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ScienceDirect
Trans. Nonferrous Met. Soc. China 33(2023) 3210−3221
Transactions of Nonferrous Metals Society of China
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Adsorption mechanism of copper and gold thiosulfates onto activated carbon

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Received 30 April 2022; accepted 20 July 2022

Abstract: The adsorption mechanism of activated carbon toward copper and gold thiosulfate complexes was investigated. Both adsorption kinetics of copper and gold thiosulfate complexes onto activated carbon conform to the pseudo-second-order model. The adsorption isotherm of activated carbon toward the copper thiosulfate complex is in accordance with the Freundlich model, while that of the gold thiosulfate complex fits the Langmuir model. The bonding characteristics of the loaded carbon suggest that the adsorption mechanism of copper thiosulfate is different from that of gold thiosulfate. The adsorption capacity of the activated carbon toward copper reaches 79.04 mg/g under the experimental conditions, which is approximately two orders of magnitude higher than that of gold. This implies that the use of activated carbon for gold recovery from thiosulfate leachate may face great challenges due to the low adsorption capacity of gold, as well as the competitive adsorption of copper and thiosulfate.

Key words: activated carbon; adsorption; gold; copper; thiosulfate

1 Introduction

In recent years, researchers are trying to find an environmentally viable option to substitute the conventional cyanidation process, which is considered to be hazardous to the environment and public security [1]. Thiosulfate is believed to be the most promising alternative to cyanide due to its non-toxicity, relatively low cost and high leaching efficiency [2−4]. Gold leaching from ores or concentrates using copper−ammonia−thiosulfate solutions has been extensively investigated, and its mechanism has been well documented [5,6]. To overcome the potential environmental challenge of ammonia, some novel thiosulfate-based leaching systems, including using copper−citrate [7−9], copper−tartrate [10], copper−glycine [11], copper−EDTA [12], and copper−EDA [13,14] as the leaching catalyst, have been developed. Some additives, such as ammonium alcohol polyvinyl phosphate (AAPP), cetyltrimethyl ammonium bromide (CTAB), carboxymethyl cellulose (CMC), triethanolamine (TEA), humic acid (HA), sulfite, and sulfate, have also been tested in various thiosulfate solutions for leaching gold [15−18]. These studies have greatly promoted the development of gold−thiosulfate leaching processes.

However, limited studies have been carried out on gold recovery from thiosulfate leaching solutions [19,20]. It was reported that the aurous cyanide or aurous thiosulfate complex can be reduced to metallic gold using zinc, iron and copper as cementing agents [21,22]. There are also various

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DOI: 10.1016/S1003-6326(23)66328-9

studies on using ion resins for gold recovery from pregnant thiosulfate leaching solutions [23,24]. However, whether activated carbon can be used as an absorbent for gold recovery from thiosulfate solutions is still questionable. Some studies indicate that activated carbon is not a suitable choice due to its significantly low affinity for the aurous thiosulfate complex [25,26]. Researchers have attempted several modified activated carbons by adding thiol groups and impregnating 1-methyl-5-mercapto-1,2,3,4-tetrazole (MMT) or cupric ferrocyanide (CuFC) and have achieved some encouraging results [27−30]. A higher gold capacity and gold recovery can be obtained from the simulated thiosulfate leaching solutions. The results indicated that gold adsorption on the modified activated carbon may act via a ligand exchange mechanism. For untreated activated carbon, JIANG et al [31] used thiosemicarbazide (TSC) as an additive for gold recovery from pregnant thiosulfate solutions. A gold loading capacity of 42.6 kg/t can be achieved under the optimal conditions after five-stage adsorption, and a gold desorption performance of 95.3% with the N,N-dimethylformamide (DMF) desorbent was obtained following 24 h for carbon containing 5 kg/t gold.

However, because a significant amount of copper is usually used as the catalyst in the gold thiosulfate leaching system, it is inevitable that the pregnant leachate will contain a much higher content of copper than gold [7−10]. Thus, it is meaningful to examine the adsorption behavior of copper thiosulfates and to illustrate their potential influence on gold recovery from thiosulfate solutions. In this work, the adsorption behavior of copper and gold thiosulfate complexes onto activated carbon in aqueous solutions was comparatively studied. Various adsorption kinetics models were used to fit the adsorption process to illustrate the adsorption mechanism of copper and gold thiosulfates onto activated carbon. The potential challenge of using activated carbon for gold recovery from thiosulfate solutions is also discussed.

2 Experimental

2.1 Materials

Reagents of analytical grade, including sodium thiosulfate, sodium hydroxide, sulfuric acid, copper sulfate, and gold standard solutions all from Shanghai Chemical Sinopharm Reagent Co. Ltd. (SCRC), China, were used in the tests. The coconut shell activated carbon used in these adsorption tests was of analytical grade and obtained from SCRC, and its main physicochemical properties are listed in Table 1. Scanning electron microscopy (SEM) images show the microstructure of the activated carbon (Fig. 1). The activated carbon has a large specific surface area (500−1000 m^2/g) and clear grains.

