

## Article

# A Kinetic Study on Enhanced Cementation of Gold Ions by Galvanic Interactions between Aluminum (Al) as an Electron Donor and Activated Carbon (AC) as an Electron Mediator in Ammonium Thiosulfate System

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**Abstract:** The enhanced cementation technique by galvanic interaction of aluminum (Al; electron donor) and activated carbon (AC; electron mediator) to recover gold (Au) ions from the ammonium thiosulfate solution is a promising technique to eliminate the challenges of poor recovery in the system. This study presents the kinetics of Au ion cementation in an ammonium thiosulfate lixiviant as functions of initial Au concentration, size/amount of Al and AC, temperature, and shaking speed. The recovery results basically followed first order kinetics and showed that the cementation rate increased with a higher initial concentration of Au, smaller electron donor size, greater both electron donor and mediator quantity, decrease in temperature, and higher shaking speed in the system, while size of electron mediator did not significantly affect Au recovery.

**Keywords:** gold; cementation; galvanic interaction; aluminum; activated carbon; kinetics; ammonium thiosulfate solution; mass transfer



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## 1. Introduction

Climate change is an urgent global issue affecting industries and communities alike. To reduce greenhouse gas emissions for achieving a climate-neutral world, countries worldwide aim to fulfill a Paris Agreement aligned to a target of transitioning to low/zero-carbon energy sources by promoting next-generation vehicles and developing mobility business by the mid-century [1,2]. For the initiatives towards decarbonization, mineral resources/metallurgy fields try to strengthen the exposure to precious metals for supporting electric/hydrogen vehicles, especially gold (Au).

In Au-hydrometallurgy, copper (Cu)-catalyzed ammonium thiosulfate leaching has gained increasing attention as an alternative to the conventional cyanide solvent due to its non-toxicity, low corrosiveness, and high selectivity for Au [3–5]. Although the leaching in this eco-friendly solvent, ammonium thiosulfate, is well established [6–9], the system is, however, commercially underdeveloped so far, because there are few acceptable methods to recover Au ions from the pregnant solutions. The adsorption of Au ions onto activated carbon (AC) has been the mainstay of Au-hydrometallurgy for several decades in cyanide-based lixiviants due to its high efficiency, relatively low cost, and high purity of the products [10]; however, its application is not preferred in the ammonium thiosulfate system. Gallagher with co-authors reported that the effectiveness of AC in adsorbing Au ions from aqueous solutions decreases in the following ligand order:

$\text{SCN}^- > \text{SC}(\text{NH}_2)_2 > \text{CN}^- \gg \text{S}_2\text{O}_3^{2-}$ , indicating that the Au thiosulfate complex does not effectively adsorb onto AC [11], hence the carbon-in-pulp (CIP) or carbon-in-leach (CIL) is not properly applicable to the thiosulfate system. Cementation (i.e., reductive precipitation), a conventional recovery process whereby Au ions are reduced to metallic Au via electron transfer, can be employed by using zero-valent base metals (i.e., cementing agents). Zero-valent copper, zinc (ZVZn), aluminum (Al), and iron (ZVI) are reasonable choices in cyanide-based lixiviants [10,12–14] but their application to thiosulfate solution is difficult because of the dissolution of the cementing agents (i.e., Cu and Zn) or the formation of the oxide/sulfide layers on the cementing agents (i.e., Al and Fe). The abundant sulfur and Cu ions in the solution also restrict the application of solvent extraction and electrowinning as well due to the contamination of the products and the increased energy requirements [10].

A previous study of the authors developed a new recovery technique, which uses the galvanic interactions between Al as an electron donor and AC as an electron mediator to the Au thiosulfate complex [15]. The results showed that when only Al or AC was employed to recover Au ions from the ammonium thiosulfate solution, the recovery of Au in that system was negligible. On the other hand, when both Al and AC were employed in the recovery process, over 99% of Au ions could be recovered under the following conditions [15]: 0.15 g Al and 0.15 g of AC with a solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_4\text{OH}$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  (pH between 9.5–10) with 100 mg/L of Au ions at 25 °C for 24 h with oxygen condition. Although the possibility of Au ion recovery from the ammonium thiosulfate medium by this simple and highly efficient technique is well established, the kinetics considering the various parameters that affect Au ion recovery (i.e., initial Au concentration, size and amount ratio of Al and AC, temperature, and shaking speed) have not been studied to date. Furthermore, there are many kinetic studies on cementation of Au ions by a single cementation agent (e.g., Al, Zn, Cu or Fe) in an ammonium thiosulfate system [16,17], whereas there remains some uncertainty regarding the cementation of Au ions enhanced by galvanic interaction between two materials. A better understanding of the Al and AC galvanic interaction on recovery of Au ions is essential before its application to industrial mining, and this will lead to better design on an industrial scale for Au mining employing ammonium thiosulfate solvent as an eco-friendly solution.

To this end, the present study investigated the kinetics of enhanced Au ions cementation by galvanic interaction between Al and AC in ammonium thiosulfate lixiviant with batch-type experiments as functions of initial Au concentration, size of Al and AC particles, their mixing ratio, and temperature as well as shaking speed, and a morphology study on the cemented Au was also carried out.

## 2. Materials and Methods

The ammonium thiosulfate solutions containing Au ions (i.e., Au-ammonium thiosulfate solution) were prepared by dissolving Au powder (99.999%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) in ammonium thiosulfate solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  (pH between 9.5 and 10) by a thermostat water bath shaker at 25 °C for 24 h with constant shaking amplitude and frequency of 40 mm and 120  $\text{min}^{-1}$ , respectively.

