competitive adsorption effects of copper (I) thiosulfate complexes and polythionates, one feasible measure is to minimize their generation during leaching through the elaborate control of reaction conditions. Another more effective measure is the replacement of traditional copper–ammonia catalysis with other metals, such as nickel- and cobalt-based catalysts. Arima (2003) studied the gold recovery from nickel-catalyzed ammonium thiosulfate solution by strongly basic anion exchange resin [23]. The results indicated that 95 kg-Au/t-resin can be obtained under the optimal gold loading conditions on a 1 g/dm^3 strongly base anion exchange resin. The maximum gold recovery by 2.5 mol/dm^3 ClO_4^- was around 98%, with the stripped resin assayed as 0.2 kg/t Au. Xu et al. (2019) conducted the test of gold recovery by resin adsorption from cobalt–ammonia–thiosulfate pregnant solutions [24]. The results demonstrated that the competitive adsorption of cobalt with gold did not occur owing to the weak affinity of the strong base anion resin for cobalt complex ions. Therefore, the elution of gold on loaded resin only needs to perform a simple one-stage process instead of the complex two-stage elution process for the copper–ammonia–thiosulfate system, which will contribute to reducing the cost of gold recovery from the pregnant solution.

However, to the best of our knowledge, studies on the performance of gold adsorption from copper–tartrate–thiosulfate solutions by ion-exchange resins have not been reported. Thus, three different types of ion-exchange resins were selected here for gold recovery from copper–tartrate–thiosulfate solutions. Effects of experimental parameters, including resin dosage, solution pH, temperature, and copper, tartrate, and thiosulfate concentration, have been examined. The XPS and FT-IR analyses were performed to illustrate the adsorption mechanism of gold thiosulfates onto resins. The potential challenges of using ion-exchange resins for gold recovery from copper–tartare–thiosulfate solutions are also discussed.

2. Material and Methods

2.1. Materials

Reagents of analytical grade include sodium thiosulfate, sodium tartrate ($Na_2C_4H_4O_6$, henceforward indicated as Na_2L), copper sulfate, sodium hydroxide, sulfuric acid, and gold standard solution, all from Shanghai Chemical Sinopharm Reagent Co. LTD (SCRC, Shanghai, China), were used in the tests. The resins (D201, 717, D301) used in these adsorption tests were of analytical grade and obtained from Tianjin Jinda Zhengtong Environmental Protection Co., LTD (Tianjin, China). Table 1 shows the main physicochemical properties of the resins. The D201 and 717 resins belong to strongly alkaline resin, while the D301

resin is a weakly alkaline resin. The concentration of the standard gold solution and its acidic matrix was 1000 mg/L. Before each experiment, a certain amount of the sample was diluted with deionized water to a required concentration of gold for subsequent use. The lixiviant was prepared with the required content of copper sulfate, sodium tartrate, sodium thiosulfate, and deionized water. Detailed adsorption conditions were specified for each experimental session.

Table 1. Some physicochemical properties of the resins.

Resin	D201	717	D301
CAS	9050-97-9	9002-24-8	201615-38-5
Type	Strongly alkaline	Strongly alkaline	Weakly alkaline
Functional group	[-N(CH_3)$_2$]	[-N(CH_3)$_2$]	[-N(CH_3)$_2$]
pH	1–14	1–14	1–9
Particle size (0.315–1.25 mm)	≥95%	≥95%	≥95%

2.2. Methods

The resins were conditioned with a 10% HCl solution for 12 h to remove the metal ions and then washed with deionized water until neutral. Thiosulfate solution was used to dilute the gold standard solution, and the volume was fixed at 100 mL; the pH of the prepared gold solution was then adjusted with diluted NaOH to 9.0 to stabilize the $Au(S_2O_3)_2^{3-}$ anion [25]. The concentration of gold used in these experiments was 30 mg/L (unless otherwise specified). Effect of resin dosage (0.10–1.00 g), solution pH (8.5–11.5), adsorption time (10–360 min), temperature (25–70 °C), concentrations of copper (0.001–0.2 mol/L), tartrate (0.05–0.4 mol/L), and thiosulfate (0.10–0.50 mol/L) on the gold adsorption process were systematically studied. Mixing was provided by a thermostatic oscillator at a constant frequency of 150 rpm/min. A water bath was used to maintain the required temperature. Solution samples were withdrawn with a set time to determine the gold concentration in the solutions by atomic adsorption spectrometry (AAS) (AA240FS, Agilent Technologies Inc, Santa Clara, CA, USA). Fourier transform infrared spectroscopy (FT-IR) was used to obtain the infrared transmission spectra of the materials, and the data were recorded in the range of 400–4000 cm^{-1} (Nicolet iS10, Thermo Fisher, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed to study the chemical composition on the surface of the samples (ESCALAB 250, Thermo Scientific, Waltham, MA, USA).

The adsorption capacity (q) of gold onto the resins was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where

q_t is the adsorption capacity of $Au(S_2O_3)_2^{3-}$ at time t,
C_0 and C_t are the gold concentrations at time 0 (initial) and t, respectively,
V is the volume of the solution,
m is the mass of the resin.

Pseudo-first-order and pseudo-second-order models were conducted to describe the process of $Au(S_2O_3)_2^{3-}$ adsorption.

Pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (2)$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot {q_e}^2} + \frac{t}{q_e} \quad (3)$$

where

q_e and q_t are the $Au(S_2O_3)_2^{3-}$ adsorption at equilibrium and time t,
k_1 and k_2 are adsorption rate constants.

3. Results and Discussion

3.1. Adsorption Kinetics

Three basic ion-exchange resins (D201, 717, D301) were selected for the comparative test of the adsorption of gold from copper–tartrate–thiosulfate solutions, and the results are shown in Figure 1. It is clear that the capacity of gold adsorption onto resins increases with increasing time in the initial stage of adsorption. Peak adsorption was observed at an adsorption time of approximately 180 min, and then the gold adsorption process reached a steady state, indicating that the equilibrium adsorption of gold onto resins was basically established. Moreover, the performance of gold adsorption using D201 resin is much more pronounced than that of the 717 and D301 resins. The equilibrium gold adsorption capacity of the $Au(S_2O_3)_2^{3-}$ complex following 180 min on D201 resin reaches up to 15.9 mg/g, which is higher than that of 717 and D301 resins with 9.7 mg/g and 5.8 mg/g, respectively. Thus, D201 resin was selected for the subsequent adsorption tests.