Table 1 Some physicochemical properties of activated carbon

Parameter	Value
Specific surface area/($m^2 \cdot g^{-1}$)	500−1000
Particle size/mm	0.63−2.75
pH (50 g/L, 25 °C)	5.0−7.0

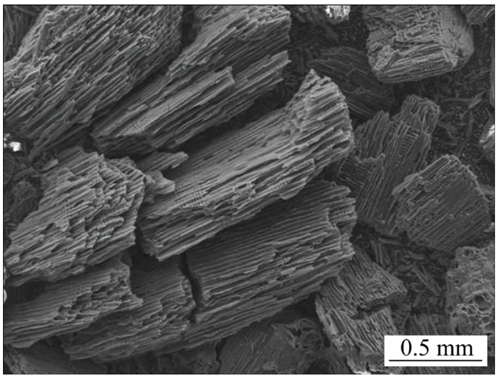


Fig. 1 Microstructure of activated carbon

2.2 Methods

The copper thiosulfate solutions were prepared by mixing suitable amounts of $CuSO_4$ and $Na_2S_2O_3$ in deionized water, and NaOH/H_2SO_4 was used for pH control. Thiosulfate is readily oxidized by copper ions to form the cuprous thiosulfate complex and tetrathionate:

$$2Cu^{2+}+6S_2O_3^{2-}=2Cu(S_2O_3)_2^{3-}+S_4O_6^{2-} \tag{1}$$

For the preparation of gold thiosulfate solutions, an appropriate amount of gold standard solution was first placed into the beaker and heated on an electric heating plate at 100 °C to obtain needle-like crystalline tetrachloroauric acid. Then, a certain amount of sodium thiosulfate reagent was weighed and dissolved in deionized water. 1 mol/L NaOH solution and the prepared sodium thiosulfate solution were added to dissolve the tetrachloroauric acid crystal. After that, the mixture solution was diluted to a given concentration of $Au(S_2O_3)_2^{3-}$ for the adsorption experiment. The related reaction equation is shown as follows:

$$HAuCl_4+4NaOH=Au(OH)_3+H_2O+4NaCl \tag{2}$$

$$Au(OH)_3+NaOH=Na[Au(OH)_4] \tag{3}$$

$$Na[Au(OH)_4]+4Na_2S_2O_3=Na_3[Au(S_2O_3)_2]+Na_2S_4O_6+4NaOH \tag{4}$$

For the adsorption tests, a solution with a volume of 50 or 100 mL was used with a given mass of activated carbon. Mixing was provided by a thermostatic oscillator at a constant speed of 130 r/min. A water bath was used to maintain the required temperature. Solution samples were withdrawn with a set time to determine the concentration of gold and copper in the solutions by atomic adsorption spectrometry (AAS) (4530F, Shanghai, China). Scanning electron microscopy (SEM) (S−520, Hitachi, Japan) was conducted to determine the morphological characteristics of the activated carbon. 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} (WQF−410, Beijing, China). X-ray photoelectron spectroscopy (XPS) was performed to study the chemical composition on the surface of the samples (ESCALAB 250, Thermo, USA).

The adsorption capacity (q) of the metal onto the activated carbon was calculated according to the following reaction (gold, for example):

$$q=\frac{(C_0-C_t)\cdot V}{m} \tag{5}$$

where q is the adsorption capacity of gold, C_0 and C_t are the gold concentrations at time 0 (initial) and t, respectively, V is the volume of the solution, and m is the mass of activated carbon.

Adsorption isotherm data were fitted to the Langmuir and Freundlich models as shown below:
Langmuir model:

$$q_e=\frac{q_m\cdot K_L\cdot C_e}{1+K_L\cdot C_e} \tag{6}$$

Freundlich model:

$$q_e=K_F\cdot C_e^{1/n} \tag{7}$$

where C_e is the $Au(S_2O_3)_2^{3-}$ concentration at equilibrium, q_e is the $Au(S_2O_3)_2^{3-}$ amount adsorbed at equilibrium, K_L and K_F are Langmuir and Freundlich adsorption constants, respectively, and q_m is the maximum gold adsorption capacity.

Three kinetics models were used to describe the process of $Au(S_2O_3)_2^{3-}$ adsorption:
Pseudo-first-order model:

$$\ln(q_e-q_t)=\ln q_e-k_1t \tag{8}$$

Pseudo-second-order model:

$$\frac{t}{q_t}=\frac{1}{k_2\cdot q_e^2}+\frac{t}{q_e} \tag{9}$$

Elovich model:

$$q_t=\left(\frac{1}{\beta_E}\right)\ln\left(\frac{\alpha_E}{\beta_E}\right)+\left(\frac{1}{\beta_E}\right)\ln t \tag{10}$$

where q_t is the $Au(S_2O_3)_2^{3-}$ adsorption at time t, k_1, k_2, and α_E are adsorption rate constants, and β_E is the desorption rate constant.

3 Results and discussion

3.1 Adsorption kinetics

Tests for copper adsorption kinetics were carried out with 100 mL copper thiosulfate solutions with an initial copper concentration of 3 g/L. The molar ratio of thiosulfate to copper is 8:1. Unless otherwise stated, 0.5 g of activated carbon was used for adsorption tests.

Figure 2 shows the adsorption kinetics of $Cu(S_2O_3)_2^{3-}$ onto activated carbon. The adsorption capacity of activated carbon toward copper increases dramatically in the first 1 h and then decreases slightly and tends to be stable. The peak

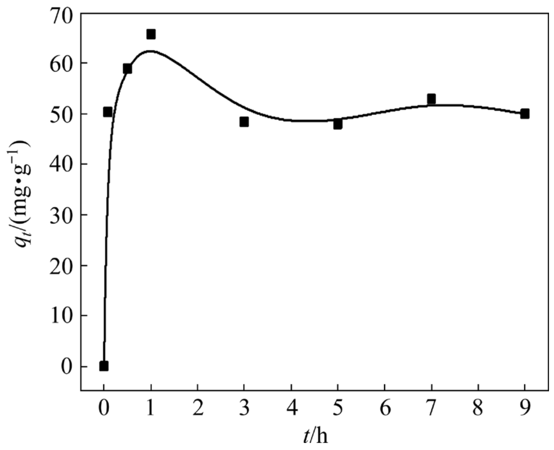


Fig. 2 Adsorption kinetics of $Cu(S_2O_3)_2^{3-}$ complex on activated carbon (Initial Cu 3 g/L, $n(S_2O_3^{2-})$:n(Cu)=8:1, pH (8.5±0.05), and 298 K)

period is probably due to supersaturation adsorption of the $Cu(S_2O_3)_2^{3-}$ complex on the interface of the activated carbon. The release of the over-adsorbed $Cu(S_2O_3)_2^{3-}$ complex from the activated carbon lasts approximately 2 h before an equilibrium is established. This indicates that the adsorption process of the copper thiosulfate complex on activated carbon may belong to multimolecular adsorption. The overloaded adsorption behavior of activated carbon may be attributed to its large specific surface area and porous structure.

