Extraction and determination of humic acids in carbonaceous gold ores

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Abstract: Carbonaceous gold ores, containing carbonaceous matters which rob gold, is a kind of refractory gold ore. Humic acids are one of the gold-robbing carbons. In this paper, humic acids were extracted by mixed alkali heating leaching method from the gold concentrate of a carbonaceous gold mine in Guizhou, and the extraction rate was determined by the potassium dichromate oxidation-titration method. The influencing factors which were researched, were sodium hydroxide concentration, sodium pyrophosphate concentration, solid-liquid ratio, leaching temperature and stirring leaching time. The results showed that the optimum extraction conditions were sodium hydroxide concentration 0.3 mol/L, sodium pyrophosphate concentration 0.06 mol/L, solid-liquid ratio 1:4, leaching temperature 70°C, stirring leaching time 24 h, and the productivity of humic acids was 1.1049%.

1. Introduction
Carbonaceous gold ores, containing preg-robbing carbonaceous matters, is a kind of refractory gold ore and mainly contain ‘Carbonaceous Carlin-type Gold Ores’. Elemental carbons and organic carbons (humic acids and hydrocarbons) are commonly found in this type of gold ores [1-3]. At present, the more unified view is that the gold-robbing carbonaceous matters only include elemental carbons and humic acids [2-4]. It is generally believed that when the content of organic carbons in gold ore is greater than or equal to 0.2%, the complexation of gold with cyanide ion will be seriously affected during cyanidation[5-6]. The content of organic carbons in carbonaceous gold ores is often higher than 0.2% [7-10], so it is necessary to extract humic acids from carbonaceous gold ores.

2. Experimental

2.1. Materials
The gold concentrate of a carboniferous gold ore in Guizhou Province is used as experimental material. The main elements are Fe 23.17%, S 24.7%, As 3.41%, Au 15.9g/t and organic carbons 4.36%. The reagents used in the experiment are sodium hydroxide, sodium pyrophosphate, potassium dichromate,
ammonium ferrous sulfate, phenanthroline and concentrated sulfuric acid, all of which are analytical pure.

2.2. Methods
In the experiment, a mixture of sodium hydroxide and sodium pyrophosphate with a certain concentration ratio was used to mix with gold concentrate in accordance with a certain solid-liquid ratio, and then heated and stirred in water bath to extract humic acids. The effects of sodium hydroxide concentration, sodium pyrophosphate concentration, solid-liquid ratio, leaching temperature and time on the productivity of total humic acids were investigated. The productivity of total humic acids was determined by the method, which is called “potassium dichromate oxidation-ammonium ferrous sulfate titration” [11].

3. Experimental results and discussion
In the experiment of extracting humic acids by alkali, the orthogonal experimental design of five factors and four levels was carried out. The specific experimental conditions and results are shown in Table 3.1.

Table 3.1 Orthogonal experimental conditions and results of alkali extraction.

| Experimental number | Experimental conditions | Assessment indicators |
|---------------------|-------------------------|-----------------------|
|                     | NaOH concentration (mol/L) | Na4P2O7 concentration (mol/L) | Solid-liquid ratio (g/mL) | Temperature (℃) | Time (h) | Productivity (%) |
| 1                   | 0.1                      | 0.06                   | 1:3                      | 50               | 6        | 0.3691           |
| 2                   | 0.1                      | 0.08                   | 1:4                      | 60               | 12       | 0.4566           |
| 3                   | 0.1                      | 0.10                   | 1:5                      | 70               | 18       | 0.5347           |
| 4                   | 0.1                      | 0.04                   | 1:6                      | 80               | 24       | 0.6844           |
| 5                   | 0.3                      | 0.06                   | 1:4                      | 70               | 24       | 1.0491           |
| 6                   | 0.3                      | 0.08                   | 1:3                      | 80               | 18       | 0.7061           |
| 7                   | 0.3                      | 0.10                   | 1:6                      | 50               | 12       | 0.3387           |
| 8                   | 0.3                      | 0.04                   | 1:5                      | 60               | 6        | 0.3963           |
| 9                   | 0.3                      | 0.06                   | 1:5                      | 80               | 12       | 0.4976           |
| 10                  | 0.5                      | 0.08                   | 1:6                      | 70               | 6        | 0.2519           |
| 11                  | 0.5                      | 0.10                   | 1:3                      | 60               | 24       | 0.8051           |
| 12                  | 0.5                      | 0.04                   | 1:4                      | 50               | 18       | 0.7083           |
| 13                  | 0.7                      | 0.06                   | 1:6                      | 60               | 18       | 0.6041           |
| 14                  | 0.7                      | 0.08                   | 1:5                      | 50               | 24       | 0.7293           |
| 15                  | 0.7                      | 0.10                   | 1:4                      | 80               | 6        | 0.2352           |
| 16                  | 0.7                      | 0.04                   | 1:3                      | 70               | 12       | 0.4889           |
| I                   | 2.0448                   | 2.5199                 | 2.3692                   | 2.1454           | 1.2525   |                  |
| II                  | 2.4902                   | 2.1439                 | 2.4492                   | 2.2621           | 1.7818   |                  |
| III                 | 2.2629                   | 1.9137                 | 2.1579                   | 2.3246           | 2.5332   |                  |
| IV                  | 2.0575                   | 2.2779                 | 1.8791                   | 2.1233           | 3.2679   |                  |
| K1                  | 0.511200                 | 0.629975               | 0.59230                  | 0.536350         | 0.313125 | T=8.8554         |
| K2                  | 0.622550                 | 0.535975               | 0.61230                  | 0.565525         | 0.445450 |                  |
| K3                  | 0.565725                 | 0.478425               | 0.539475                 | 0.581150         | 0.638300 |                  |
| K4                  | 0.514375                 | 0.569475               | 0.469775                 | 0.530825         | 0.816975 |                  |
| R                   | 0.111350                 | 0.151550               | 0.142525                 | 0.015625         | 0.503850 |                  |
By comparing the above 16 test results directly, the best scheme was found. Obviously, the highest productivity of total humic acids was the scheme No.5. Under these conditions, the productivity of total humic acids was 1.0491%. The optimum solution is 0.3 mol/L of sodium hydroxide, 0.06 mol/L of sodium pyrophosphate, 1:4 g/mL of solid-liquid ratio, 70°C of leaching temperature and 24 h of leaching time.