The recovery of Au ions was carried out using a mixture of Au-ammonium thiosulfate solution and Al (99.99%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) with AC (99.99%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) in 50-mL Erlenmeyer flasks at 25 °C for 1 h under the nitrogen purging condition at thermostat water bath shaker (shaking amplitude of 40 mm and frequency of 120  $\text{min}^{-1}$ ). Subsequently, the filtrate and the residue were separated, the latter was washed with deionized (DI) water (18  $\text{M}\Omega\cdot\text{cm}$ , Mill-Q<sup>®</sup> Integral Water Purification System, Merck Millipore, Burlington, MA, USA), dried in a vacuum oven at 40 °C for 24 h, and analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, Superscan SSX-550, Shimadzu Corporation,

Kyoto, Japan). The filtrate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan) (margin of error =  $\pm 2\%$ ).

### 3. Results and Discussion

#### 3.1. Recovery of Au Ions with Varying Initial Gold Concentrations

The cementation of Au ions from the ammonium thiosulfate solution with varying initial concentrations of Au (i.e., 1, 10, 50, 100 mg/L) was examined using the Al/AC mixture. The standard conditions were as follows: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  (pH between 9.5 and 10) with 100, 50, 10, or 1 mg/L of Au, and 0.3 g mixture (0.15 g Al ( $-45 \mu\text{m}$ ) + 0.15 g AC ( $-45 \mu\text{m}$ )) at 25 °C. In this recovery system, Al likely acted as the primary electron donor (i.e., anode) and the attached AC served as an electron mediator from Al to Au-thiosulfate complex ( $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ ), a configuration that promoted both galvanic interactions and Au recovery, cementation [15]. Generally, the cementation of Au ions has been found to obey first-order kinetics with the rate controlled by mass transfer of metal ions in the solution phase [14,16,18–20]. As reported in the previous study relating to the present system, Au was generally cemented on AC attached to Al and it exists with Cu in the same area (deposition order: Au-Cu-AC-Al), indicating that the cementation reaction rate is expected to be a function of the surface area of Al according to the following first-order expression:

$$\ln([\text{Au}]_t/[\text{Au}]_0) = -kAt/V, \quad (1)$$

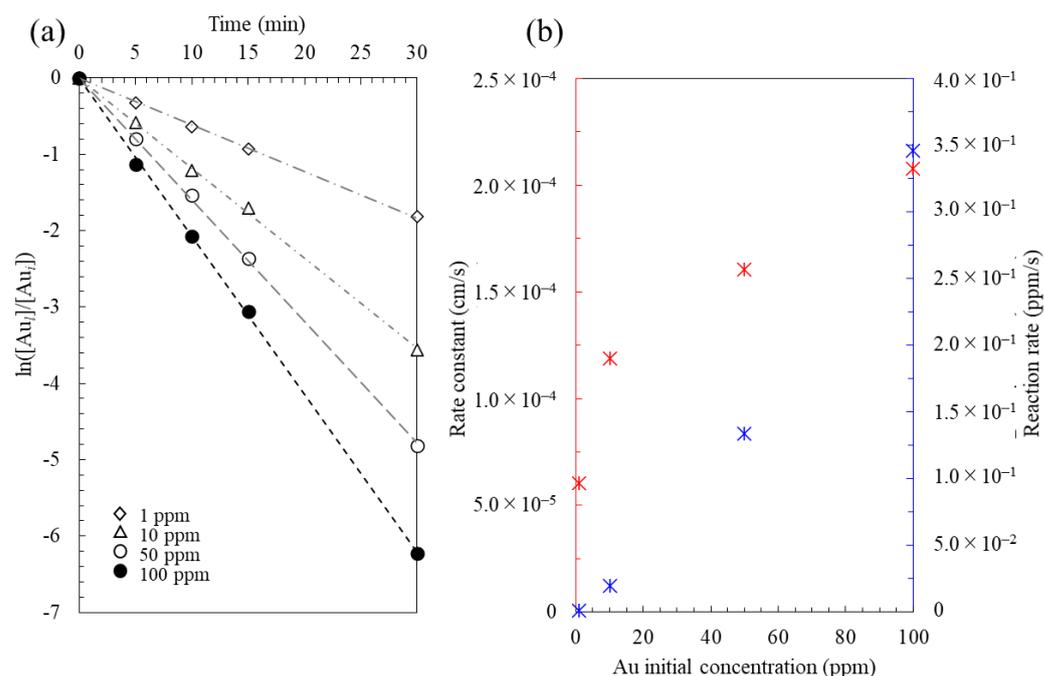
where  $[\text{Au}]_t$  is the Au concentration at time  $t$  (mg/L),  $[\text{Au}]_0$  is the initial Au concentration (mg/L),  $k$  is the rate constant (cm/s),  $A$  is initial surface area of substrate (electron donor: Al) ( $\text{cm}^2$ ),  $t$  is time (s), and  $V$  is a solution volume ( $\text{cm}^3$ ).

Figure 1a shows the variations for different initial Au concentrations in the solution with time, and the slope of  $\ln([\text{Au}]_t/[\text{Au}]_0)$  vs. time indicates the reaction constant. The results showed that, as many researchers have mentioned, the cementation of Au ions using single materials (e.g., Cu or Zn) followed first-order kinetics [16,20]. The Au cementation in the present system using galvanic interaction of Al and AC also obeyed first-order kinetics and showed 83.7% of the recovery at 30 min for 1 mg/L of initial Au concentration, while the recovery reached up to about 99.8% of the recovery at 30 min for 100 mg/L of initial Au concentration, indicating that the rate increases with increasing the initial concentration of Au ions in the solution. The reaction rates of Au cementation were in the following order: 100 mg/L > 50 mg/L > 10 mg/L > 1 mg/L of initial Au concentration.

To calculate the rate constant, the surface area of the substrate ( $A$ ) is required, which was calculated based on the following assumption: the shape of the Al is a sphere, and all the precipitates are present on Al. The calculated rate constants of Au ions cementation onto Al–AC are (cm/s):  $k_{100 \text{ mg/L}} = 2.08 \times 10^{-4}$ ,  $k_{50 \text{ mg/L}} = 1.61 \times 10^{-4}$ ,  $k_{10 \text{ mg/L}} = 1.19 \times 10^{-4}$ , and  $k_{1 \text{ mg/L}} = 6.05 \times 10^{-5}$  (Table 1), and the reaction rate also showed a positive correlation with initial Au concentration as shown in Figure 1a,b.

