

Efficient recovery of Au(III) from acidic chloride solutions by microwave-induced carbonized persimmon tannin adsorbent

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Abstract. A new adsorbent has been developed by microwave-induced carbonization with persimmon tannin, and its adsorption behaviors and mechanism towards Au(III) were studied in hydrochloric acid medium. The adsorption of Au(III) was found to be dependent on acidity, temperature, reaction time. The maximum adsorption capacity was above 700 mg g⁻¹. The selective recovery of Au(III) by adsorption-elution experiment was tested to be effective, and the loaded metals can be easily desorbed by acidic thiourea. Characterized by FTIR and SEM, the adsorption mechanisms of Au(III) was proposed to be redox-reduction.

1. Introduction

Gold is one of precious metals, and it exhibits increasing application including electrical and electronic devices, telecommunication, chemical engineering and medical industry [1]. Electronic waste contains a large number of valuable metals and toxic and harmful components such as gold, lead and plastics, which can lead to waste of resources and pose serious risks to the ecological environment and human health. In 2014, a total of 41.8 million tons of electronic waste was generated globally, and about 6 million tons of electronic waste was generated in China. However, the annual disposal of electronic waste accounted for 70 % of the global total [2, 3]. Currently, only 15 per cent of e-waste is properly recycled or reused. Electronic waste containing a large number of valuable metals is known as "urban mine". The recycling of electronic waste has become a major issue in China and even in the world. In particular, the precious metals rich in used circuit boards are the main economic drivers of recycling and utilization, so efficient recovery of precious metals such as gold from the "urban mine" is of sustainable value [4, 5].

In recent years, adsorption has been widely adopted for metal recovery and proven to be an effective method [6]. Due to rich in sources, low in cost, and rich in phenolic hydroxyl groups. In the past decade, plant tannin-based materials as adsorbents is widely employed for metal ions recovery from aqueous solutions. The reported tannin adsorbents are tannin phenolic resin., tannin grafting polymer composite materials and their derivatives, and the adsorption objects include heavy metals, precious metals, radioactive metals, dyes, small molecules, etc [7, 8].

However, the acid leaching dilute solution of circuit board has high acidity and contains a large number of common ions such as copper, nickel, iron, and lead, which puts forward higher requirements for the functionality, acid stability, and selectivity of tannin adsorption materials. In this study, a new and highly effective adsorbent microwave-induced carbonized persimmon tannin



adsorbent (MCP) was prepared for selective recovery of Au(III) ions from acidic chloride solutions. The adsorption behaviors and mechanism of MCP towards Au(III) were studied in hydrochloric acid medium, and the recovery effectiveness of the metal leaching solution was evaluated.

2. Materials and methods

2.1. Materials

Oil persimmon (*Diospyros oleifera* Cheng) was collected in the persimmon repository of Huazhong Agricultural University, Wuhan, China. The persimmon fruits were sliced and the kernel was removed, after vacuum freezing, they were ground into fine powder. The tannin content was determined 28 % by the Folin-Ciocalteu method [9]. The preparation procedures are as follows. 10 g persimmon powders were mixed with 20 mL 50% phosphoric acid solution for 6 h to yield a homogeneous paste, and then it was placed in a glass reactor fixed in the chamber of 2450 MHz and 900 W microwave oven (Galanz G70F20CN1L) where the carbonized reaction was performed for 8 min. The carbonized product was washed severally with de-ionised water, dried at 65°C for 12 h and stored in the dessicator used as the adsorbent for gold adsorption investigation in the present study, named as microwave-induced carbonized persimmon (MCP) adsorbent. The percentage yield of MCP with respect to persimmon powders was 35.6 %. Chloroauric acid tetrahydrate and all the other reagents applied in the present study were of analytical grade without any purification and purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China.

2.2. Instrumentation

Metal ion concentrations of samples were measured by atomic adsorption spectrophotometer (AAS, Beijing Purkinje General Instrument, TAS-990AFG). Fourier transform infrared spectra (FT-IR) were recorded by Nicolet 6700 spectrophotometer using KBr pellet method. Scanning electron microscope (SEM) images were acquired using a Jeol JSM-5610LV instrument.

2.3. Batch adsorption studies

The effects of different pH (acidity), adsorption time, temperature, initial concentration of gold ions and coexisting ions on the adsorption effect were studied by static adsorption. In a typical batch adsorption experiment, 15 mg adsorbent MOP and 15 mL Au(III) working solution were mixed in the sealed conical flasks and shaken at a speed of 200 rpm in a gas bath thermostat oscillator (ZHWY-200B). Then the mixture was filtered and the concentration of the filtrate was measured. The adsorption capacity (q_e , mg g⁻¹) and adsorption rate (%Adsorption) were calculated through the following equations.