It can be seen from Table 3.1 that, depending on the size of the Range, in the process of extracting humic acids, the degree of influence of various factors on the productivity of total humic acids is as follows: leaching time > sodium pyrophosphate concentration > solid-liquid ratio > sodium hydroxide concentration > Leaching temperature. The horizontal change of factors is taken as abscissa and the average value of indicators is taken as ordinate. For the sake of clarity, the relationship between levels and indicators is drawn, that is the trend map of the influence of factors on productivity in the experiment of extracting humic acids.

3.1. Effect of NaOH concentration
According to the four mean values of sodium hydroxide concentration in orthogonal Table 3.1, the trend diagram of the influence of sodium hydroxide concentration on the productivity of total humic acids is drawn, as shown in Figure 3.1.

As can be seen from Figure 3.1, when the concentration of sodium hydroxide is 0.3 mol/L, the productivity of total humic acids reaches the maximum value of 0.622550%. When the concentration of sodium hydroxide increases from 0.1 mol/L to 0.3 mol/L, the productivity of total humic acids increases rapidly with the increase of the concentration of sodium hydroxide. This is due to the increase of the concentration of sodium hydroxide, the contact probability between humic acid molecules and sodium ions increases, and the formation of sodium humate is easier. When the concentration exceeds 0.3 mol/L, the productivity of total humic acids decreases gradually with the increase of the concentration. Because the concentration of alkali added is higher than the alkali concentration required to extract humic acids, that is, the sodium ion concentration is too high, resulting in the same ion effect which causes the reaction of free humic acids to react with the extracting solution to form a sodium humate to the left, as shown in the reaction (1). Therefore, in the alkali extraction experiment of humic acid, the optimum concentration of sodium hydroxide should be 0.3 mol/L.

\[
\text{R-(COOH)}_4 + 4\text{NaOH} \rightleftharpoons \text{R-(COONa)}_4 + 4\text{H}_2\text{O} \quad (1)
\]

![Figure 3.1](image.png)
3.2. Effect of Na₄P₂O₇ concentration

According to the four mean values of sodium pyrophosphate concentration in orthogonal Table 3.1, the trend diagram of the influence of sodium pyrophosphate concentration on the productivity of total humic acids is drawn, as shown in Figure 3.2.

As can be seen from figure 3.2, when the concentration of sodium pyrophosphate is 0.06 mol/L, the productivity of total humic acids reaches the maximum of 0.629975%. When the concentration of sodium pyrophosphate increases from 0.04 mol/L to 0.06 mol/L, the productivity of total humic acids increases rapidly with the increase of the concentration of sodium pyrophosphate. This is due to the increase of the concentration of sodium pyrophosphate, which causes the reaction between complex humic acids and sodium pyrophosphate to proceed to the right, as shown in the reaction (2). When the concentration increases from 0.06 to 0.10 mol/L, the productivity of total humic acids decreases rapidly. This is because the concentration of added alkali solution is higher than that required for extracting complex humic acids, that is, the concentration of sodium ion is too high, which produces the same ion effect, which makes the reaction of insoluble humic acids combined with Ca and Mg ions react with extract solution to produce soluble sodium humate to the left. See reaction (2). Therefore, in the alkali extraction experiment of humic acids, the optimum concentration of sodium pyrophosphate should be 0.06 mol/L.

\[
R-(COO)₄Ca₂ + Na₄P₂O₇ \rightleftharpoons R-(COONa)₄ + Ca₂P₂O₇
\]  

(2)

![Figure 3.2](image)

**Figure 3.2** Effect of Na₄P₂O₇ concentration on the productivity of total humic acids.

3.3. Effect of solid-liquid ratio

According to the four mean values of solid-liquid ratio in orthogonal Table 3.1, the trend diagram of the influence of solid-liquid ratio on the productivity of total humic acids is drawn, as shown in Figure 3.3.