**Table 1.** Summary of rate constant for the cementation of Au onto the Al as a function of initial Au concentration (base conditions: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$ , and 0.3 g mixture (0.15 g Al ( $-45 \mu\text{m}$ ) and 0.15 g AC ( $-45 \mu\text{m}$ )) at 25 °C).

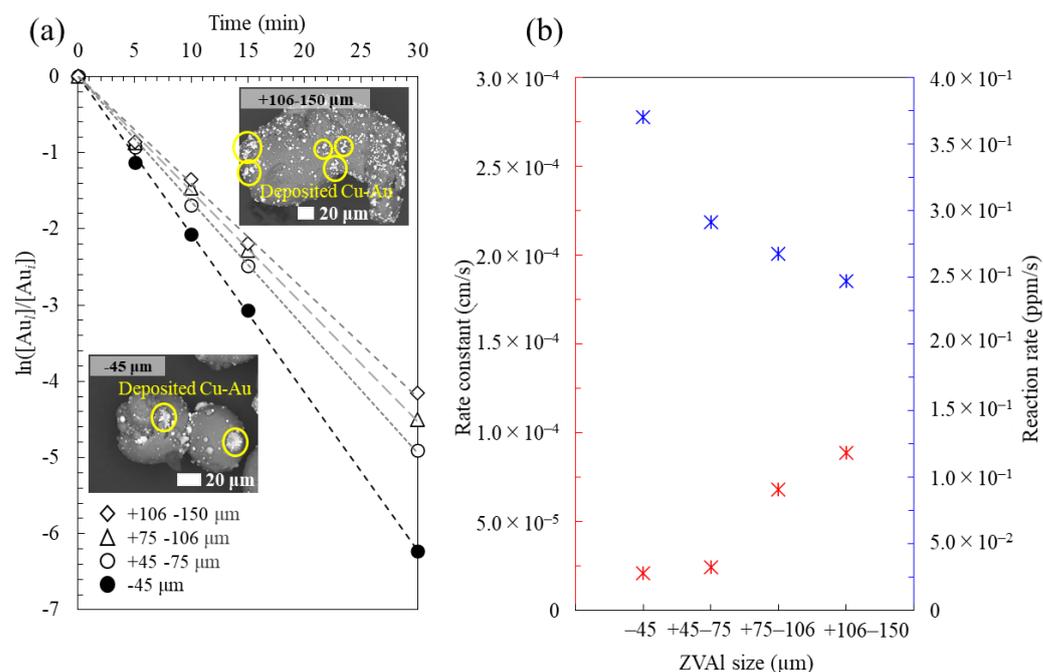
Initial Au Conc.	Al Area ( $\text{cm}^2$ )	Rate Constant (cm/s)	Reaction Rate (ppm/s)	$R^2$
1 ppm	166.7	$6.05 \times 10^{-5}$	$-1.08 \times 10^{-1}$	0.9996
10 ppm	166.7	$1.19 \times 10^{-4}$	$-2.11 \times 10^{-1}$	0.9997
50 ppm	166.7	$1.61 \times 10^{-4}$	$-2.87 \times 10^{-1}$	0.9997
100 ppm	166.7	$2.08 \times 10^{-4}$	$-3.70 \times 10^{-1}$	0.9998



**Figure 1.** (a) The effects of initial Au concentration on the recovery of Au ions, and (b) the plot of rate constant/reaction rate vs. initial Au concentration for the cementation reaction by galvanic interaction of Al and AC in the ammonium thiosulfate system (Note that reaction rate has a minus value).

### 3.2. Recovery of Au Ions with Varying Size of Al

Recovery of Au ions from ammonium thiosulfate solution using different sizes of the electron donor Al, and a constant size of AC was examined under the following conditions: 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  with 100 mg/L of Au, and 0.15 g of Al (size:  $-45$ ,  $+45-75$ ,  $+75-106$ ,  $+106-150$   $\mu\text{m}$ ) and 0.15 g of AC (size:  $-45$   $\mu\text{m}$ ) at 25 °C. The results are expected to be a function of the surface area of the Al according to the first order, as illustrated in Equation (1). The results evidently showed that the smaller the size of Al particles, the faster the reaction rate, indicating that the reaction rate was related to the surface area of electron donor, Al, for the electron transfer (Figure 2a,b). For the  $-45$   $\mu\text{m}$  size of Al powder, the reduction of Au ions onto the Al–AC obeys first-order kinetics, and  $\sim 99.8\%$  Au recovery was achieved for 30 min. As the range of Al particle size increased to  $+106-150$   $\mu\text{m}$ , the cementation reaction also obeyed first-order kinetics and had a recovery up to about 98.4%, which is slightly decreased compared to the result using the  $-45$   $\mu\text{m}$  size of Al. The rate constants ( $k$ ) with different sizes of Al, i.e.,  $-45$ ,  $+45-75$ ,  $+75-106$ ,  $+106-150$   $\mu\text{m}$ , were calculated to be  $2.08 \times 10^{-4}$ ,  $2.45 \times 10^{-4}$ ,  $6.82 \times 10^{-4}$ , and  $8.86 \times 10^{-4}$   $\text{cm}^{-1}\text{s}^{-1}$ , respectively (Table 2). As the Al particle size increased, the rate constant indicating the rate at which cementation occurs per unit area, also increased, while the total cementation rate decreased (Figure 2b). The results suggested that as the surface area of the electron donor increased, this could more readily transfer the electrons from the Al–AC to the Au-thiosulfate complex ( $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ ) in an ammonium thiosulfate medium, while the cementation reaction rate per unit area decreased. Similarly, Hiskey and Lee [16] performed Au cementation from a thiosulfate solution using a different size of cementing agent—copper powder (150  $\times$  200 and  $-200$  mesh)—and reported that as the particle size of the cementing agent increased, the cementation rate of Au ions decreased. The SEM-EDX results showed that particles located in an area brighter than the background (i.e., the surface of the Al) present Au and Cu [15], and the larger the surface area, the more Au was noticeably recovered onto the Al surface (inset, Figure 2a).