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\% \text{Adsorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where C_i (mg L⁻¹) and C_e (mg L⁻¹) are initial and equilibrium concentration of Au(III) in solution, respectively, m (mg) is the weight of MOP and V (mL) is the volume of Au(III)-solution. All the experiments were repeated three times and mean values with standard deviation were present.

The effects of pH (acidity) and temperature were conducted with 200 mg L⁻¹ Au(III) in varied acidic chloride solutions (1 mol L⁻¹, 0.1 mol L⁻¹, pH 2-6) at 298, 308, 318 K, respectively. The samples of the kinetic experiment were collected at different time intervals (5-1800 min) to determine the adsorption equilibrium time at 298 K. For isotherm study, varied initial concentrations of Au(III) ranging from 600 to 3000 mg L⁻¹ were employed at 298 K. Also, a solution containing both light and

heavy metal ions Mg(II), Zn(II), Fe(III), Cu(II), Na(I), Ca(II) was prepared in the same concentration 200 mg L⁻¹ to understand the selectivity of MOP at 298 K.

2.4. Column adsorption studies

Column adsorption can simulate industrial applications and be used to assess the selectivity, industrial applicability, and effectiveness of bioadsorbent. Discarded circuit board after shredding was kindly provided by Jingmen GEM New Materials Co. Ltd., Jingmen, China. The metal concentrations of Au(III)-bearing liquor of PCBs leached by aqua regia was determined to be Au(III) 53 mg L⁻¹, Mg(II) mg L⁻¹, Zn(II) 20 mg L⁻¹, Fe(III) 10 mg L⁻¹, Cu(II) 16 mg L⁻¹, Na(I) 30 mg L⁻¹, Pb(II) 40 mg L⁻¹, the pH value was tested to 0.93.

A dynamic column experiment was carried out using a glass column (1 cm internal diameter and 30 cm height) equipped with a constant flow pump (DHL-A) and an automatic fraction collector (BSA-100). Firstly, 100 mg MCP 8, immersed in deionized water for 12 h before use, was packed into the column. Secondly, the packed column was conditioned by passing deionized water for 24 h. Thirdly, Au(III)-bearing liquor was pumped through the column at a constant flow rate of 8.0 mL h⁻¹. The effluent solution from the column was collected hourly for measurement of metal concentration. Then, the loaded metal ions were desorbed by 0.5 M HCl + 0.5 M thiourea as eluting agent. The eluted solution was also collected and analysed.

The bed volume (B.V.) of the effluent is defined as:

$$B.V. = \frac{v \cdot t}{V} \quad (3)$$

Where v , t and V are the flow rate of the solution, the time for which the feed solution was pumped through the bed, and the wet volume of the packed adsorbent, respectively.

3. Results and discussion

3.1. Effect of acidity

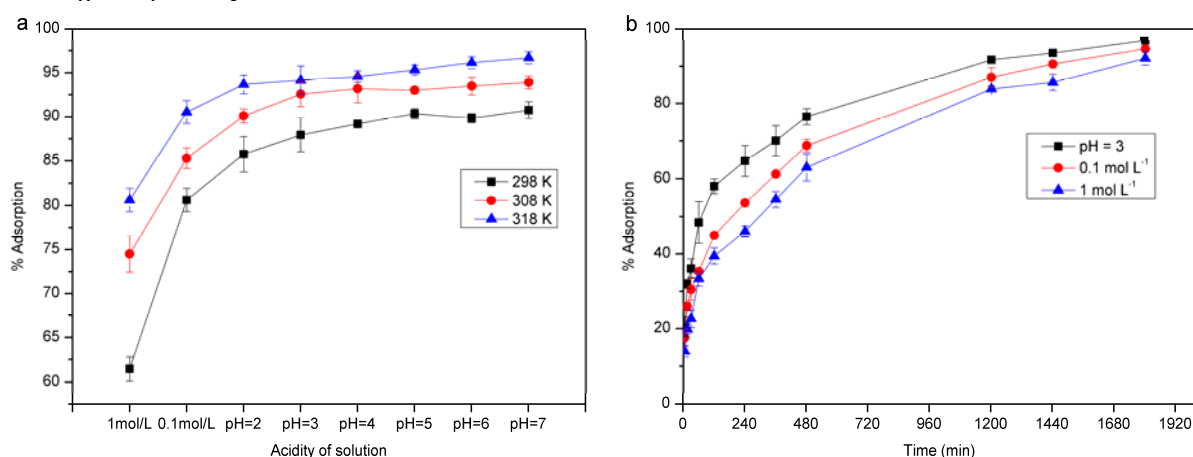


Figure 1. Effect of (a) acidity and (b) time on Au(III) adsorption by MCP. Adsorbent dosage = 1 g L⁻¹, $C_i = 200$ mg L⁻¹