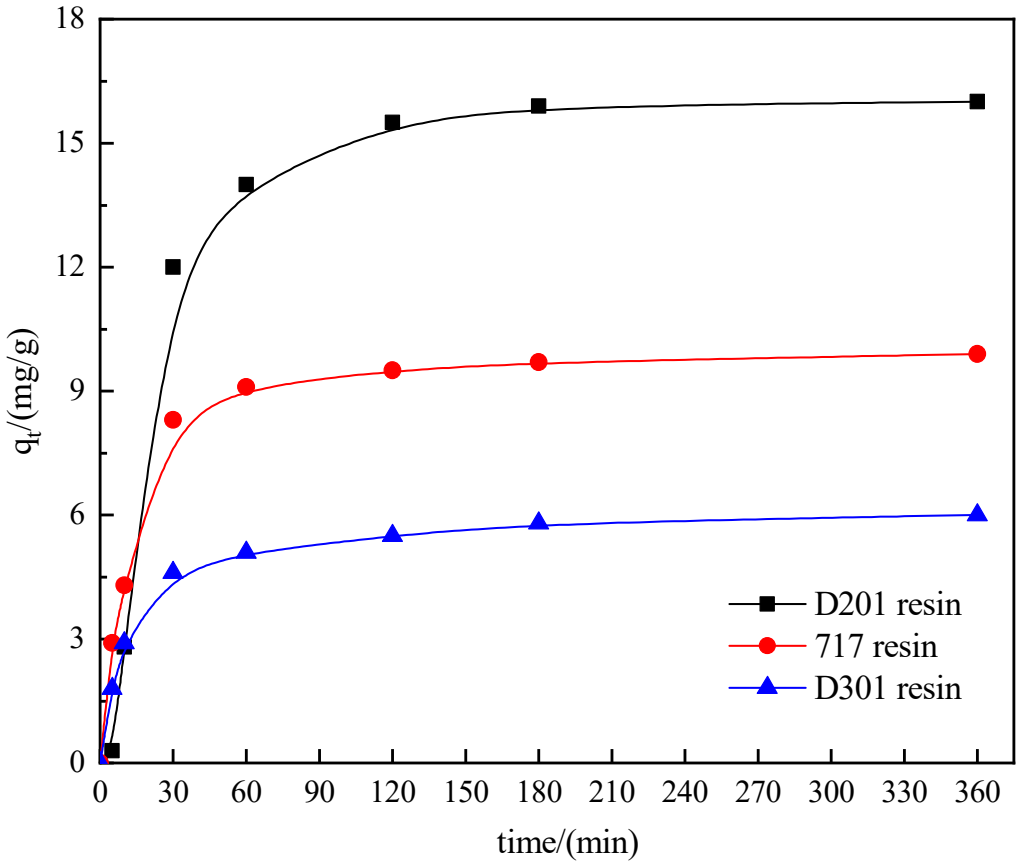


Figure 1. Kinetics of gold adsorption with three ion-exchange resins (initial Au 100 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, pH = 11.5, 25 °C, and 0.5 g resin).

3.2. Effect of Resin Dosage

Figure 2 illustrates the effect of the resin dosage on gold adsorption performance. The capacity of gold adsorption on resins increases with increasing adsorption time. The rate of gold adsorption onto the resins is very fast in the initial 30 min, and then the amount of gold adsorption increases slightly with the extended time. When the adsorption time exceeds 30 min, however, the gold adsorption rate gradually decreases. The adsorption

process basically attains equilibrium after 180 min, and the amount of adsorbed gold on the resins tends to be stable.

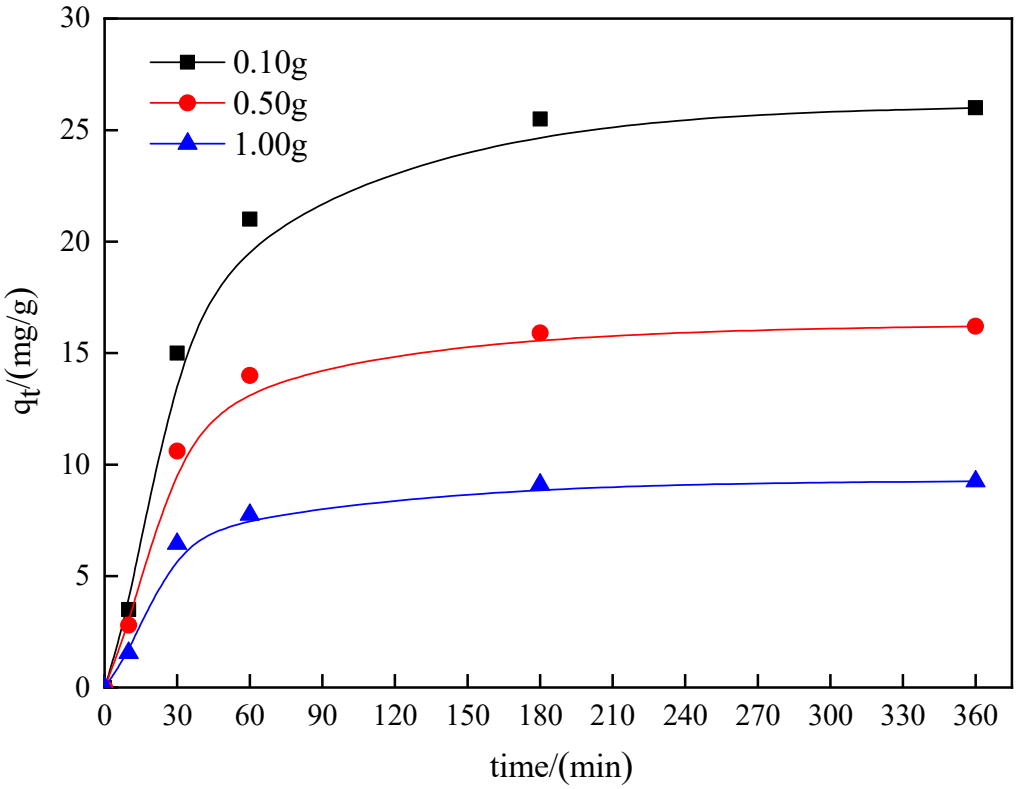


Figure 2. Effect of the resin dosage on gold adsorption performance (initial Au 100 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, pH = 11.5, and 25 °C).