Table 2 gives the parameters fitted to the pseudo-first-order, pseudo-second-order and Elovich kinetic models based on the test results. This implies that the pseudo-second-order kinetic model is more suitable (R^2=0.997) for the adsorption kinetics process than the pseudo-first-order or Elovich kinetic model. The equilibrium adsorption capacity of the $Cu(S_2O_3)_2^{3-}$ complex on activated carbon is 50.15 mg/g according to the fitted line of pseudo-second-order kinetic model (Fig. 3).

Table 2 Parameters related to pseudo-first-order, pseudo-second-order and Elovich kinetic model

Kinetics model	Concentration of copper/ $(g\cdot L^{-1})$	R^2	$q_e/(mg\cdot g^{-1})$	
			Calculated	Experimental
Pseudo-first-order	3	0.798	33.58	50.00
Pseudo-second-order	3	0.997	50.15	50.00
Elovich	3	0.080	55.33	50.00

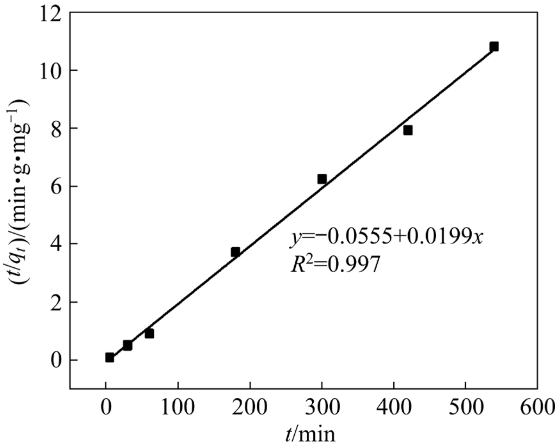


Fig. 3 Pseudo-second-order kinetic model of copper adsorption on activated carbon (Initial Cu 3 g/L, $n(S_2O_3^{2-})$:n(Cu)=8:1, pH (8.5±0.05), and 298 K)

Tests for gold adsorption were carried out with 100 mL gold thiosulfate solutions with an initial concentration of 50 mg/L gold. The molar ratio of thiosulfate to gold is 8:1. Unless otherwise stated, 1.0 g of activated carbon was used for adsorption tests.

Figure 4 shows the adsorption kinetics of gold onto activated carbon. The adsorption capacity of activated carbon toward gold rapidly increases in the initial stage. Peak adsorption is observed at an adsorption time of approximately 3 h. Then, gold adsorption slightly decreases, indicating that the equilibrium adsorption of gold onto activated carbon is basically established.

Table 3 summarizes the parameters fitted to pseudo-first-order, pseudo-second-order, and Elovich adsorption kinetic models. Similar to that of copper, the pseudo-second-order kinetic model exhibits a better linear correlation (R^2=0.996) for the gold adsorption kinetics than the pseudo-first-order and Elovich kinetic models. The equilibrium gold adsorption capacity of the $Au(S_2O_3)_2^{3-}$ complex

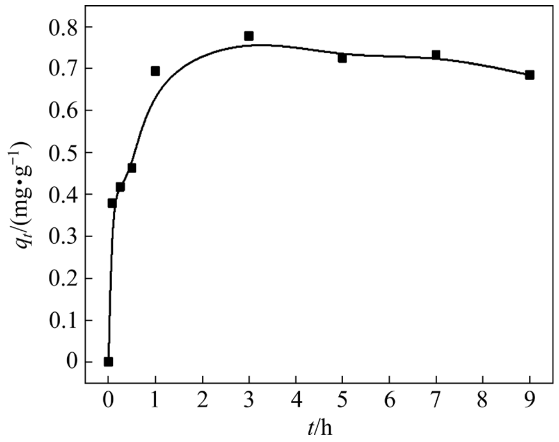


Fig. 4 Adsorption kinetics of $Au(S_2O_3)_2^{3-}$ complex on activated carbon (Initial Au 50 mg/L, $n(S_2O_3^{2-})$:n(Au)= 8:1, pH (8.5±0.05), and 298 K)

Table 3 Parameters related to pseudo-first-order, pseudo-second-order and Elovich adsorption isotherm models

Kinetics model	Concentration of gold/ $(mg\cdot L^{-1})$	R^2	$q_e/(mg\cdot g^{-1})$	
			Calculated	Experiment
Pseudo-first-order	50	0.661	0.489	0.685
Pseudo-second-order	50	0.996	0.712	0.685
Elovich	50	0.801	0.493	0.685

on activated carbon is 0.712 mg/g according to the fitted line (Fig. 5), which is very close to the experimental result of 0.685 mg/g.