**Figure 2.** (a) The effects of Al particle size (i.e., –45, +45–75, +75–106, +106–150  $\mu\text{m}$ ) on recovery of Au ions with the SEM photomicrographs, and (b) the plot of rate constant/rate vs Al size for the cementation reaction by galvanic interaction of Al and AC in an ammonium thiosulfate system (Note that reaction rate has a minus value).

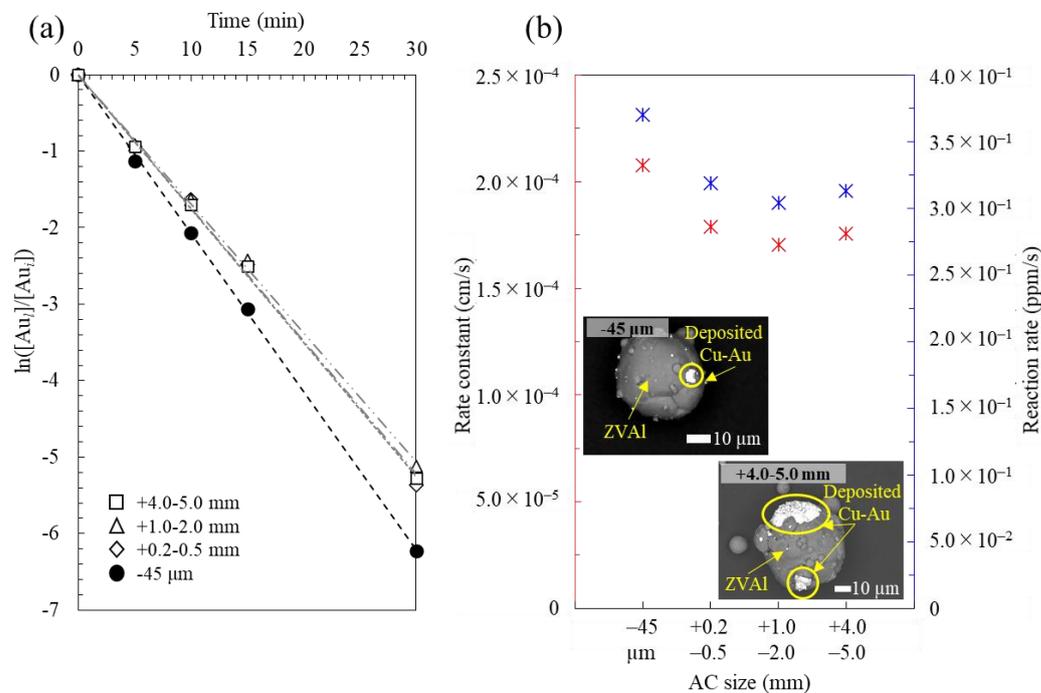
**Table 2.** Summary of rate constant for the cementation of Au onto the Cu-AC-Al as a function of electron donor (Al) size (base conditions: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$ , and 0.3 g mixture (0.15 g Al and 0.15 g AC (–45  $\mu\text{m}$ )) at 25  $^\circ\text{C}$ ).

Al Size	Al Area ( $\text{cm}^2$ )	Rate Constant (k, cm/s)	Reaction Rate (ppm/s)	$R^2$
–45 $\mu\text{m}$	166.7	$2.08 \times 10^{-4}$	$-3.70 \times 10^{-1}$	0.9998
+45–75 $\mu\text{m}$	111.1	$2.45 \times 10^{-4}$	$-2.92 \times 10^{-1}$	0.9996
+75–106 $\mu\text{m}$	36.63	$6.82 \times 10^{-4}$	$-2.68 \times 10^{-1}$	0.9994
+106–150 $\mu\text{m}$	26.04	$8.86 \times 10^{-4}$	$-2.47 \times 10^{-1}$	0.9985

### 3.3. Recovery of Au Ions with Varying Size of AC

Recovery of Au ions from an ammonium thiosulfate solution using different sizes of the electron mediator, AC, and a constant size of Al particles was examined under the following conditions: 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  with 100 mg/L of Au, and 0.15 g of Al (size: –45  $\mu\text{m}$ ) and 0.15 g of AC (size: –45  $\mu\text{m}$ , +0.2–0.5 mm, +1.0–2.0 mm, +4.0–5.0 mm) at 25  $^\circ\text{C}$ . The results continued to exhibit first-order kinetics and showed similar results to those of the previous section; that is, the cementation rate using the smallest particle size of AC (–45  $\mu\text{m}$ ) showed the fastest reaction rate (Figure 3). Although, as the particle size of AC was increased, the reaction rate seemed to be less responsive, indicating that the effects of electron mediator size are not so significant in the system. For the –45  $\mu\text{m}$  size of AC, the recovery showed up to about 99.8% at 30 min, while for the upper size ranges of AC, the recovery irregularly showed about 99.4–99.5%. This can be explained by the fact that once the activated carbon was added in the system, small AC particles (about 0.2–2  $\mu\text{m}$ ) detached from the original AC, became attached to the surface of Al [15], and acted as an electron mediator, making the original particle size of the AC not so important to the reaction rate. The residue

analysis results also showed that there are no significant differences between  $-45\ \mu\text{m}$  and  $+4.0-5.0\ \text{mm}$  size of AC. The calculated rate constants of Au ions cementation onto Al-AC are ( $\text{cm}\cdot\text{s}^{-1}$ ):  $k_{-45\ \mu\text{m}} = 2.08 \times 10^{-4}$ ,  $k_{+0.2-0.5\ \text{mm}} = 1.79 \times 10^{-4}$ ,  $k_{+1.0-2.0\ \text{mm}} = 1.71 \times 10^{-4}$ , and  $k_{+4.0-5.0\ \text{mm}} = 1.76 \times 10^{-4}$  (Table 3).



