Study on enhancing the chromium separation efficiency from tannery sludge by bioleaching

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Abstract： On the base of studies carried on by the former topic group, the article mainly carried on study on enhancing the heavy metal chromium separation efficiency in tannery sludge by bioleaching, through changing the filters material, the solid separation condition, as well as low pH nutrients and so on. Simultaneously the article inspected chromium separation efficiency of chemistry Leaching (1∶1H_2SO_4) under the same condition. The experiment showed that it could enhance the separation efficiency with the acid liquor (1∶1H_2SO_4 configuration).In bioleaching when the pH dropped to 1.80, the separation efficiency could achieve 94.65%, compared to using the distilled water. In chemistry leaching when the pH value dropped to 1.0, the separation efficiency could achieve 96.70%, the surplus chromium content in the sludge may achieve the standard of making the leather sludge as agriculture fertilizer.

Key words： leather making sludge; chromium; bioleaching; chemical leaching

1 Introduction

Bioleaching is adopted to treat the heavy metal chromium in tannery sludge to release it from the slu-dge efficiently. The aim of bioleaching is to enhance the safety of agricultural sludge, expand agricultural application of sludge and lower the accumulation of heavy metals in soil [1].The basic principles of biolea-ching is that it makes use of catalytic oxidation by specific types and self-support acidophilic Thiobacilli to reduce the pH of the sludge system. Then the insoluble forms of heavy metals are dissolved out from the solid-phase into the liquid. Finally, heavy metals are removed from the sludge through the sludge dew-atering [2,3].The scholars of Canada have carried out much system research. It is found that the removal of many heavy metals in sludge can reach 85%～100%,whereas less 40% of the chromium. Up to now the bioleaching technology is internationallly adopted the treatment of urban sewage sludge. Though it is studied to treat tannery sludge to a certain extent[4],the removal of heavy metal chromium is not enough to meet the standard of agricultural sludge. On the basis of the optimal conditions of tannery sludge cultiva-tion obtained by the former task, the removal of chromium is achieved 70% [5]. However, the remaining chromium content in the excess sludge is still far from agricultural safety standards.

In order to enhance the chromium separation efficiency from tannery sludge by bioleaching, the artic-le mainly studied the influence on chromium separation efficiency with changing the filters material, the solid separation condition, as well as low pH nutrients and so on. It was shown that the chromium separa-tion efficiency was increased considerably, making the remaining chromium content in the excess sludge meet the standard of agricultural sludge. It not only eliminated chromium pollution but also provided the condition of recycling bioleaching filtrate, to achieve environmental protection and energy saving require-ments.

2 Materials and methods

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2.1 Materials

Concentrated sulfuric acid(chemically pure, 1.84 of relative density);

Elemental sulfur (analytically pure, Haijing Fine Chemical Factory, Hebei District in Tianjin);

Concentrated nitric acid (analytically pure 65% ～ 68%, Xi'an Chemical Reagent Factory) ; Perchloric acid (analytically pure 70.0%～72.0%, Chengdu Chemical Reagent Factory) ;

Tannery activated sludge from Zibo, Shandong.

2.2 Determination of tannery activated sludge

The pH value, solid phase content, chromium content in the supernatant fluid of sludge and settling sludge was determined through pH meter of pHS-25, constant weight test and acidic potassium permanganate oxidation test respectively. Joint resolution of three strong oxidizing acids was adopted to counteract the sludge.

2.3 Bioleaching experiment of tannery activated sludge

600ml activated sludge and 12g sulfur were added into 1000ml beaker. Then the beaker was put in a stable temperature Horizontal shaking bather with 30℃± and 400r±·min^{-1}, the pH value was tested every day. When the pH value of the miscible liquids was dropped to 3.5±, 2.5g tannery dry sludge and 4g sulfur were added into the beaker. The total added dry sludge and sulfur were separated into three times until the pH value no longer dropped. Meantime blank experiment without activated sludge was done. Four separation methods, the distilled water washing, the homologous pH acid liquor washing (1∶1H_2SO_4 configuration), the acid and submersed liquor washing, acid liquor washing and vacuum filtration, were used to obtain supernatant fluid. The filter medium was crocus cloth. The excess sludge was oven-dried. The chromium content in the supernatant fluid and the excess sludge were determined.