3.2 Adsorption isotherms

Copper thiosulfate solutions with different initial copper concentrations were used for tests. Figure 6 shows the adsorption isotherms of copper on activated carbon at different temperatures. It can be seen that the copper adsorption capacity on activated carbon increases with an increase in initial copper concentration but slightly decreases with increasing temperature in the range of 298−318 K. This implies that the copper adsorption process is an exothermic process. Figure 7 illustrates the plots of $\ln C_e$ versus $\ln q_e$ for the copper adsorption isotherms at different temperatures. The good linear correlation (R^2) indicates the high suitability of the Freundlich model for the copper adsorption isotherms. Figure 8 shows plots of C_e/q_e vs q_e for the copper adsorption isotherms; however, the poor linear correlation (R^2) suggests that the Langmuir model is not fit for the copper adsorption isotherms. Table 4 summarizes the parameters of different adsorption isotherm models calculated from the slope and intercept of the correlation line. It can be safely concluded that $Cu(S_2O_3)_2^{3-}$ adsorption on activated carbon follows Freundlich isotherms, indicating that copper adsorption is a multi-molecular chemical adsorption process.

Figure 9 shows the adsorption isotherms of gold onto activated carbon. The amount of gold thiosulfate complex adsorbed by activated carbon increases gradually with increasing initial gold concentration. The adsorption isotherms of gold at 308 and 318 K are quite close to the data for 298 K,

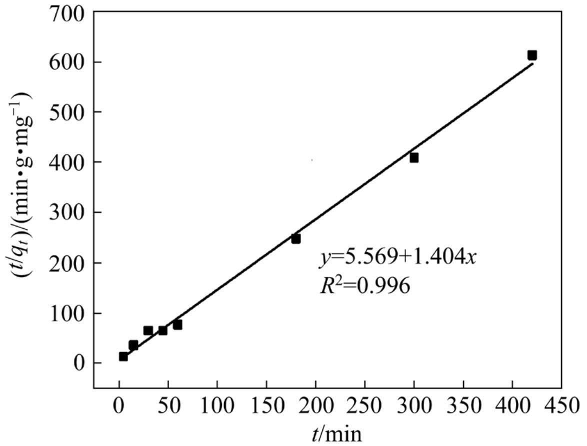


Fig. 5 Pseudo-second-order kinetic model of gold adsorption on activated carbon (Initial Au 50 mg/L, $n(S_2O_3^{2-})$:n(Au)=8:1, pH (8.5±0.05), and 25 °C)

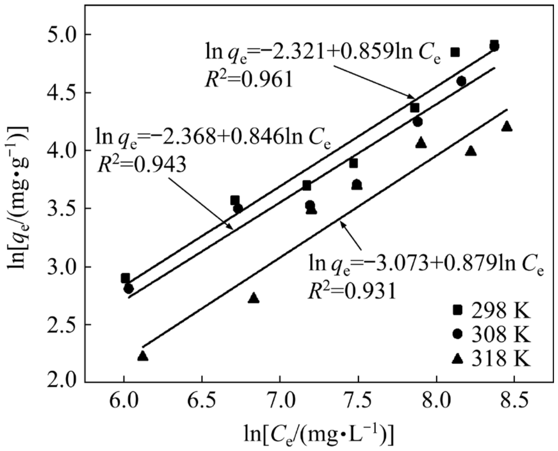


Fig. 7 Freundlich adsorption isotherms of copper adsorption on activated carbon at 298, 308, and 318 K ($n(S_2O_3^{2-})$:n(Cu)=8:1, and pH (8.5±0.05))

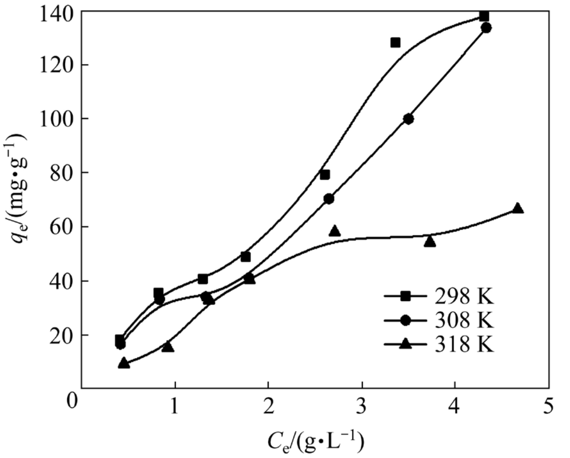


Fig. 6 Adsorption isotherm of copper adsorption on activated carbon at 298, 308, and 318 K ($n(S_2O_3^{2-})$:n(Cu)=8:1, and pH (8.5±0.05))

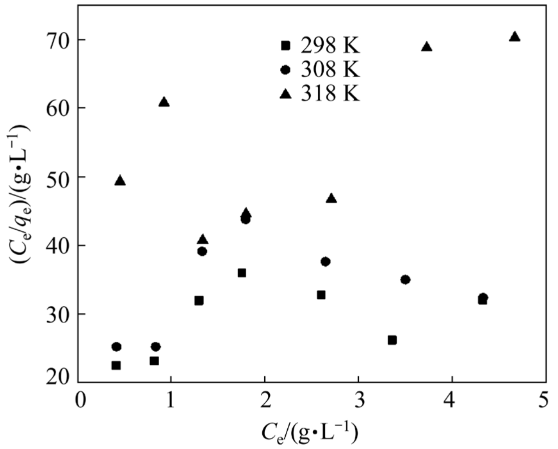


Fig. 8 Langmuir adsorption isotherms of copper adsorption on activated carbon at 298, 308, and 318 K ($n(S_2O_3^{2-})$:n(Cu)=8:1, and pH (8.5±0.05))

Table 4 Parameters related to Freundlich and Langmuir adsorption isotherm models for copper on activated carbon

Temperature/K	Freundlich parameter			Langmuir parameter		
	R^2	K_F	n	R^2	K_L	q_m/(mg·g^{-1})
298	0.961	0.370	1.164	0.179	7.7×10^{-5}	500
308	0.943	0.357	1.182	0.097	6.5×10^{-5}	500
318	0.931	−0.286	1.138	0.439	11.6×10^{-5}	200