Fig. 1a shows the Au(III) adsorption behaviour of MCP in varied acidic chloride solutions at 298, 308, 318 K, respectively. It was found that there is little difference in adsorption rate at pH 1-7. As the pH of the solution increased, the adsorption rate also increased. As the temperature increases, the adsorption rate increased significantly, which shows that the adsorption reaction was endothermic, and increasing the temperature would help increase the adsorption rate. It is noted that the filtrates

collected from Au(III) solutions after adsorption showed colorless (1 mol L^{-1} , 0.1 mol L^{-1} HCl), brick red color (pH 3.0-4.0) and slate gray color (pH 5.0-7.0). This phenomenon can be explained by the distribution of Au(III) species like AuCl_4^- and $\text{AuCl}_3(\text{OH})^-$ in different acidic media [10].

3.2. Effect of time

Fig. 1b presents the plots of Au(III) adsorption versus contact time (5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 20 h, 24 h, 30 h) at 298 K. It can be seen that the adsorption of Au(III) occurred almost half at 120 min and then increased gradually with the increasing of contact time from 120 to 1920 min. And its adsorption rate tends to 100 % at 32h. So, the reaction time had a very significant effect on the adsorption rate, and the adsorption rate increases until it is completely adsorbed. Also, lower acidity is conducive to Au(III) adsorption by MCP. To ensure the complete equilibrium, the samples were shaken for 30 h in the adsorption isotherms tests.

3.3. Effect of initial Au(III) concentration

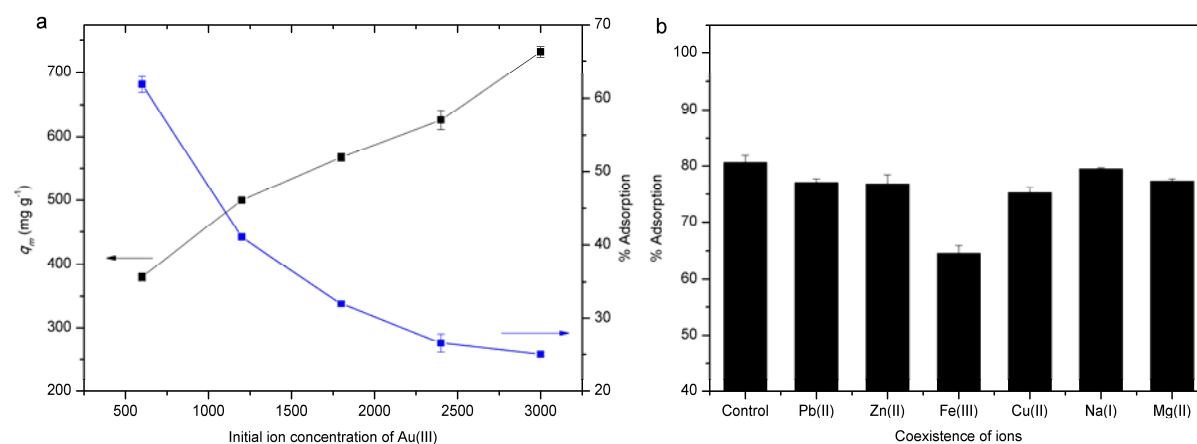


Figure 2. Effect of (a) initial Au(III) concentration and (b) coexisting ions on Au(III) adsorption by MCP. Adsorbent dosage = 1 g L^{-1} , 0.1 mol L^{-1} HCl acidic chloride solution

Fig. 2a shows the Au(III) adsorption rate and adsorption capacity in varied initial metal concentration ($600\text{--}3000 \text{ mg L}^{-1}$). The adsorption capacity was positively correlated to the initial solution concentration. It can be seen that the adsorption capacity of Au(III) by MCP increased with the increase of initial ion concentration while the adsorption rate decreased, and the maximum adsorption capacity has potential enhancement with increasing metal concentration further. So, the adsorbent MCP had a great saturation adsorption capability on Au(III).