2.4 chemical leaching experiments

7.5g lapped finishing tannery dry sludge and 200ml distilled water were added into 500ml beaker in stir condition, and the 1∶1H_2SO_4 solution was used to reduce the pH value. When the pH value were dropped respectively to 3.0±、2.0±、1.0±, the four separation methods were adopted to separate the mixture if the pH value no longer reduced after standing 2～3h. The filter medium was crocus cloth. The excess sludge was oven-dried. The chromium content in the supernatant fluid and the excess sludge were determined.

3 Results

3.1 Results of determination of tannery activated sludge

3.1.1 Determination of the pH value

The original pH value of tannery activated sludge was 7.9±, showing alkalescent phase. It was concluded that chromium was mostly existent in the form of $Cr(OH)_3$ in tannery sludge. It was needed to reduce pH value to dissociate chromium (III) [6]. Chemical leaching needed much sulphuric acid, causing diseconomy. But bioleaching made use of catalytic oxidation of specific types and self-support acidophilic Thiobacilli to reduce the pH of the sludge system to dissociate chromium (III) from the sludge into liquid phase. Then chromium was removed through sludge dewatering. Bioleaching was economical and simple.

3.1.2 Determination of solid phase content

The results of solid and liquid phase content in the tannery activated sludge were as follows in Tab.1.

Tab.1 The determined data of solid content in tannery activated sludge

No.	*The weight of evaporating dish /g*	*The total weight of evaporating dish and sludge /g*	*The dried weight of dish and sludge /g*	*Liquid phase content*	*Solid phase content*

1#	9.4582	11.8862	9.4897	98.70%	1.30%
2#	8.9680	10.4710	8.9869	98.74%	1.26%
medium value	—	—	—	98.72%	1.28%

The influence of sludge concentration on the pH value of bioleaching is that the cushioning capacity of the leaching system to pH value reduction become increased with the higher sludge concentration. It was shown that the lower sludge concentration could reduce the pH value rapidly to dissociate heavy metals [7]. Fang Di pointed out that after 4d with the 2%～6% concentration of sludge, the pH value dropped under 2, whereas after 6d with 6% concentration beyond [8]. But in view of different sludge in this experiment, solid concentration only played a small part in factors influencing the pH value reduction.

3.1.3 Determination of chromium content in the tannery activated sludge

The results of chromium content in the the supernatant fluid and activated sludge were as follows in Tab.2.

Tab.2 The determined data of chromium content in tannery activated sludge and supernatant fluid

No.	*The weight of driedsludge /g*	*chromium content /(mg·L^{-1})*	*chromium content /(mg·kg^{-1})*	*chromium content in the supernatant fluid /(mg·kg^{-1})*
1#	0.1344	0.67	1246.28	0.194
2#	0.1345	0.691	1284.39	0.195
medium value	—	—	1265.34	0.1945

It was shown that the original chromium content in tannery sludge from Zibo, Shandong was lower. The reason was that amounts of chromium was precipitated by added chemical agent in primary settling tank. Chromium was mostly existent in the form of $Cr(OH)_3$ in tannery sludge in the activated sludge, whereas low levels of sludge supernatant.

3.2 Results of bioleaching experiment

3.2.1 Cultivation result of tannery activated sludge from Zibo

In the process of cultivation of tannery activated sludge from Zibo, the pH value kept reducing, such as in the Fig. 1 shown.