It is noted that the total amount of adsorbed gold in the resins increases with the increasing amount of resin, but the amount of gold per unit mass of the resin gradually decreases. When the initial amount of resin was 0.10 g, the amount of adsorbed gold in the resin reached 15.0, 21.0, and 25.5 mg/g after adsorption for 30, 60, and 180 min, respectively. However, when the resin mass was 1.00 g, the gold content of the resin was 6.45, 7.75, and 9.10 mg/g following adsorption for 30, 60, and 180 min, respectively. The results indicate that increasing the amount of resin is beneficial to the adsorption of gold in the solutions, but excessive resin may adsorb more impurities from the solutions, which may affect the eluent process and increase the operation cost [19]. Thus, a suitable amount of 0.5 g resin was used for the subsequent adsorption tests.

Table 2 summarizes the parameters fitted to pseudo-first-order and pseudo-second-order adsorption kinetic models. The results indicate that the pseudo-second-order kinetic model exhibits a higher linear correlation (R^2 = 0.985) for the gold adsorption kinetics than the pseudo-first-order kinetic model. Moreover, the equilibrium gold adsorption capacity of the $Au(S_2O_3)_2^{3-}$ complex on resins was 17.27 mg/g according to the fitted line (Figure 3) when the resin was 0.50 g, which is closer to the experimental result of 16.20 mg/g.

Table 2. Parameters related to pseudo-first-order and pseudo-second-order kinetic models.

Kinetics Model	Concentration of Gold (mg/L)	R^2	q_e (mg/g)	
			Calculated	Experiment
Pseudo-first-order	100	0.839	8.69	16.20
Pseudo-second-order	100	0.985	17.27	16.20

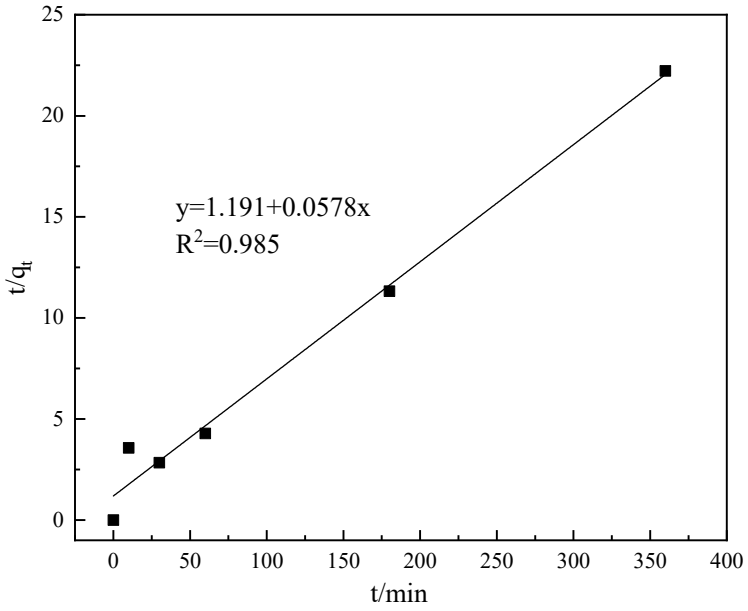


Figure 3. Pseudo-second-order kinetic model for gold adsorption onto D201 resin (initial Au 100 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, pH = 11.5, 25 °C and 0.5 g resin).

3.3. Effect of the Composition of Solutions

3.3.1. Effect of Solution pH

Figure 4 shows the effect of solution pH on gold adsorption from copper–tartrate–thiosulfate solutions. The capacity of gold adsorption dramatically increases with increasing solution pH from 8.5 to 10.5 and then slightly increases with a continuous increase in solution pH to 11.5. The adsorbed gold on resin increases with increasing adsorption time over the entire range studied. The gold adsorption capacity of the $Au(S_2O_3)_2^{3-}$ complex on D201 resin reached 3.5, 6.4, 9.3, and 9.9 mg/g following 360 min adsorption when the initial solution pH was 8.5, 9.5, 10.5, and 11.5, respectively. Apparently, the performance of gold adsorption is more encouraging under strongly alkaline conditions with the D201 resin.

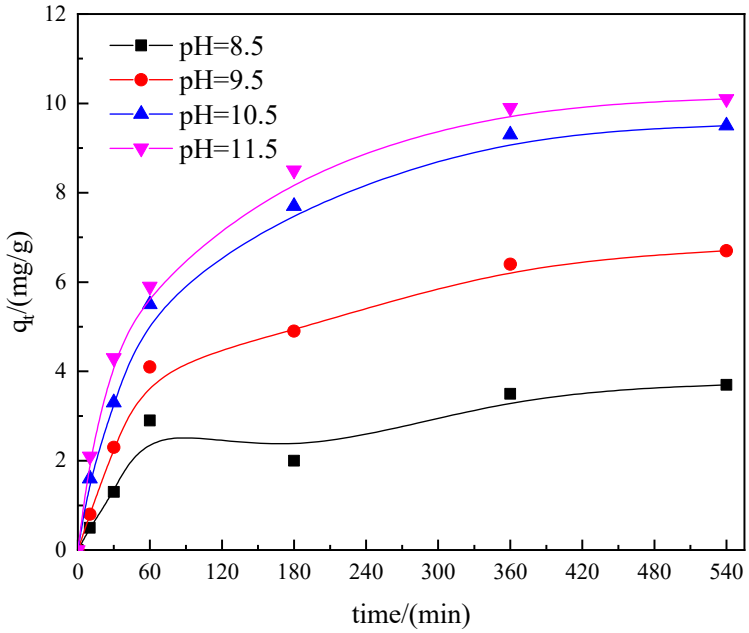


Figure 4. Effect of solution pH on gold adsorption performance (initial Au 30 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, 25 °C and 0.5 g resin).