**Figure 3.** (a) The effects of AC size on the recovery of Au ions, and (b) the plot of rate constant/rate vs AC size for the cementation reaction by galvanic interaction of Al and AC in ammonium thiosulfate system (Note that reaction rate has a minus value).

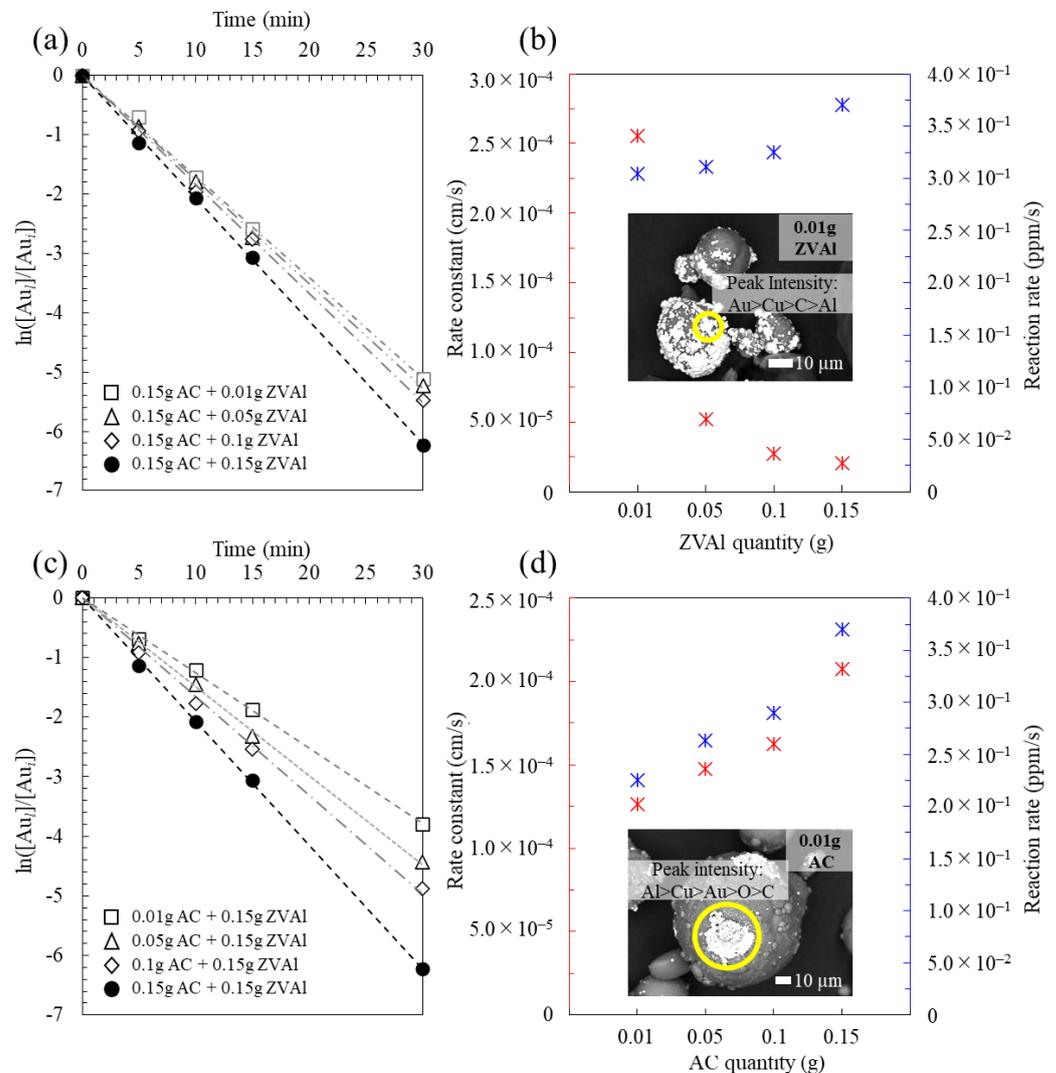
**Table 3.** Summary of rate constant for the cementation of Au onto the Cu-AC-Al as a function of AC size (base conditions: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$ , and 0.3 g mixture (0.15 g Al and 0.15 g AC) at  $25\ ^\circ\text{C}$ ).

AC Size	Al Area ( $\text{cm}^2$ )	Rate Constant ( $k$ , $\text{cm}\cdot\text{s}^{-1}$ )	Reaction Rate ( $\text{ppm}\cdot\text{s}^{-1}$ )	$R^2$
$-45\ \mu\text{m}$	166.7	$2.08 \times 10^{-4}$	$-3.67 \times 10^{-1}$	0.9998
$+0.2-0.5\ \text{mm}$	166.7	$1.79 \times 10^{-4}$	$-3.19 \times 10^{-1}$	0.9986
$+1.0-2.0\ \text{mm}$	166.7	$1.71 \times 10^{-4}$	$-3.04 \times 10^{-1}$	0.9993
$+4.0-5.0\ \text{mm}$	166.7	$1.76 \times 10^{-4}$	$-3.13 \times 10^{-1}$	0.9995