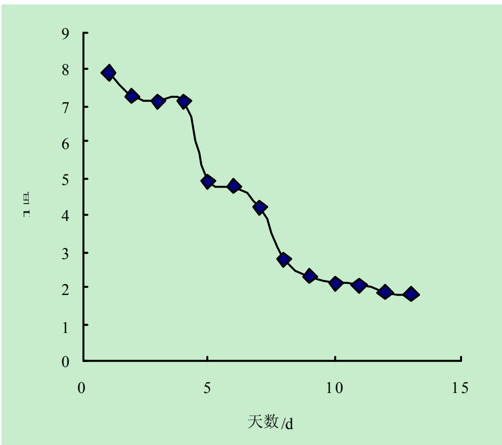

Fig. 1 The variation trend of pH value in Tannery activated Sludge

The pH value continuing to reduce was resulted by catalytic oxidation of acidophilic Thiobacilli which was able to oxidize elemental sulfur to sulphuric acid. The microbial activity of activated sludge was relatively weak owing to lack of nutrients. Because of adaptive phase needed after adding sulfur powder (20g·L^{-1}) [9], the initial drop in pH value is relatively slow in early cultivation. Then glucose, ammonium chloride and potassium dihydrogen phosphate were supplemented in order to provide N、P、K nutrition. The pH value reached to 1.80 in 13d. As shown in the former studies [10,11], the pH value only dropped to 2.0± in the conventional bioleaching. However, it reached to much lower level in this test. It was concluded that nutrient substance played an important role.

3.2.2 Bioleaching result of tannery sludge

Bioleaching was adopted to separate chromium in the tannery sludge. The filter medium was crocus cloth. Different separation methods were used to obtain supernatant fluid. The chromium content in the supernatant and the excess sludge were determined. When the pH dropped to 1.80, it was shown that if 1：1H_2SO_4 acid liquor washing used to separate chromium, the chromium content in the supernatant and the excess sludge were 0.56 mg·L^{-1}, 0.15 mg·g^{-1} respectively. The separation efficiency was 81.45%. If the acid and submersed liquor washing used, the chromium content were 0.60 mg·L^{-1}, 0.08 mg·g^{-1} respectively. The separation efficiency was 87.35%. If acid liquor washing and vacuum filtration used, the chromium content were 0.65 mg·L^{-1}, 0.03 mg·g^{-1} respectively. The separation efficiency was 94.65%, which was much higher than that with the distilled water washing to separate chromium.

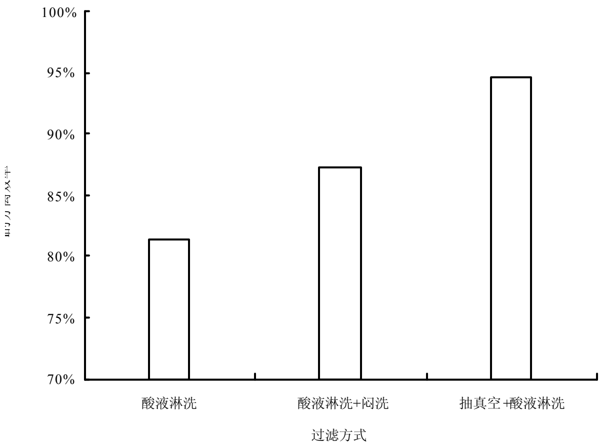

Fig. 2 The variation trend of different solid separation conditions by bioleaching (pH1.80)

It was demonstrated that the bioleaching efficiency was effected not only by temperature, O_2 and CO_2 concentration, initial pH, sludge type and concentration, type and concentration of substrate, inhibitor, Fe^{3+} concentration[11-13], but also filter medium and filter washing way.

When the pH value dropped to 1.80 in this test, the bioleaching efficiency was much more increased by the different separation methods mentioned. The optimum separation efficiency was 94.65%. The reason that acid liquor washing, the acid and submersed liquor washing, acid liquor washing and vacuum filtration increased separation efficiency was that washing with distilled water would make the pH value increased, then chromium transferred into the liquid phase may be re-adsorbed on the remaining sludge, affecting the separation efficiency. But washing with acid liquor of the same pH value could reduce the adsorption of chromium, chromium dissolution was almost complete.