3.3.2. Effect of Temperature

Figure 5 illustrates the effect of temperature from 25 °C to 70 °C on the gold adsorption performance. In the first 60 min, the capacity of gold adsorption onto resins increases with increasing temperature. However, when the adsorption time exceeds 60 min, the adsorbed gold in the resins gradually increases until 540 min with the temperature at 25 and 40 °C but rises just a little more and reaches a plateau with the temperature at 55 and 70 °C. This shows that the resin adsorption process of the gold thiosulfate complex is an endothermic process; however, high temperatures may accelerate the decomposition of thiosulfate. The sulfur-bearing species may competitively occupy the active site of the resin with gold, resulting in a decline in the adsorbed gold. This shows that the D201 resins also readily adsorb other undesirable anions, such as $S_3O_6^{2-}$, $S_4O_6^{2-}$, SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-}, and consequently show poor selectivity for the $Au(S_2O_3)_2^{3-}$ complex [19]. The gold adsorption capacity toward the resins was 9.9, 10.6, 8.2, and 7.6 mg/g following 360 min adsorption when the temperature was 25, 40, 55, and 70 °C, respectively. The presence of these competitive anions will greatly decrease the gold loading capacity of the resins.

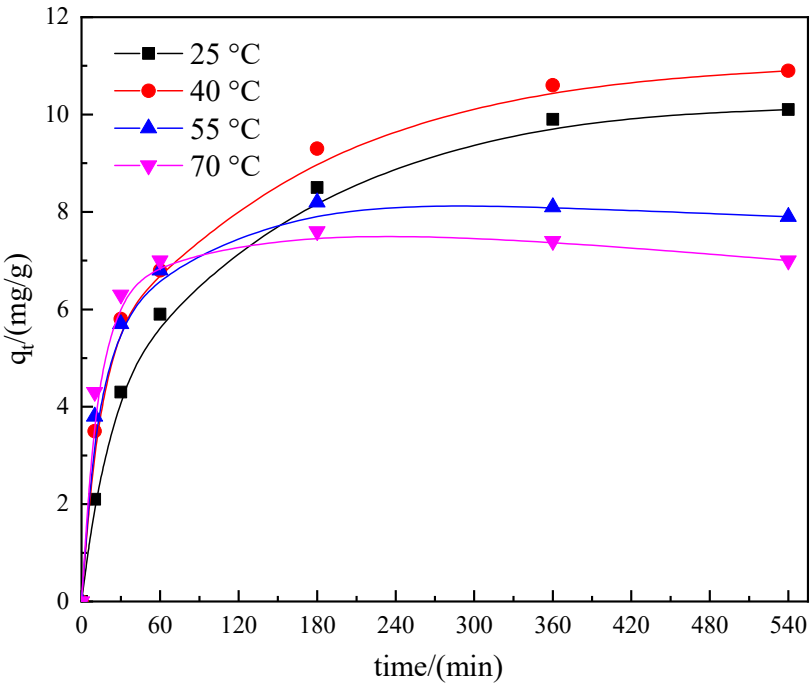


Figure 5. Effect of temperature on gold adsorption performance (initial Au 30 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, pH = 11.5 and 0.5 g resin).

3.3.3. Effect of Copper Concentration

Copper ions play a key role in accelerating the gold dissolution process, and there is inevitably a higher copper ion concentration than that of gold in the solutions [3]. Thus, it is necessary to consider the effect of copper ions on the gold adsorption performance, and the results are shown in Figure 6. The gold adsorption capacity on the resins increases with an increase in adsorption time and then attains a steady state but significantly decreases with an increasing copper concentration in the range from 0.001 mol/L to 0.200 mol/L. Copper ions can also oxidize thiosulfate to tetrathionate ($S_4O_6^{2-}$), which may further oxidize to $S_3O_6^{2-}$, SO_3^{2-} and SO_4^{2-}, as shown in Equations (4)–(7). Meanwhile, copper ions will be reduced to cuprous ions, and the $Cu(S_2O_3)_3^{5-}$ complex is the dominant form of cuprous ions. The adsorption capacity of the resins toward the gold thiosulfate complex reached 13.9, 11.8, 9.9, and 5.4 mg/g following 360 min of adsorption when the initial copper concentration was 0.001, 0.010, 0.050, and 0.200 mol/L, respectively.

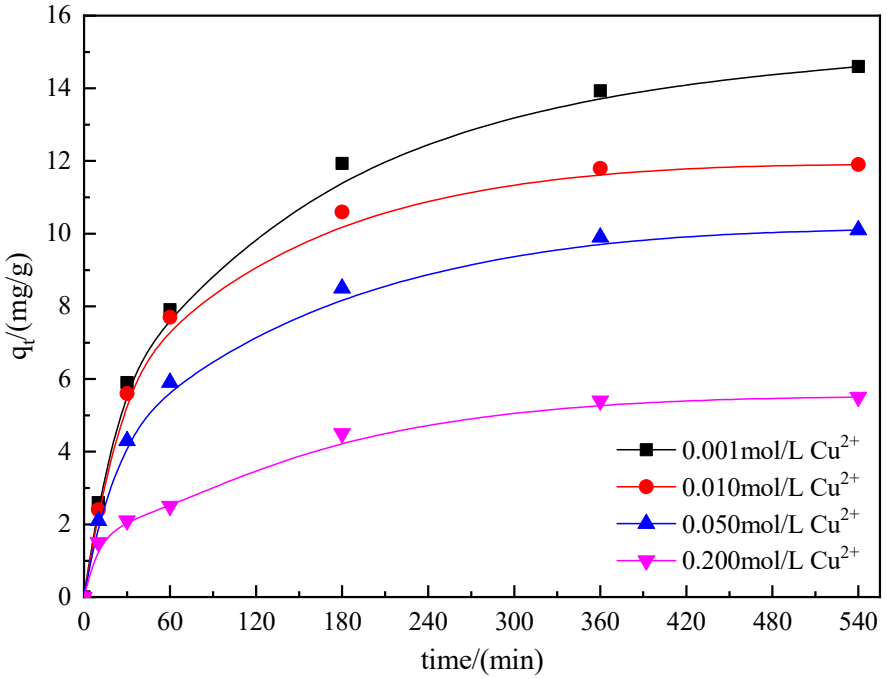


Figure 6. Effect of copper concentration on gold adsorption performance (initial Au 30 mg/L, 0.3 mol/L $S_2O_3^{2-}$, 0.1 mol/L L^{2-}, pH = 11.5, 25 °C and 0.5 g resin).