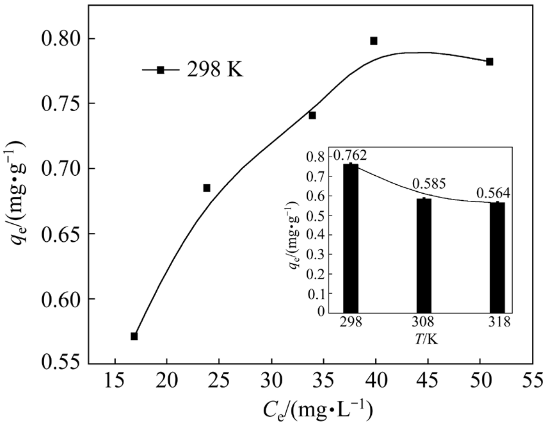


Fig. 9 Adsorption isotherm of gold adsorption on activated carbon ($n(S_2O_3^{2-})$:n(Au)=8:1, and pH (8.5±0.05))

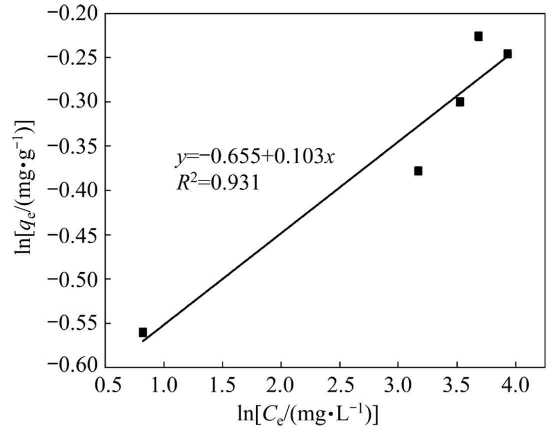


Fig. 10 Freundlich adsorption isotherm of gold adsorption on activated carbon at 298 K ($n(S_2O_3^{2-})$:n(Au)=8:1, and pH (8.5±0.05))

indicating that the effect of temperature on gold adsorption in the temperature range of 298−313 K is insignificant. The slight decrease in the equilibrium adsorption capacity of gold suggests that the gold adsorption process is an exothermic process.

Figures 10 and 11 show the plots of ln C_e versus ln q_e and C_e/q_e versus q_e for the gold adsorption isotherms at 298 K. From the slope and intercept of the correlation line, relevant parameters of different adsorption isotherm models for a temperature of 298 K were calculated and are listed in Table 5. Clearly, the adsorption process of gold thiosulfate by activated carbon conforms to the Langmuir model, indicating that gold adsorption is a monomolecular adsorption process.

It should be noted that the maximum adsorption capacity of gold by activated carbon is relatively low (only approximately 0.762 mg/L at 298 K). The adsorption capacity of the activated carbon toward copper reaches 79.04 mg/g under similar conditions, which is approximately two orders of magnitude higher than that of gold. Additionally, the competitive adsorption of thiosulfate ions must be considered. Thus, the use of activated carbon for gold recovery from thiosulfate solutions may face great challenges.

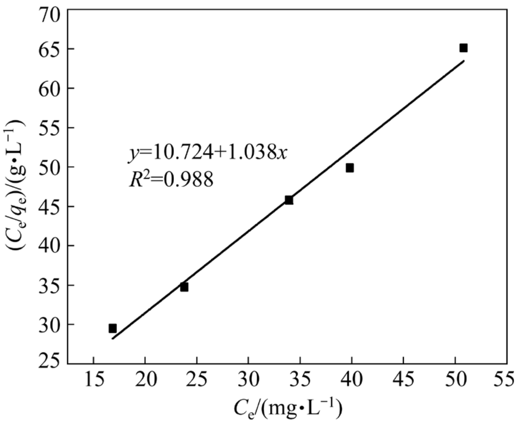


Fig. 11 Langmuir adsorption isotherm of gold adsorption on activated carbon at 298 K ($n(S_2O_3^{2-})$:n(Au)=8:1, and pH (8.5±0.05))

Table 5 Parameters related to Freundlich and Langmuir adsorption isotherm models for gold on activated carbon

Temperature/K	Freundlich parameter			Langmuir parameter		
	R^2	K_F	n	R^2	K_L	q_m/(mg·g^{-1})
298	0.931	1.925	9.708	0.988	0.097	0.963

3.3 Effect of molar ratio of $S_2O_3^{2-}$ to Cu/Au

Figure 12 shows the effect of the molar ratio of $S_2O_3^{2-}$ to Cu on the copper adsorption capacity by activated carbon. The adsorption capacity of activated carbon toward copper significantly decreases with increasing ratio of thiosulfate to copper when it varies from 2:1 to 8:1. When the molar ratio of thiosulfate to copper is higher than 8:1, it exhibits little influence on copper adsorption. The effect of the molar ratio of $S_2O_3^{2-}$ to Au on gold adsorption capacity exhibits similar behavior to that of copper (Fig. 13). Excessive thiosulfate may competitively occupy the active sites on the surface of activated carbon, leading to a reduction in the copper or gold adsorption capacity.