3.3 Results of chemical leaching

3.3.1 1：1H_2SO_4 chemical leaching

1：1H_2SO_4 chemical leaching was used to separate chromium in dried tannery sludge from Xuzhou. The filter medium was crocus cloth. Different separation methods were used to separate mixture when the pH dropped to 3.0±、2.0±、1.0± respectively. The chromium content in the supernatant and the excess sludge were determined.

When the pH dropped to 3.0±（2.89）, the chromium content in the supernatant was 2.99 $mg \cdot g^{-1}$ with the distilled water washing, and the separation efficiency was 20.95%. The corresponding chromium content in the supernatant and their leaching efficiency were 3.80 $mg \cdot g^{-1}$，3.97 $mg \cdot g^{-1}$，4.23 $mg \cdot g^{-1}$，and 26.45%,27.90%,29.35% respectively with the 1：1H_2SO_4 acid liquor washing, the acid and submersed liquor washing, acid liquor washing and vacuum filtration.

When the pH dropped to 2.0±（1.96）, the chromium content in the supernatant was 8.05 $mg \cdot g^{-1}$ with the distilled water washing, and the separation efficiency was 56.66%. The corresponding chromium content in the supernatant and their leaching efficiency were 8.66 $mg \cdot g^{-1}$，8.81$mg \cdot g^{-1}$，9.11 $mg \cdot g^{-1}$，and 60.75%,61.70%,64.20% respectively with the 1：1H_2SO_4 acid liquor washing, the acid and submersed liquor washing, acid liquor washing and vacuum filtration.

When the pH dropped to 1.0±（0.99）, the chromium content in the supernatant was 11.96$mg \cdot g^{-1}$ with the distilled water washing, and the separation efficiency was 83.75%. The corresponding chromium content in the supernatant and their leaching efficiency were 12.60 $mg \cdot g^{-1}$, 12.93 $mg \cdot g^{-1}$, 13.77 $mg \cdot g^{-1}$, and 88.55%,90.95%,96.70% respectively with the 1：1H_2SO_4 acid liquor washing, the acid and submersed liquor washing, acid liquor washing and vacuum filtration.

The determined results were demonstrated as follows in Fig.3, Fig.4 and Fig.5.In the Figs, the distilled water washing, 1：1H_2SO_4 acid liquor washing, the acid and submersed liquor washing, acid liquor washing and vacuum filtration were represented by No. 1,2,3,4.

Fig.3 The variation trend of different solid separation conditions by chemical leaching (pH2.89)

Fig.4 The variation trend of different solid separation conditions by chemical leaching (pH1.96)

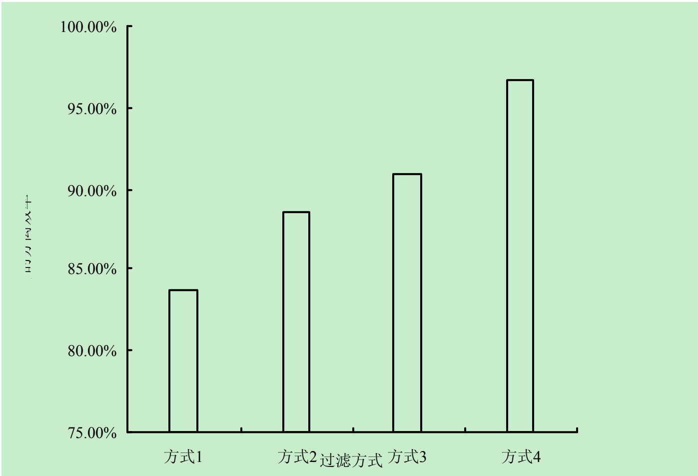

Fig.5 The variation trend of different solid separation conditions by chemical leaching(pH0.99)

It was drawn the conclusion from chemical leaching results that in the same separation conditions, with the decline in pH value, the rate of leaching increased gradually. When the pH value was 2.0, a significant increase in leaching rate appeared. When the pH value dropped to 1.0, the leaching efficiency was more than 96%, which proved that the pH value had an important influence on leaching efficiency. The study has shown that the pH value was the most critical factor in the process of chromium dissolution [14]. If the pH value was less than 2, the chromium removal of sludge can reach more than 80%.While it dropped to 1.6, chromium dissolution was almost complete.