### 3.4. Recovery of Au Ions with Varying Quantity of Al and AC

Subsequently, the effects of Al quantity (0.01, 0.05, 0.1, 0.15 g) and AC quantity (0.01, 0.05, 0.1, 0.15 g) on the kinetics of Au ion cementation onto AC-Al are presented in Figure 4a-d under the following conditions: 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  with 100 mg/L of Au, and both  $-45\ \mu\text{m}$  particle size of Al and AC at  $25\ ^\circ\text{C}$ . As shown in Figure 4a,c, the Au cementation by galvanic interaction obeys first-order kinetics, and the quantity of Al and AC affects cementation of Au ions; especially, the cementation of Au ions rapidly increased even when only a small amount of Al was present together with AC in the system. For the mixture of 0.01 g AC and 0.15 g of Al (Figure 4c), the reduction of Au ions was about 97.8% recovery at 30 min, while for the mixture of 0.15 g AC and 0.01 g of Al (Figure 4a), the recovery showed about 99.4% at 30 min. Meanwhile, the maximum reduction of Au was achieved with 0.15 g Al and

0.15 g AC where 99.8% of Au was recovered. It can be explained by the fact that electron transfer is readily enabled when the electron donor quantity increases, leading to high Au recovery, and this suggests that the electron donor quantity is a more pronounced mediator in cementation of Au ions in this galvanic system



**Figure 4.** The effects of (a) Al and (b) AC quantity on recovery of Au ions, and the plot of rate constant/rate vs (c) Al and (d) AC quantity for the cementation reaction by galvanic interaction of Al and AC in an ammonium thiosulfate system (Note that reaction rate has a minus value).

The rate constant in the system for the different quantity of Al (i.e., 0.15 g AC + 0.01, 0.05, 0.1, or 0.15 g of Al) were calculated to be  $2.56 \times 10^{-4}$ ,  $5.22 \times 10^{-4}$ ,  $2.74 \times 10^{-4}$ , and  $2.08 \times 10^{-4}$   $\text{cm s}^{-1}$ , while for the different quantity of AC (i.e., 0.01, 0.05, 0.1, or 0.15 g of AC + 0.15 g of Al), the calculated rate constants were  $1.27 \times 10^{-4}$ ,  $1.48 \times 10^{-4}$ ,  $1.63 \times 10^{-4}$ , and  $2.08 \times 10^{-4}$   $\text{cm s}^{-1}$ , respectively (Table 4). The insets in Figure 4b,d are the back-scattered electron (BSE) photomicrographs of the residues obtained with 0.15 g AC + 0.01 g Al (inset, Figure 4b) and 0.01 g AC + 0.15 g Al (inset, Figure 4d) after 30 min cementation, respectively. The EDX point analysis of the residue with 0.15 g AC + 0.01 g Al (inset, Figure 4b) had strong signals of Au, Cu, AC and Al, while the residue with 0.01 g AC + 0.15 g Al (inset, Figure 4d) had Al and Cu as major signals and Au and C as minor signals, both of which were relatively lower than those observed at point in Figure 4b. This supports the aforementioned explanation of the momentous role of the electron donor in

creating a high and fast cementation rate for Au ions by the galvanic interactions between Al and AC in an ammonium thiosulfate system.

**Table 4.** Summary of rate constant for the cementation of Au onto the Cu-AC-Al as a function of Al and AC quantity (base conditions: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$ , and 0.3 g mixture (Al and AC) at 25 °C).

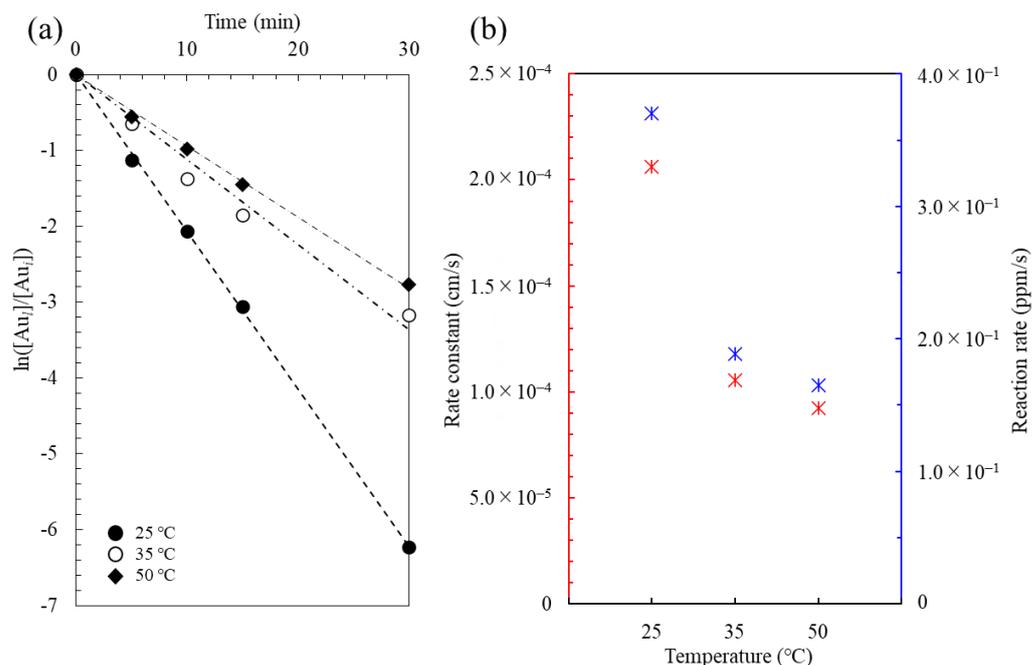
Al Quantity	Al Area (cm <sup>2</sup> )	Rate Constant (k, cm/s)	Reaction Rate (ppm/s)	R <sup>2</sup>
0.01 g	11.11	$2.56 \times 10^{-4}$	$-3.04 \times 10^{-1}$	0.9993
0.05 g	55.56	$5.22 \times 10^{-4}$	$-3.11 \times 10^{-1}$	0.9997
0.1 g	111.1	$2.74 \times 10^{-4}$	$-3.25 \times 10^{-1}$	0.9996
0.15 g	166.7	$2.08 \times 10^{-4}$	$-3.70 \times 10^{-1}$	0.9998
AC quantity	Al area (cm <sup>2</sup> )	Rate constant (k, cm/s)	Reaction rate (ppm/s)	R <sup>2</sup>
0.01 g	166.7	$1.27 \times 10^{-4}$	$-2.26 \times 10^{-1}$	0.9996
0.05 g	166.7	$1.48 \times 10^{-4}$	$-2.64 \times 10^{-1}$	0.9995
0.1 g	166.7	$1.63 \times 10^{-4}$	$-2.90 \times 10^{-1}$	0.9991
0.15 g	166.7	$2.08 \times 10^{-4}$	$-3.70 \times 10^{-1}$	0.9998