3.4. Effect of coexisting ions

It is well-known that the presence of one metal may hinder the adsorption of other metals. Thus, the investigation of effects of coexisting metal ions is useful at industrial scale. Adsorption of Au(III) in presence of coexisting cations (Pb(II), Zn(II), Fe(III), Cu(II), Mg(II), and Na(I)) was evaluated in binary metal ion systems containing 200 mg L^{-1} metal ions. Fig. 2b shows that the adsorption percentage of Au(III) in control was higher than that in binary metal ion systems. This can be attributed to the competition between heavy metal ions, and the effects of competing cations on Ni(II) adsorption reduced in the orders of $\text{Fe(III)} \gg \text{Cu(II)} > \text{Pb(II)}, \text{Zn(II)}, \text{Mg(II)}$. The presence of Na(I) had no significant effects on the adsorption of Au(III).

3.5. Applicability for industrial Au(III)-bearing liquor

As seen in Fig. 3a, the breakthroughs of Mg(II), Na(I), Pb(II) and Zn(II) occurred immediately after the start of flow, then there was a small amount of adsorption for Fe(III) and Cu(II). Au(III) ions were

adsorbed in large quantities on the adsorbent and its breakthroughs started at 400 B.V. This indicates that Au(III) can be separated from coexisting base metals by continuous operation. Once the column adsorption was saturated, the loaded metal ions were eluted by acidic thiourea solution. Fig. 3b shows the elution profiles, Au(III) was eluted with preconcentration factors of 2.3. The precious metal Au(III) containing leach liquor was successfully recovered by MCP, demonstrating a strategy of precious metals recovery from acidic leached liquor of PCBs.

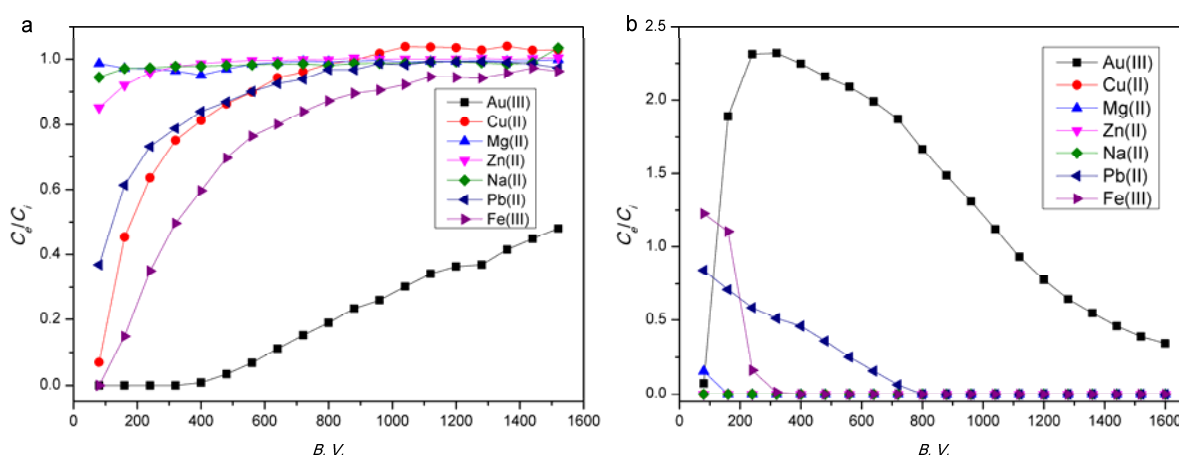


Figure 3. Breakthrough profiles (a) and elution profile (b) of Au(III), Cu(II), Mg(II), Zn(II), Na(I), Pb(II), Fe(III) from acidic leached liquor of PCBs. Flow rate = 0.1 mL min^{-1} , room temperature.

3.6. Characterization of the adsorbent and adsorption process

Fig. 4 shows the FTIR spectra of MCP before and after adsorption of Au(III). In the spectra of MCP, the broad band at 3395 cm^{-1} is assigned to phenolic O-H stretching vibration, the sharp bands at 1692 and 1607 cm^{-1} represents C=O stretching vibration of ester and ketone groups, the peaks observed at 1235 cm^{-1} , 1084 cm^{-1} are assigned to C=C-O stretching, and C-O stretching vibrations, respectively. After adsorption of Au(III), the peaks at 1710 cm^{-1} and 1614 cm^{-1} assigned for quinone type C=O were increased, indicating that the phenolic hydroxyl groups of MCP are oxidized to carbonyl groups.