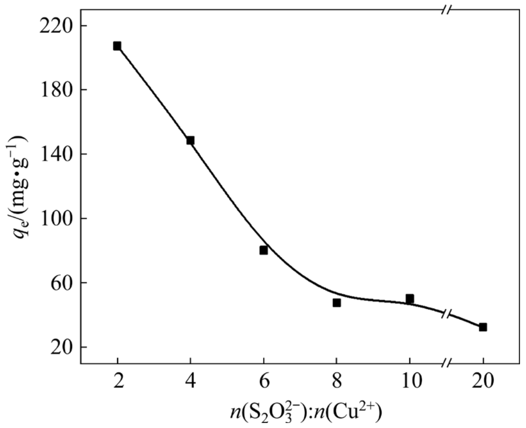


Fig. 12 Effect of molar ratio of thiosulfate to copper on copper adsorption (pH (8.5±0.05), and 298 K)

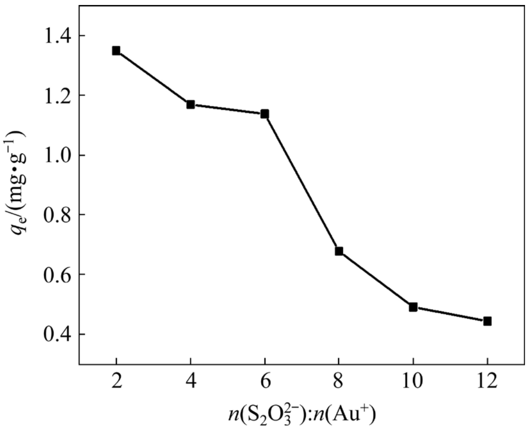


Fig. 13 Effect of molar ratio of thiosulfate to gold on gold adsorption (pH (8.5±0.05) and 298 K)

It is believed that some aurous thiosulfate complexes adsorbed on the activated carbon may be reduced to metallic gold [30,32]. Once metallic gold is formed, this species may be dissolved by thiosulfate to form the $Au(S_2O_3)_2^{3-}$ complex in solution. Thus, thiosulfate ions can also play the role of a desorption reagent, and excessive thiosulfate content may depress the adsorption capacity of activated carbon toward gold. For copper adsorption, excessive thiosulfate may react with copper ions to form copper sulfides (CuS, Cu_2S), and thiosulfate itself may be decomposed to elemental sulfur and other sulfur-bearing species due to the instability nature of thiosulfate. The presence of sulfur or copper sulfides may occupy the active site of activated carbon; therefore, the carbons are poisoned. Furthermore, cupric or cuprous ions can also be reduced to metallic copper upon activated carbon [33], causing a decrease in the copper adsorption capacity.

3.4 Potential adsorption mechanism

Figure 14 shows the FTIR spectra of the original activated carbon and the carbon loaded with copper and gold. The peaks at approximately 3430, 1600 and 1100 cm^{-1} are related to O—H, C═O, and C—O stretching vibrations, respectively [34]. The carbonyl peaks (C═O) after adsorption are basically higher than those before adsorption, and the increase is more obvious for copper adsorption. For loaded carbon with copper, the peak

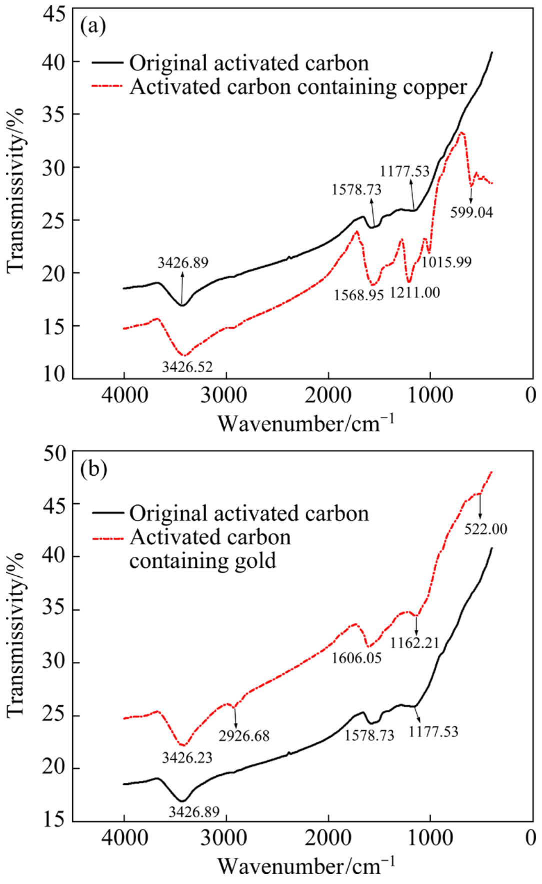


Fig. 14 FTIR spectra of original activated carbon and carbons containing copper (a) and gold (b)

at 1100 cm^{-1} almost disappears, but two obvious peaks appear at 1211 and 1016 cm^{-1}, which are believed to be derived from the stretching vibration of ethers (—C—O—C—) [35]. A new peak at 2922 cm^{-1} is introduced on the loaded carbon with gold, probably from the stretching of alkyl (—CH_2) groups [36]. For both loaded carbons, a weak adsorption peak near 500−600 cm^{-1} appears, which corresponds to the S═O or S—O bond. The analysis of the infrared spectrum shows that the functional groups existing in the original activated carbon include hydroxyl (—OH), carbonyl (C═O) and oxygen bonds (—C—O—). After adsorption, the strength of hydroxyl (—OH) and carbonyl (C═O) bonds increases, and the carbon–oxygen bond (—C—O—) for the loaded carbon with copper almost disappears. It is suggested that the adsorption mechanism of gold onto the activated carbon is different from that of copper.