### 3.5. Recovery of Au Ions with Varying Temperature

The conditions of the recovery experiments under varying temperature were the same as the standard conditions as follows: 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$  with 100 mg/L of Au, and both  $-45 \mu\text{m}$  particle size of Al and AC. Figure 5 shows the effects of temperature on the kinetics at values ranging from 25 °C to 50 °C. The results obey first-order kinetics, and the rate were observed to decrease with increase in temperature under the current condition: For the reaction temperature at 25 °C, the reduction of Au ions was about 99.8%, while it showed 95.8% and 93.7% of the recovery at 35 °C and 50 °C, respectively. This is understandable for the following reasons: In general, cementation results show positive proportional increase with temperature [21]. The present cementation results by the galvanic interaction between Al and AC, however, showed that reaction rate decreased as temperature increased. This can be explained by the fact that there was an improved formation of the oxide layer on the aluminum surface [22]: Wahab et al. (2013) mentioned that the formation of the insulating film, i.e., oxyhydroxide layer on the surface of Al (electron donor) can be enhanced as the temperature increases, which contributes greatly to electrochemical reactions, i.e., cementation [22]. The rate constant in the system for different temperatures (i.e., 25, 35, and 50 °C) were calculated to be  $2.06 \times 10^{-4}$ ,  $1.06 \times 10^{-4}$ , and  $9.24 \times 10^{-5}$ , respectively (Table 5).

**Table 5.** Summary of rate constant for the cementation of Au as a function of temperature (base conditions: 10 mL solution containing 1 M of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.5 M of  $\text{NH}_3$ , 0.25 M of  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM of  $\text{CuSO}_4$ , and 0.3 g mixture (0.15 g Al and 0.15 g AC) at 25, 35, and 50 °C).

Temperature	Al Area (cm <sup>2</sup> )	Rate Constant (k, cm/s)	Reaction Rate (ppm/s)	R <sup>2</sup>
25 °C	166.7	$2.08 \times 10^{-4}$	$-3.67 \times 10^{-1}$	0.9998
35 °C	166.7	$1.06 \times 10^{-4}$	$-1.88 \times 10^{-1}$	0.9912
50 °C	166.7	$9.24 \times 10^{-5}$	$-1.65 \times 10^{-1}$	0.9987



**Figure 5.** (a) The effects of temperature on recovery of Au ions, and (b) the plot of rate constant/rate vs temperature for the cementation reaction by galvanic interaction of Al and AC in ammonium thiosulfate system (Note that reaction rate has a minus value).

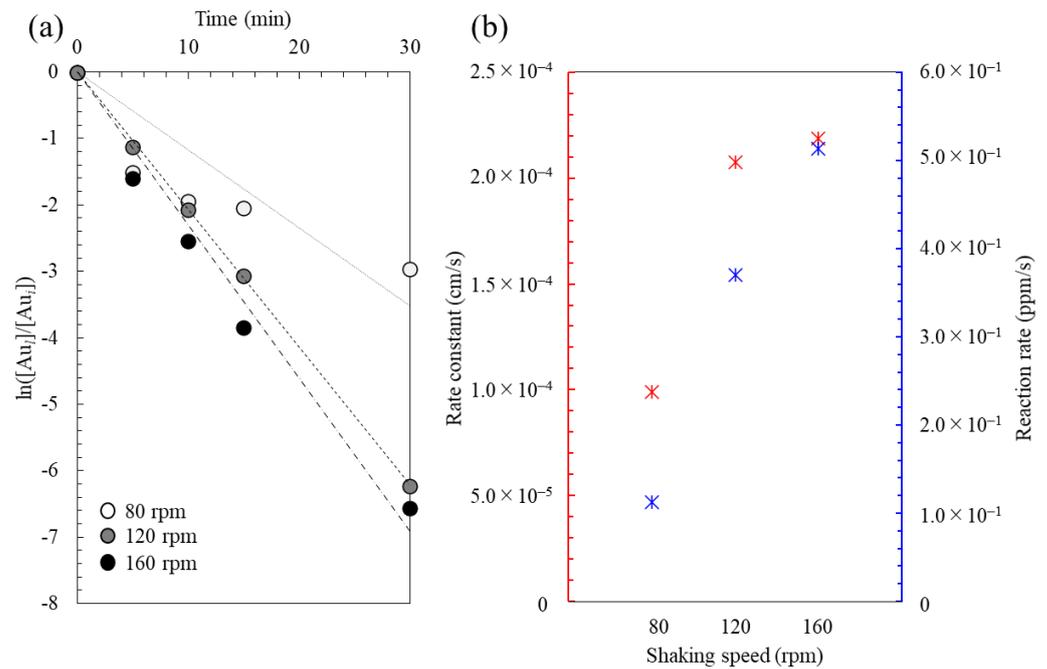
3.6. Recovery of Au Ions with Varying Shaking Speed

Kinetic results are presented in Figure 6 for  $\ln([Au]_t/[Au]_0)$  as a function of time for shaking speeds from 80 to 200 rpm. The basic experimental conditions were as follows: 1 M of  $Na_2S_2O_3$ , 0.5 M of  $NH_3$ , 0.25 M of  $(NH_4)_2SO_4$  and 10 mM of  $CuSO_4$  with 100 mg/L of Au, and 0.15 g of Al and AC (both sizes:  $-45 \mu m$ ) at 25 °C. The results also obeyed first-order kinetics, and the reaction rate increased as the shaking speed increased: the recovery results showed that about 94.9% of Au was recovered at 80 rpm for 30 min and it increased to 99.9% at 160 rpm. The rate constant (k) at 80, 120, and 160 rpm were calculated to be  $0.99 \times 10^{-4}$ ,  $2.08 \times 10^{-4}$ , and  $2.19 \times 10^{-4}$ , respectively (Table 6).