Probably, the copper- or sulfur-bearing species may competitively occupy the active sites on the surface of the resin, resulting in a reduction in the gold adsorption capacity. In addition, although the affinity of the resin for the $Cu(S_2O_3)_3^{5-}$ anion is weaker than that for the $Au(S_2O_3)_2^{3-}$ anion, the concentration of the $Cu(S_2O_3)_3^{5-}$ anion is much higher than that of the $Au(S_2O_3)_2^{3-}$ anion in copper–tartrate–thiosulfate solutions [19]. As a result, the simultaneous loading of a considerable amount of copper with gold on the resins has become one of the primary factors affecting gold recovery from pregnant thiosulfate solutions.

$$2Cu^{2+} + 8S_2O_3^{2-} = 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} \quad (4)$$

$$4S_4O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (5)$$

$$2S_3O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (6)$$

$$S_2O_3^{2-} + 2OH^- = SO_4^{2-} + S^{2-} + H_2O \quad (7)$$

3.3.4. Effect of Thiosulfate Concentration

Thiosulfate is the only complexing agent for aurous ions, which provides the driving force for gold dissolution in copper–tartrate–thiosulfate solutions [26]. Figure 7 illustrates the effect of thiosulfate concentration on gold adsorption performance. The rate of resin adsorption toward the gold thiosulfate complex is very fast in the first 60 min and then slightly increases with prolonged adsorption time. Increasing the thiosulfate concentration provides the driving force for gold leaching, thus accelerating the gold dissolution process [12]. However, excessive thiosulfate content may depress the gold adsorption process because thiosulfate ions can also competitively occupy the active sites on the surface of resin [3]. The equilibrium adsorption capacity of the resins toward the gold thiosulfate complex reached 10.5, 9.9, and 8.3 mg/g following 360 min of adsorption when the initial thiosulfate concentration was 0.1, 0.3, and 0.5 mol/L, respectively. These results indicate that thiosulfate ions may have a great impact on the equilibrium loading of gold.

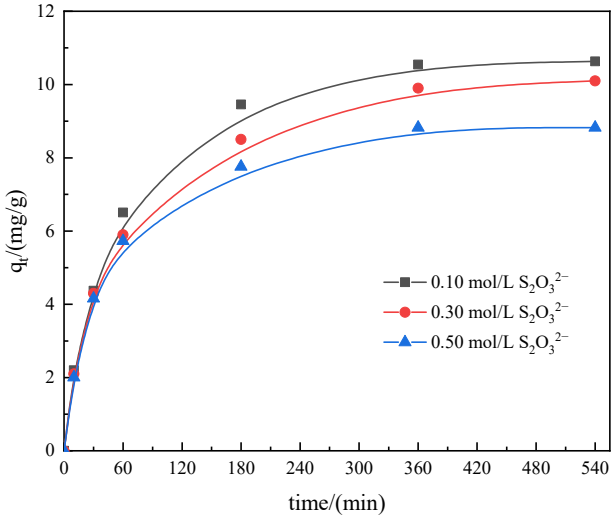


Figure 7. Effect of thiosulfate concentration on gold adsorption performance (initial Au 30 mg/L, 0.05 mol/L Cu^{2+}, 0.1 mol/L L^{2-}, pH = 11.5, 25 °C and 0.5 g resin).

3.3.5. Effect of Tartrate Concentration

Tartrate does not participate in the gold dissolution process directly but works as a copper ligand to prevent copper precipitation in alkaline media [26]. Figure 8 shows the effect of tartrate concentration on gold adsorption performance. The adsorption capacity of the resins toward the gold thiosulfate complex was 8.1, 9.9, 11.1, and 9.0 mg/g following 360 min of adsorption when the initial tartrate concentration was 0.05, 0.1, 0.2, and 0.4 mol/L, respectively. A moderate increase in tartrate concentration is beneficial for the gold adsorption, but excessive tartrate depresses the adsorption process. Increasing the tartrate concentration can effectively complex with copper ions (Equation (8)) and then eliminate the occurrence of side reactions and cause a reduction in sulfur-bearing species content. Therefore, the effect of decomposition products on the adsorption of gold thiosulfates with resin can be obviously reduced. However, excessive tartrate may competitively occupy the active sites on the surface of the resin, leading to a reduction in the gold adsorption capacity.

$$Cu^{2+} + 2L^{2-} + 4OH^- = CuL_2H_{-4}^{6-} + 4H_2O \quad (8)$$

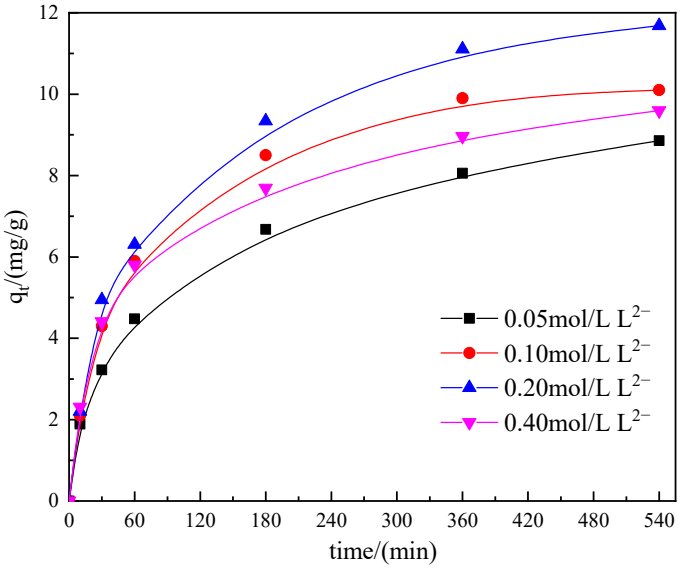


Figure 8. Effect of tartrate concentration on gold adsorption performance (initial Au 30 mg/L, 0.05 mol/L Cu^{2+}, 0.3 mol/L $S_2O_3^{2-}$, pH = 11.5, 25 °C and 0.5 g resin).