In the same condition of the pH value, the changes in separation conditions could improve leaching efficiency. Leaching rate from low to high order were as follows: the distilled water washing, the homologous pH acid liquor washing (1∶1H_2SO_4 configuration), the acid and submersed liquor washing, acid liquor washing and vacuum filtration. In particular, the leaching efficiency reached up to 96.70% with acid liquor washing and vacuum filtration, so that the remaining chromium content in tannery sludge （530mg·kg^{-1}）could achieve the agricultural standard in acid soils （《1000mgCr·kg^{-1}）.

3.3.2 Chromium content Determination in tannery dried sludge

The result of original chromium content in tannery dried sludge from Xuzhou was shown in Tab.3.

Tab.3 The determined data of Chromium content in Tannery dry Sludge

No.	*The weight of dried sludge /g*	*Chromium content /(mg·g^{-1})*	*The average chromium content /(mg·g^{-1})*
1#	0.1279	14.01	
2#	0.1210	14.36	14.18
3#	0.1206	14.17	

After chemical leaching, the pH value of sludge system dropped to 0.99. With separation of supernatant, the chromium content determined in the excess sludge was shown in Tab.4.

Tab.4 The determined data of Chromium content in absolute dry Tannery Sludge by chemistry leaching (pH0.99)

No.	The weight of dried sludge /g	Chromium content /(mg·g-1)	The average chromium content /(mg·g-1)
1#	0.1008	0.50	
2#	0.1100	0.59	0.53
3#	0.1020	0.54	

It was concluded from determined results that tannery sludge contains a large number of chromium. The content was more 14.20 times than that （1000mgCr·kg-1）regulated in the pollutant control standards of China's agricultural sludge (GB4284-84).In this study, the leaching efficiency reached up to 96.70% in the use of acid liquor washing and vacuum filtration. The remaining chromium content in the sludge was far from that in control standards. Therefore, the key to chemical leaching is to make the sludge pH value dropped to below 1.0 to leach more chromium.

4 Conclusions

(1) In order to enhance chromium separation efficiency in tannery sludge by bioleaching, the pH value needs to drop to less than 1.80.

(2) When the pH value of 1.80 by bioleaching, the optimum leaching efficiency reach up to 94.65% with acid liquor washing and vacuum filtration.

(3) When the pH value of 1.0± by chemical leaching, the separation efficiency of chromium is increased remarkably. The optimum leaching efficiency is 96.70% with acid liquor washing and vacuum filtration.

Compared to chemical leaching, in the treatment of tannery sludge, sulphur needed in bioleaching is inexpensive to cost savings. Bio-leaching liquor derived from tannery sludge contains amounts of chromi -um which can be reused in tanning process. The study by Ma Hongrui and Zhou Lixiang[15] have shown that compared with regular tanned hide by using Cr tanning agent, the hide tanned bio-leachate contained 3-4mg/L of Fe. However, the shrinkage temperature and Cr content of the hides were almost similar to re -gular tanned hide. Heavy Fe content could influence Cr absorption in hide and changed color of the hide. Because of high Fe content in bio-leachate, Fe needs to be separated in the reuse process. In the study by Ma Hongrui[16], solvent extraction of Iron(Ⅲ)and chromium(Ⅲ) was studied by bis(2-ethylhexy1) phosph -oricacid(D2EHPA), and the associate effect of tributy1 phosphate(TBP)was also examined by mixed with D2EHPA in research. The results shows that completely removal of Fe(Ⅲ) from the leachate could be achieved by 5％ D2EHPA in n—hexane at equilibrium pH 2.2.

The chromium content in the excess sludge can measure up to the sludge agricultural standard. However, the sludge has the problem of high acidity, so it can not be directly used for agricultural fertilizer. Lime will be added as acidity regulator which will increase self-cost. But compared to chromium pollution, bioleaching adopted to treat tannery sludge still has broad prospects.

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