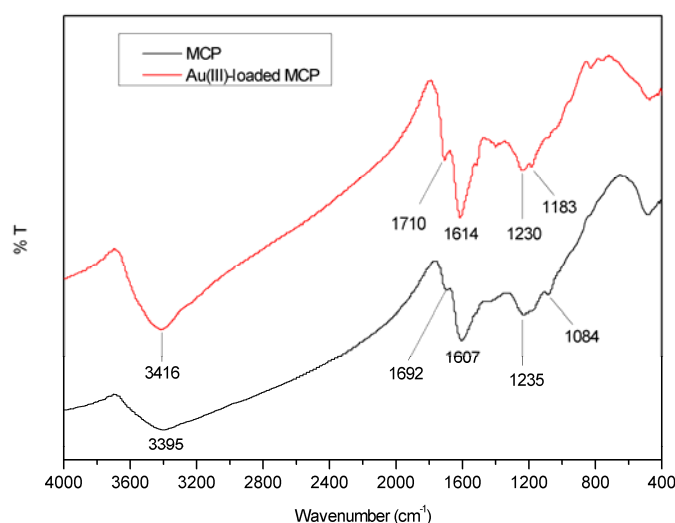


Figure 4. FT-IR spectra of the adsorbent MCP before and after adsorption of Au(III)

SEM images is shown in Fig. 5. It was observed that the adsorbent MCP is irregular and coarse before adsorption. After adsorption of Au(III), an abundant of metallic gold particles are formed and aggregated. Large particles of gold were also observed by naked eyes after adsorption. The adsorption mechanism between MCP and Au(III) could be explained by reduction adsorption [11, 12].

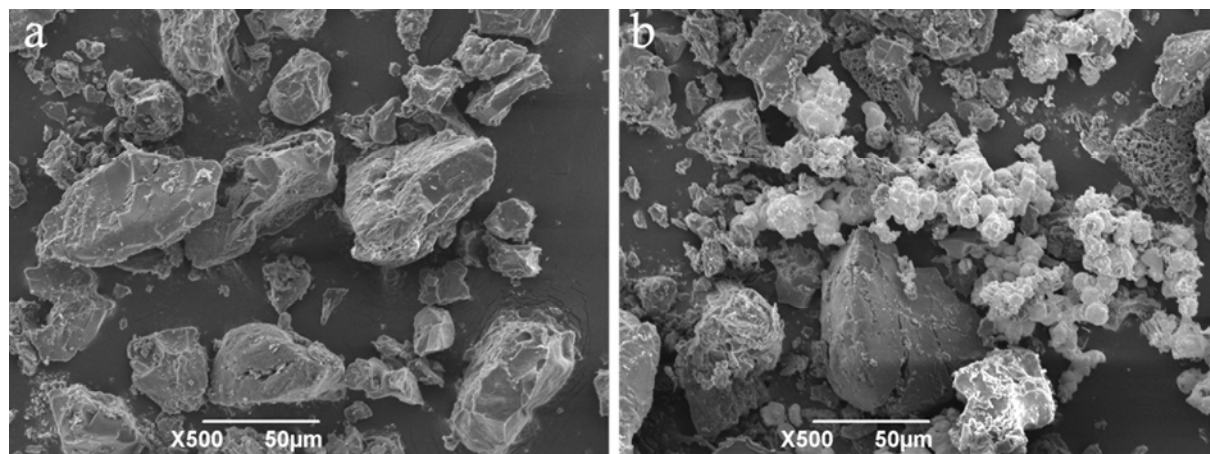


Figure 5. SEM images of the adsorbent MCP before (a) and after adsorption of Au(III)(b)

4. Conclusion

Microwave-induced carbonized persimmon tannin adsorbent (MCP) was prepared by simple reactions. The present studies have demonstrated that MCP can be used for the effective adsorption of Au(III) from hydrochloric acidic solutions. The adsorption of Au(III) was found to be dependent on acidity, temperature, reaction time. The maximum adsorption capacity was above 700 mg g^{-1} . The selective recovery of Au(III) by adsorption-elution experiment was tested to be effective, and the loaded metals can be easily desorbed by acidic thiourea. Characterized by FTIR and SEM, the adsorption mechanisms of Au(III) was proposed to be redox-reduction.

Acknowledgments

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