Figure 15 shows the XPS spectra of the loaded carbon with copper. The Cu 2p, S 2p, O 1s, and C 1s peaks appeared in Fig. 15(a). In the analysis of Cu 2p peaks (Fig. 15(b)), the peaks of Cu^{2+} $2P_{1/2}$ and Cu^{+} $2p_{1/2}$, and Cu^{2+} $2p_{3/2}$ and Cu^{+} $2p_{3/2}$ are very close; therefore, it is difficult to distinguish Cu^{2+} from Cu^{+} directly by the binding energy of Cu 2p

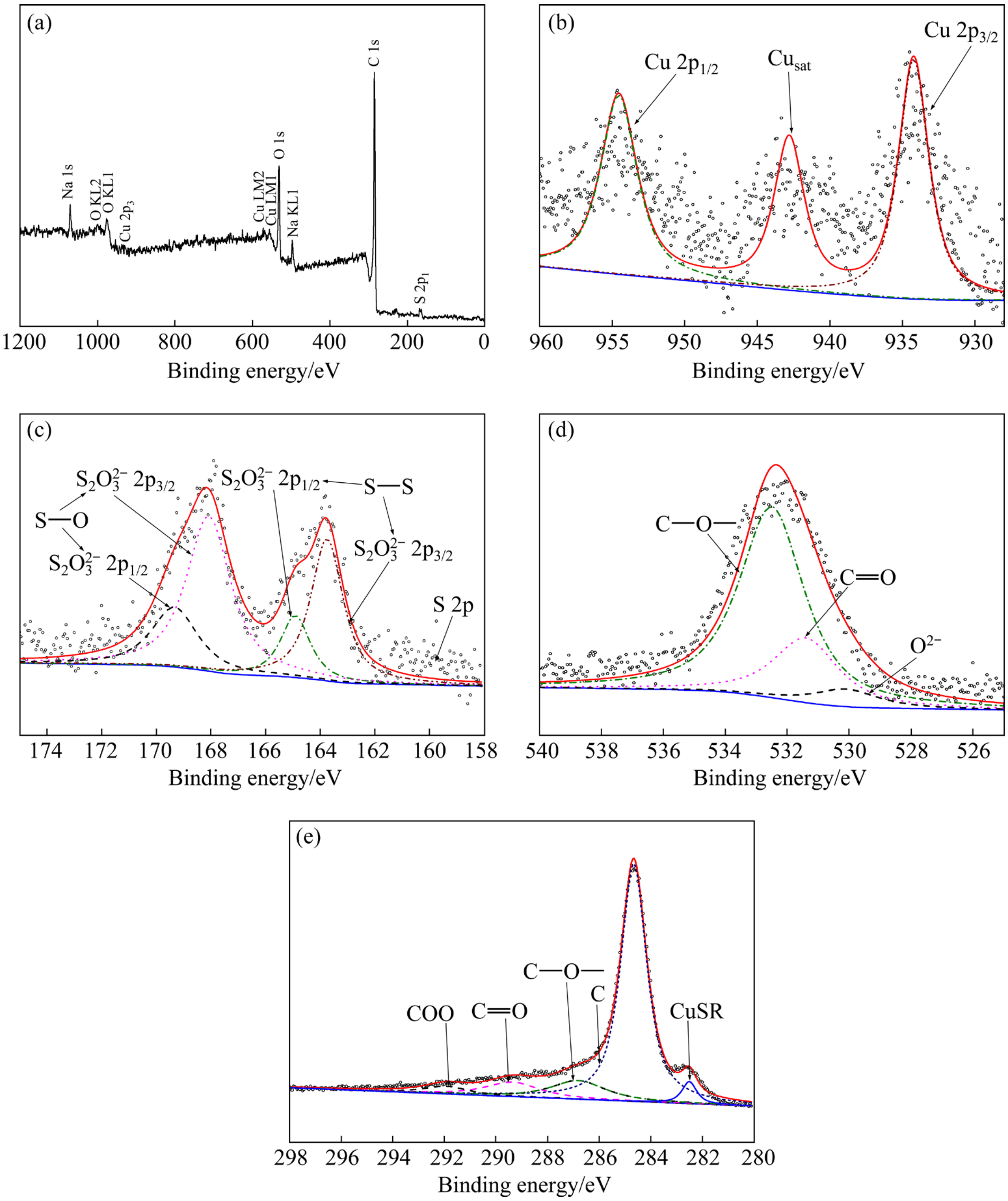
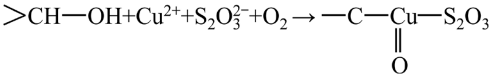


Fig. 15 XPS spectra of full spectrum (a), Cu 2p (b), S 2p (c), O 1s (d), and C 1s (e) of activated carbon containing copper

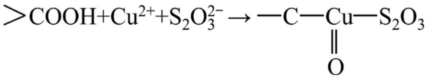
peaks. According to the theory proposed by HAYEZ et al [37] the Cu^{2+}, Cu^{+} and Cu^{0} peaks can be distinguished by satellite peaks of Cu 2p presented in the range of 940−945 eV. Thus, it is proven that Cu mainly exists in the form of Cu^{2+} on the carbon due to the obvious satellite peak observed at 942.8 eV.

It was reported that there were two distinct peaks in the XPS spectrum of thiosulfate ions ($S_2O_3^{2-}$), and the intensity ratio of the S—S peak to the S—O peak was approximately 1 [38]. The intensity ratio of S(S—O) to S(S—S) observed in Fig. 15(c) is approximately 1.07. Moreover, a weak peak is found at approximately 160 eV, indicating that the thiosulfate ions may be disproportionated on the surface of activated carbon, resulting in the enhancement of the S(S—O) photoelectron peak signal and slight weakening of the S(S—S) photoelectron peak signal. It should be noted that sulfur mainly exists in the form of $S_2O_3^{2-}$ on the activated carbon, with only very small amounts of S and SO_4^{2-}.