3.4. Characterization of the Resin

3.4.1. FT-IR Analysis

Figure 9 shows the FT-IR analysis of the resin. The peaks at approximately 1490 cm^{-1}, 1631.5 cm^{-1}, 2920 cm^{-1}, and 3246 cm^{-1} were related to the benzene ring skeleton, C=C, -CH_2, and N-H stretching vibrations, respectively. Some new infrared peaks were present in the resin at 1230 cm^{-1}, 1116 cm^{-1}, and 1015 cm^{-1}, which belonged to the sulfonic acid S=O asymmetric stretching peak, sulfonic acid S=O symmetric stretching peak, and sulfonate S=O symmetric stretching peak. This shows that the functional groups of the D201 resin and thiosulfate or sulfate in the solutions may have a chemical reaction to generate a new sulfonate functional group.

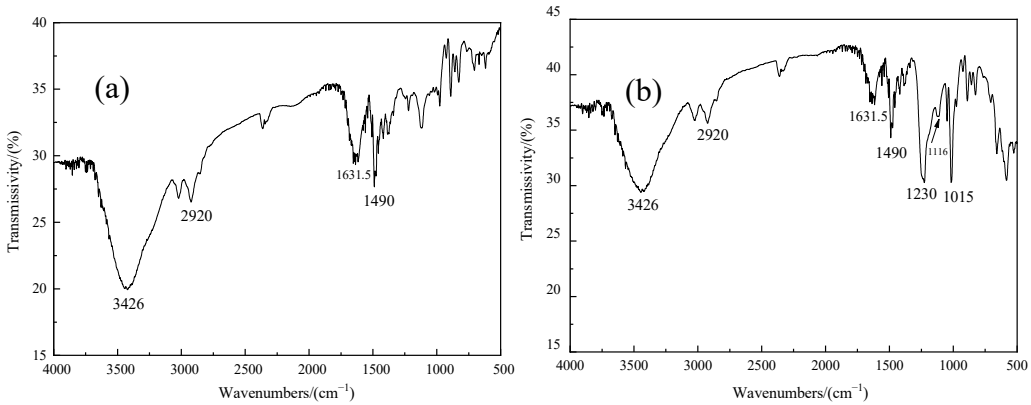


Figure 9. FT-IR spectra of the resin (**a**) before adsorption and (**b**) after adsorption (initial Au 30 mg/L, 0.05 mol/L Cu^{2+}, 0.20 mol/L L^{2-}, 0.3 mol/L $S_2O_3^{2-}$, pH = 11.5, 25 °C and 0.5 g resin).

3.4.2. XPS Analysis

Figure 10a illustrates the full XPS spectra of the resin. New peaks of Cu 2p, Au 4f, and S 2p were present on the resin surface after adsorption. It is noted that the peaks of Cu^{2+} 2p1/2 and Cu^{+} 2p1/2, and Cu^{2+} 2p3/2 and Cu^{+} 2p3/2 are very close; therefore, it is difficult to distinguish Cu^{2+} from Cu^{+} directly by the binding energy of Cu 2p peaks. Severino et al. [27] studied the locations of different binding energies of Cu^{2+}, Cu^{+}, and Cu^{0} under X-ray photoelectron spectroscopy, and their results showed that the characteristic satellite peak of Cu^{2+} 2p was in the range of binding energies from 938 eV to 945 eV. However, no obvious characteristic peak of divalent copper was observed (Figure 10b). Moreover, Hayez et al. [28] proposed that the Cu^{2+}, Cu^{+}, and Cu^{0} peaks can be distinguished by satellite peaks of Cu 2p presented in the range of 940 eV to 945 eV. Thus, it proves that Cu mainly exists in the form of Cu^{+} on the resin [21]. Figure 10c shows that there are two obvious peaks at binding energies of 88.29 eV and 84.55 eV. According to the analysis results of Deutsch et al., [29] the photoelectron peaks at the 4f 5/2 and 4f 7/2 levels of Au^{+} correspond to binding energies of 88 eV and 84 eV, respectively. Therefore, it is proven that Au exists in the form of Au^{+} on the resin surface. The peaks of S 2p appear at 167.7–168.9 eV and 162.9–164.2 eV, which are likely derived from SO_4^{2-} and $S_2O_3^{2-}$ [30]. The results show that sulfur mainly exists in the form of SO_4^{2-} and $S_2O_3^{2-}$ on the resin surface. The peaks of O 1 s shown in Figure 10e at approximately 532 eV, 531 eV, and 530 eV correspond to the electron binding energies of C-O-, C=O, and O^{2-}, respectively [31]. The O 1 s electron binding energy is between 531.5 eV and 533.6 eV, and its value depends on the type of organic groups and their chemical environment. Moreover, the peaks of C 1 s shown in Figure 10f at approximately 285 eV, 286 eV, and 287 eV correspond to the binding energy of C, C-O-, and C=O, which is consistent with the results of Terzyk et al. [32] These results indicate that oxygen- or carbon-containing groups in the resin have no significant change after adsorption.