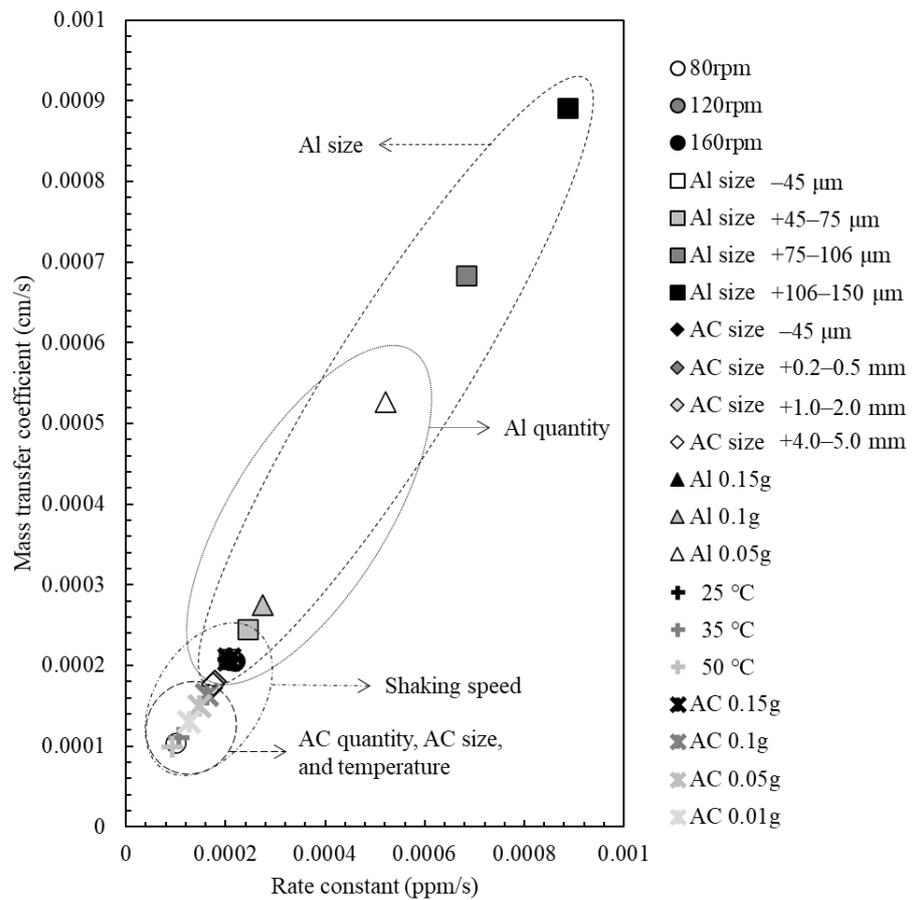
**Table 6.** Summary of rate constant for the cementation of Au as a function of shaking speed (base conditions: 10 mL solution containing 1 M of  $Na_2S_2O_3$ , 0.5 M of  $NH_3$ , 0.25 M of  $(NH_4)_2SO_4$  and 10 mM of  $CuSO_4$ , and 0.3 g mixture (0.15 g Al and 0.15 g AC) at 25 °C).

Shaking Speed	Al Area (cm <sup>2</sup> )	Rate Constant (k, cm/s)	Reaction Rate (ppm/s)	R <sup>2</sup>
80 rpm	166.7	$0.99 \times 10^{-4}$	$-1.13 \times 10^{-1}$	0.9035
120 rpm	166.7	$2.08 \times 10^{-4}$	$-3.67 \times 10^{-1}$	0.9998
160 rpm	166.7	$2.19 \times 10^{-4}$	$-5.14 \times 10^{-1}$	0.9919

Finally, the rate constant and mass transfer coefficient values based on the recovery results in the present study were plotted in Figure 7, and clearly showed a positive correlation, especially as a function of electron size, quantity, and shaking speed compared to the function of electron mediator size, quantity and temperature, which indicates that the reactions were controlled by mass transfer. Guerra and Dreisinger (1999) and Hiskey and Lee (2003) who researched the kinetic study of Au(I) thiosulfate complex were also concluded that the cementation reactions were controlled by mass transfer [6,16].



**Figure 6.** (a) The effects of shaking speed on recovery of Au ions, and (b) the plot of rate constant/rate vs shaking speed for the cementation reaction by galvanic interaction of Al and AC in ammonium thiosulfate system (Note that reaction rate has a minus value).



**Figure 7.** The plot of rate constant and mass transfer coefficient based on all recovery results in the present study.

#### 4. Conclusions

This study described the kinetics of enhanced cementation of Au ions by galvanic interaction between Al (i.e., electron donor) and AC (i.e., electron mediator) as functions of various parameters (i.e., initial Au concentration, Al and AC size, Al and AC quantity, temperature, and shaking speed) in an ammonium thiosulfate system. The results showed that the Au cementation by Al and AC basically followed first order kinetics, and the rate increased with an increase in initial Au concentration and Al/AC quantity, as well as a decrease in Al size (i.e., surface area  $\uparrow$ ), temperature, and shaking speed while AC size did not have significant effects on the reaction rate. These results could give a better understanding of the Au recovery technique using Al and AC before it is applied to industrial mining, and this will help to establish a better design on an industrial scale for Au mining employing an eco-friendly solution.

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