Figure 15(d) shows the narrow spectrum of O 1s. The binding energies of 530.1, 531.4 and 532.5 eV can be attributed to the O^{2-}, C═O and C—O— groups, respectively. This result is consistent with that reported by TERZYK and RYCHLICKI [36] regarding the adsorption of acetaminophen on the surface of activated carbon. Figure 15(e) shows the narrow spectrum of C 1s, and the binding energies of 284.6, 286.8, 289.4 and 291.9 eV confirm the C, C—O—, C═O and COO groups, respectively [36]. It is noted that an obvious peak is found at 282.6 eV on the loaded carbon with copper. The peak is probably caused by the interaction between Cu or S and the active group on the surface of activated carbon (CuSR), resulting in the deviation of the peak position of the C 1s peak. Some XPS studies on metal synthetic carbides show that the C 1s photoelectron peak at approximately 282.6 eV is caused by the covalent bond between C and metals (e.g., Cr, V, Mo, W, Zr and Ta) or some non-metallic elements (Si) [39−42]. Therefore, it is reasonable to deduce that Cu and S may partially form covalent bonds with C in the active group on the surface of activated carbon during the adsorption process. COOK et al [43] studied the adsorption mechanism of Au(CN) on the surface of activated carbon by XPS. BINIAK et al [44] adopted XPS to investigate the adsorption mechanism of $CuSO_4$ on the surface of activated carbon under different pH conditions. TERZYK and RYCHLICKI [36] studied the adsorption behavior of acetaminophen on the surface of activated carbon by XPS and FTIR. MONSER and ADHOUM [45] investigated the mechanism of adsorption of Cu, Zn and Cr cyanide by activated carbon. In the above studies, no covalent bond was reported between the metal and active groups in activated carbon. To the author's knowledge, this study is the first report on the adsorption of metal cations on the surface of activated carbon to form covalent bonds. BINIAK et al [44] proposed the adsorption mechanism of copper in thiosulfate solutions under different pH conditions. The potential adsorption mechanism of Cu^{2+} onto activated carbon may occur via the following reactions:



$$>\mathrm{CH{-}OH}+\mathrm{Cu}^{2+}+\mathrm{S_2O_3^{2-}}+\mathrm{O_2}\rightarrow -\mathrm{C}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{Cu}}-\mathrm{S_2O_3} \tag{11}$$



$$>\mathrm{COOH}+\mathrm{Cu}^{2+}+\mathrm{S_2O_3^{2-}}\rightarrow -\mathrm{C}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{Cu}}-\mathrm{S_2O_3} \tag{12}$$

Unfortunately, due to the extremely low adsorption capacity of the gold thiosulfate complex onto activated carbon, XPS analysis of the loaded carbon with gold was not available. However, some studies reported the kinetics of the process in a heterogeneous system of gold adsorption or reduction on activated carbon, which may provide useful suggestions for the kinetics analysis of gold adsorption onto activated carbons. YU et al [30,32] studied the adsorption of the gold−thiosulfate complex ion onto cupric ferrocyanide (CuFC)− or silver ferrocyanide (AgFC)−impregnated activated carbon in aqueous solutions. The experimental results indicated that the mechanism of gold adsorption onto the activated carbon can be divided into two steps: first, the gold−thiosulfate complex diffuses to the activated carbon surface, and an ion-exchange reaction for Au and Cu/Ag occurs. Then, Au(I) is likely reduced to native gold by carbon or $[Fe(CN)_6]^{4-}$. WOJNICKI et al [46,47] investigated the kinetic process of adsorption and reduction of Au(III) chloride complex ions on the activated carbon surface by various methodological technologies, such as SEM, XRD and XPS analyses. It was found that Au(III) can be reduced to the metallic form, probably due to the reduction characteristic of phenolic hydroxide superficial groups. Thus, it can be reasonable to deduce that the gold thiosulfate complex may be partly reduced to metallic gold by the functional groups on the surface of activated carbon, such as hydroxyl groups.

4 Conclusions

(1) The activated carbon exhibits a good adsorption performance toward copper but a poor selectivity for gold in thiosulfate solutions. The adsorption capacity of the activated carbon toward copper reaches 79.04 mg/g with an initial concentration of 3000 mg/L copper and at an initial pH of 8.5 and 298 K, which is two orders of magnitude higher than that of gold. The competitive adsorption of thiosulfate ions results in a significant decrease in the adsorption of copper and gold.

(2) The adsorption kinetics of copper and gold thiosulfate complexes onto activated carbon both conform to the pseudo-second-order model. The good linear correlation suggests the high suitability of the copper adsorption isotherms to the Freundlich model and the gold adsorption isotherm to the Langmuir model. This indicates that copper adsorption is multimolecular chemical adsorption, and gold adsorption is monomolecular adsorption.

(3) The FTIR and XPS analysis indicates that the potential interaction between Cu and S may partially form covalent bonds with C in the active group on the surface of activated carbon during the adsorption process. The adsorption mechanism of gold onto the activated carbon is different from that of copper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 52174271) and Fundamental Research Funds for Central Universities of China (No. N182502044). Special thanks are given to the instrumental or data analysis from the Analytical and Testing Center, Northeastern University, China.

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铜和金硫代硫酸盐在活性炭上的吸附机理

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摘 要：研究活性炭对铜和金硫代硫酸盐的吸附机理。铜和金硫代硫酸盐在活性炭上的吸附动力学均符合准二级动力学模型。活性炭对铜硫代硫酸盐的吸附等温线符合 Freundlich 模型，而对金硫代硫酸盐的吸附等温线符合 Langmuir 模型。负载活性炭的键合特性分析表明，活性炭对铜和金的吸附机理不同。在实验条件下，活性炭对铜的吸附量达到 79.04 mg/g，比金的吸附量高出约 2 个数量级。这意味着由于金的吸附量低以及铜和硫代硫酸盐的竞争吸附，用活性炭从硫代硫酸盐浸出液中回收金将面临很大的挑战。

关键词：活性炭；吸附；金；铜；硫代硫酸盐

(Edited by Bing YANG)