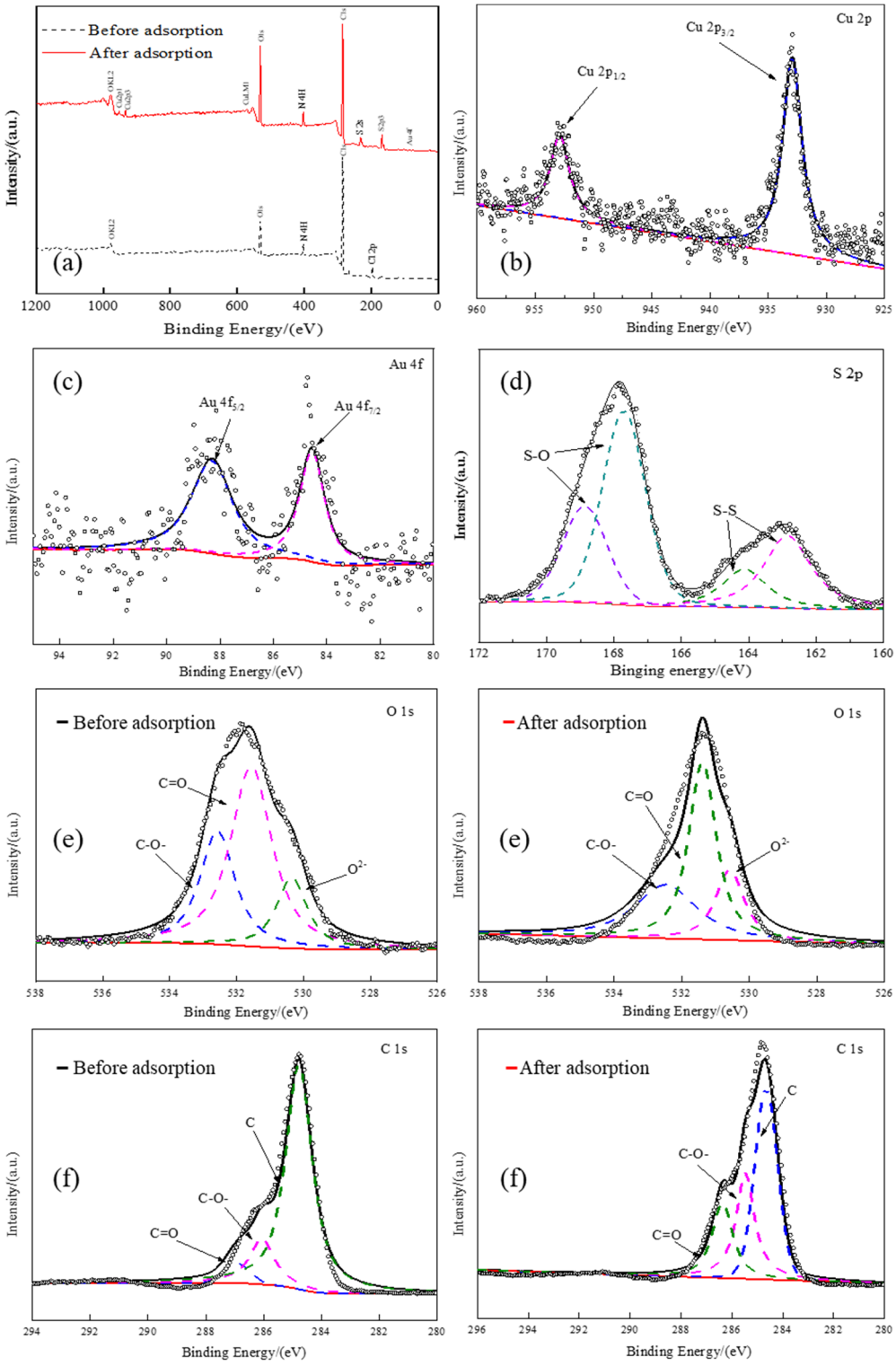


Figure 10. XPS spectra of (**a**) full spectrum, (**b**) Cu 2p, (**c**) Au 4f, (**d**) S 2 p, (e) O 1 s, and (**f**) C 1 s of the resin (initial Au 30 mg/L, 0.05 mol/L Cu^{2+}, 0.20 mol/L L^{2-}, 0.3 mol/L $S_2O_3^{2-}$, pH = 11.5, 25 °C and 0.5 g resin).

4. Conclusions

The adsorption behavior of gold from copper–tartrate–thiosulfate solutions with ion-exchange resins has been investigated in this paper. The main conclusions can be summarized as follows:

(1) The gold adsorption capacity with the D201 resin is much higher than that of the 717 and D301 resins under experimental conditions. A considerable gold adsorption capacity of 25.5 mg/g was achieved with an initial concentration of 100 mg/L gold at an initial pH of 11.5 and 25 °C following adsorption for 180 min.

(2) The adsorption kinetics of the gold thiosulfate complex onto D201 resin conform to the pseudo-second-order model, indicating that gold adsorption may belong to a chemical reaction process. Under the experimental conditions, a moderate increase in resin dosage, pH, temperature, and tartrate concentration is beneficial for gold adsorption, but excessive tartrate concentration or higher temperature depresses the adsorption process.

(3) XPS and FT-IR analyses indicate that copper and gold on the resin after adsorption mainly exist in the form of Cu^{+} and Au^{+}, and sulfur mainly exists in the form of SO_4^{2-} and $S_2O_3^{2-}$. Increasing the copper and thiosulfate concentrations may competitively occupy the active sites on the surface of the resin, leading to a reduction in the gold adsorption capacity.

(4) These results indicate that the use of ion-exchange resins for gold recovery with copper–tartrate–thiosulfate solutions may face critical challenges because there is inevitably a higher content of copper and thiosulfate.

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References

1. La Brooy, S.R.; Linge, H.G.; Walker, G.S. Review of gold extraction from ores. *Miner. Eng.* **1994**, *7*, 1213–1241. [CrossRef]
2. Hilson, G.; Monhemius, A.J. Alternatives to cyanide in the gold mining industry: What prospects for the future? *J. Clean. Prod.* **2006**, *14*, 1158–1167. [CrossRef]
3. Xie, F.; Chen, J.-N.; Wang, J.; Wang, W. Review of gold leaching in thiosulfate-based solutions. *Trans. Nonferrous Met. Soc. China* **2021**, *31*, 3506–3529. [CrossRef]
4. Liu, Z.-W.; Guo, X.-Y.; Tian, Q.-H.; Zhang, L. A systematic review of gold extraction: Fundamentals, advancements, and challenges toward alternative lixiviants. *J. Hazard. Mater.* **2022**, *440*, 129778. [CrossRef]
5. Aylmore, M.G. Alternative Lixiviants to Cyanide for Leaching Gold Ores. In *Gold Ore Processing*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 447–484. [CrossRef]
6. Molleman, E.; Dreisinger, D. The treatment of copper–gold ores by ammonium thiosulfate leaching. *Hydrometallurgy* **2002**, *66*, 1–21. [CrossRef]
7. Xu, B.; Yang, Y.B.; Li, Q.; Jiang, T.; Liu, S.Q.; Li, G.H. The development of an environmentally friendly leaching process of a high C, As and Sb bearing sulfide gold concentrate. *Miner. Eng.* **2016**, *89*, 138–147. [CrossRef]
8. Abbruzzese, C.; Fornari, P.; Massidda, R.; Vegliò, F.; Ubaldini, S. Thiosulphate leaching for gold hydrometallurgy. *Hydrometallurgy* **1995**, *39*, 265–276. [CrossRef]
9. Liu, X.; Jiang, T.; Xu, B.; Zhang, Y.; Li, Q.; Yang, Y.; He, Y. Thiosulphate leaching of gold in the Cu–NH_3–$S_2O_3^{2-}$–H_2O system: An updated thermodynamic analysis using predominance area and species distribution diagrams. *Miner. Eng.* **2020**, *151*, 106336. [CrossRef]
10. Senanayake, G. Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulfate oxidation by ammoniacal copper(II) solutions. *Hydrometallurgy* **2004**, *75*, 55–75. [CrossRef]
11. Breuer, P.L.; Jeffrey, M. An electrochemical study of gold leaching in thiosulfate solutions containing copper and ammonia. *Hydrometallurgy* **2002**, *65*, 145–157. [CrossRef]