As can be seen from Figure 3.3, when the solid-liquid ratio is 1:4 g/mL, the productivity of total humic acids reaches the maximum value of 0.612300%. The productivity of total humic acids increased slightly (0.02%) when the solid-liquid ratio decreased from 1:3 g/mL to 1:4 g/mL, and decreased rapidly when the solid-liquid ratio exceeded 1:4 g/mL. This shows that when the solid-liquid ratio is 1:4 g/mL, the humic acids in the mine can fully contact with the alkali solution and react completely. When the solid-liquid ratio continues to decrease (or the liquid-solid ratio is increased), the contact probability between the humic acids in the mine and sodium ion in the alkali solution decreases, which is not beneficial to the extraction of humic acids. Therefore, the optimum solid-liquid ratio should be 1:4 g/mL.
3.4. Effect of leaching temperature

According to the four mean values of leaching temperature in orthogonal Table 3.1, the trend diagram of the influence of leaching temperature on the productivity of total humic acids is drawn, as shown in Figure 3.4.

From figure 3.4, it can be seen that the productivity of total humic acids increases with the increase of leaching temperature between 50°C and 70°C, and reaches the highest (0.581150%) at 70°C. Therefore, the increase of leaching temperature is beneficial to the reaction between humic acids and alkali liquor, because the increase of leaching temperature intensifies the molecular thermal movement and increases the contact probability of reactants. The productivity of total humic acids decreased rapidly when the leaching temperature increased from 70°C to 80°C, which may be due to the instability of sodium pyrophosphate aqueous solution at higher than 70°C. Therefore, the optimum temperature for alkali extraction should be 70°C.
3.5. Effect of leaching time

According to the four mean values of leaching time in orthogonal table 3.1, the trend diagram of the influence of leaching time on the productivity of total humic acids is drawn, as shown in Figure 3.5.

As can be seen from Figure 3.5, with the prolongation of leaching time, humic acids in ore can be fully contacted with alkali solution, which makes the reaction complete gradually, and the productivity of total humic acids also increases gradually (the maximum is 0.816975%). According to Figure 3.5, the optimum leaching time in alkali extraction experiment should be 24 hours. However, if it is to find the most suitable leaching time, it is necessary to continue the experiment. This paper will not carry out the exploratory experiment of optimum leaching time.

![Figure 3.5 Effect of leaching time on the productivity of total humic acids.](image)

4. Conclusions

In the experiment of alkali extraction of humic acids from the carbonaceous gold ore, the concentration of sodium hydroxide, concentration of sodium pyrophosphate, solid-liquid ratio, leaching temperature and time all have effects on the productivity of total humic acids, of which the effect of leaching time is the most obvious and the effect of leaching temperature is the least.

The optimum extraction conditions obtained by orthogonal experiment were as follows: sodium hydroxide concentration was 0.3 mol/L, sodium pyrophosphate concentration was 0.06 mol/L, solid-liquid ratio was 1:4 g/mL, leaching temperature was 70°C, and leaching time was 24 h. At this time, the productivity of total humic acids was 1.1049%.

The productivity of total humic acids may still increase with the prolongation of leaching time.

Acknowledgements

The authors acknowledge the financial support of the Special Funds for the National Natural Science Foundation of China (No. U1608254), the Open Fund of State Key Laboratory of Comprehensive Utilization of Low-Grade Refractory Gold Ores (ZJKY2017 (B) KFJJ01 &ZJKY2017 (B) KFJJ02) and National Key R&D Program of China (No. 2018YFC1902002).

References

[1] Hong-ying Yang, Qian Liu, Xiang-ling Song and Jin-kui Dong 2013 Transactions of Nonferrous Metals Society of China 23(11)
[2] Xiao-yang Xu 2013 Gold Science and Technology 21(01) 82-88.
[3] Kai-chuang Cai 2014 Gold Science and Technology 22(04) 124-128
[4] Xiu-zhu Su 2017Transactions of Nonferrous Metals Society of China (smelting part) 07 48-51
[5] Qian Li, Wei Qi, Yan Zhang, Huang Shen, Jun Luo, Guang Liu, Bin, Yang Xu, Bin Yong 2018 Precious metals 39 (03) 72-78
[6] K L Rees , J S J V Deventer 2000 Hydrometallurgy 58(1) 61-80
[7] An Wang, Yong-kui Zhang, Han-zhao Liu 2000 Multipurpose Utilization of Mineral Resources (03) 4-8
[8] Zhao-hong Fang 2003 Gold Science and Technology 06 28-35
[9] Zhi-jun Xing, Jin-chang Gao, Cheng-rui Yang 2014 Gold 35 (06) 58-61
[10] Wen-jie Luo, Hong-ying Yang 2015 Multipurpose Utilization of Mineral Resources, (03) 52-54
[11] Appendix B (Normative Appendix) 2016 Method for the determination of total humic acids Humic acid (02) 47-48