12. Breuer, P.L.; Jeffrey, M. Thiosulfate leaching kinetics of gold in the presence of copper and ammonia. *Miner. Eng.* **2000**, *13*, 1071–1081. [CrossRef]
13. Gos, S.; Rubo, A. *The Relevance of Alternative Lixiviants with Regard to Technical Aspects, Work Safety and Environmental Safety*; Cyplus, Degussa AG: Hanau, Germany, 2001.
14. Wang, J.; Wang, R.; Pan, Y.; Liu, F.; Xu, Z. Thermodynamic analysis of gold leaching by copper-glycine-thiosulfate solutions using Eh-pH and species distribution diagrams. *Miner. Eng.* **2022**, *179*, 107438. [CrossRef]
15. Wang, J.; Xie, F.; Pan, Y.; Wang, W. Leaching of Gold with Copper-citrate-thiosulfate Solutions. *Miner. Process. Extr. Met. Rev.* **2021**, *43*, 916–925. [CrossRef]
16. Chen, J.N.; Xie, F.; Wang, W.; Fu, Y.; Wang, J. Leaching of Gold and Silver from a Complex Sulfide Concentrate in Copper-Tartrate-Thiosulfate Solutions. *Metals* **2022**, *12*, 1152. [CrossRef]
17. Chen, J.N.; Xie, F.; Wang, W.; Fu, Y.; Wang, J. Leaching of a carbonaceous gold concentrate in copper-tartrate-thiosulfate solutions. *Miner. Eng.* **2022**, *183*, 107605. [CrossRef]
18. Wang, J.; Xie, F.; Wang, W.; Bai, Y.L.; Fu, Y.; Dreisinger, D. Eco-friendly leaching of gold from a carbonaceous gold concentrate in copper-citrate-thiosulfate solutions. *Hydrometallurgy* **2020**, *191*, 105204. [CrossRef]
19. Dong, Z.L.; Jiang, T.; Xu, B.; Yang, Y.B.; Li, Q. Recovery of Gold from Pregnant Thiosulfate Solutions by the Resin Adsorption Technique. *Metals* **2017**, *7*, 555. [CrossRef]
20. Grosse, A.C.; Dicinoski, G.W.; Shaw, M.J.; Haddad, P.R. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* **2003**, *69*, 1–21. [CrossRef]
21. Zhang, Y.; Xu, B.; Zheng, Y.Q.; Li, Q.; Yang, Y.B.; Liu, X.L.; Jiang, T.; Lyu, X.J. Hexaamminecobalt(III) catalyzed thiosulfate leaching of gold from a concentrate calcine and gold recovery from its pregnant leach solution via resin adsorption. *Miner. Eng.* **2021**, *171*, 107079. [CrossRef]
22. Zhang, H.G.; Dreisinger, D.B. The recovery of gold from ammoniacal thiosulfate solutions containing copper using ion exchange resin columns. *Hydrometallurgy* **2004**, *72*, 225–234. [CrossRef]
23. Arima, H.; Fujita, T.; Yen, W.-T. Gold Recovery from Nickel Catalyzed Ammonium Thiosulfate Solution by Strongly Basic Anion Exchange Resin. *Mater. Trans.* **2003**, *44*, 2099–2107. [CrossRef]
24. Xu, B.; Li, K.; Li, Q.; Yang, Y.; Liu, X.; Jiang, T. Kinetic studies of gold leaching from a gold concentrate calcine by thiosulfate with cobalt-ammonia catalysis and gold recovery by resin adsorption from its pregnant solution. *Sep. Purif. Technol.* **2019**, *213*, 368–377. [CrossRef]
25. Chen, Y.; Zi, F.; Hu, X.; Lin, Y.; Du, H.; Hu, J.; Yang, P.; Zhang, Y.; Yang, B. The first effective utilization of activated carbon in gold thiosulfate system: A more eco-friendly, easier method for gold recovery and material regeneration. *Miner. Eng.* **2020**, *155*, 106441. [CrossRef]
26. Chen, J.N.; Xie, F.; Wang, W.; Fu, Y.; Wang, J. Leaching of Gold with Copper–Tartrate–Thiosulfate Solutions. *Trans. Indian Inst. Met.* **2023**, 1–8. [CrossRef]
27. Severino, F.; Brito, L.J.; Laine, J.; Fierro, J.L.G.; Agudo, A.L. Nature of Copper Active Sites in the Carbon Monoxide Oxidation on CuAl2O4and CuCr2O4Spinel Type Catalysts. *J. Catal.* **1998**, *177*, 82–95. [CrossRef]
28. Hayez, V.; Franquet, A.; Hubin, A.; Terryn, H. XPS study of the atmospheric corrosion of copper alloys of archaeological interest. *Surf. Interface Anal.* **2004**, *36*, 876–879. [CrossRef]
29. Deutsch, K.L.; Shanks, B.H. Active species of copper chromite catalyst in C–O hydrogenolysis of 5-methylfurfuryl alcohol. *J. Catal.* **2012**, *285*, 235–241. [CrossRef]
30. Turner, N.H.; Murday, J.S.; Ramaker, D.E. Quantitative determination of surface composition of sulfur bearing anion mixtures by Auger electron spectroscopy. *J. Vac. Sci. Technol. A.* **1980**, *17*, 84–92. [CrossRef]
31. Lindberg, B.J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. Molecular Spectroscopy by Means of ESCA II. Sulfur compounds. Correlation of electron binding energy with structure. *J. Electron. Spectrosc.* **1970**, *1*, 286. [CrossRef]
32. Terzyk, A.P. The influence of activated carbon surface chemical composition on the adsorption of acetaminophen (paracetamol) in vitro: Part II. TG, FTIR, and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the neutral pH. *Colloids Surf. A* **2001**, *177*, 23–45. [CrossRef]

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