Application of Acidophilic Microorganism in the Metal Enrichment of Electroplating Sludge Use the Membrane Bioreactor

Yiran Yang

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Huichao Chu

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Can Qian

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Chunyou Jia

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Shiyue Qi

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Baoping Xin (✉ xinbaoping@bit.edu.cn)

Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China <https://orcid.org/0000-0002-8105-4662>

Research

Keywords: biotechnology, membrane bioreactor, metal enrichment, electroplating sludge

Posted Date: August 10th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-54149/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Application of acidophilic microorganism in the metal enrichment of electroplating sludge use the membrane bioreactor

Yiran Yang¹, Huichao Chu¹, Can Qian¹, Chunyou Jia¹, Shiyue Qi¹, Baoping Xin^{*1}

¹ Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Abstract

Background: Bioleaching is an important technology for treating electroplating sludge. Previous researches have focus on improving the leaching rate of metals in electroplating sludge by bioleaching. However, the concentration of heavy metals in the leachate after single leaching was lower, which is quite unfavorable for subsequent metal recovery. Additionally, membrane bioreactors (MBRs) have been widely used in the field of sewage treatment. Research on the application of bioleaching technology combined with MBRs to enrich metals in electroplating sludge has not been reported. Therefore, in this study, we first combined bioleaching technology and MBRs for metal enrichment in electroplating sludge to obtain the key technology of "acid production - electroplating sludge leaching - leachate regeneration -repeated electroplating sludge leaching - achievement of valuable metal enrichment".

Results: In this research, through scaling up from the laboratory scale (shake flasks) to a factory-scale application (10 m³ membrane bioreactors), we mastered the key technology of acid production by acidophilic microorganism, and the acid solution

* Corresponding author: E-mail address: xinbaoping@bit.edu.cn (B.P. Xin).

can be repeatedly used for metal leaching. The results showed that the MBR maintained high-density cell growth ($\approx 2.1 \times 10^9/\text{mL}$) and a stable sulfuric acid production rate (850 L/h) throughout the entire operational period. Under the above conditions, the maximum cycle number (10 times) for enrichment of the target metals in the electroplating sludge was obtained. Additionally, after the end of the cycle enrichment process, the concentrations of the target metals Ni^+ , Cu^{2+} , and Zn^{2+} were 13.867 g/L, 18.118 g/L and 21.075 g/L, respectively, which were highly enriched.

Conclusions: This study first solved the difficulties in the industrialization of bioleaching electroplating sludge through combining bioleaching technology and MBRs. Furthermore, this research can provide a demonstration project for the industrial application of MBR-bioleaching technology in electroplating sludge, with a view to applying this technology to the disposal of more types of hazardous waste.

Keywords: biotechnology; membrane bioreactor; metal enrichment; electroplating sludge.

Background

Membrane bioreactors (MBRs) are a new water treatment technology that combines membrane a separation unit with a biological treatment unit. The membrane module is used to replace the secondary sedimentation tank in the traditional activated sludge process [1, 2]. Membrane bioreactors not only occupy a small area, produce less sludge, and operate flexibly and stably but also achieve high-efficiency solid-liquid separation due to the excellent interception performance of the membrane

module [3,4], which makes the effluent water quality better and enables direct recycling of the effluent to achieve wastewater reuse [5, 6]. To analyse the current research direction and trends related to MBRs, a Web of Science database was used to search for the keywords “membrane bioreactor” and “bioleaching” from January 2010 to 2020. Using CiteSpace software, the evolution of the keywords in the field of MBR in the past ten years was obtained, and the dynamic evolution of the research hotspots was analysed with respect to time. The results are shown in Fig. 1 and Fig. 2. As shown in Fig. 1, there are 11 types of clusters in the field of MBR research in the past ten years, which mainly involve water recycling, adsorption, flat membranes, online cleaning and so on. All keyword clusters presented high overlap, showing that these keywords have a strong relationship. Fig. 2 shows the dynamic evolution of the research hotspots related to MBRs in the past decade. The research fields related to MBRs are becoming increasingly detailed, and the research content is becoming increasingly abundant, showing a trend of diversified development. The research hotspots have shifted from wastewater treatment, membrane pollution and pollutant removal rate to membrane pollution control and landfill leachate treatment. In recent years, scholars have carried out extensive research on the application of MBRs in wastewater treatment and have also obtained good research results. However, the application of MBRs in the bioleaching of electroplating sludge has not been reported.

The electroplating industry produces a great deal of wastewater, which has a high chemical oxygen demand, a high heavy metal content and a complex composition [7]. Moreover, the types and concentrations of pollutants in wastewater vary with the

types of metal plating and the cleaning methods used for plating parts [8]. Therefore, it is necessary to treat electroplating wastewater to reduce the concentration of heavy metals in wastewater and to meet the relevant discharge standards. At present, electroplating wastewater is generally treated by the traditional treatment method of “pollution first, treatment later”, and a large amount of electroplating sludge is generated during the treatment process. Statistically, nearly 5×10^4 tons of electroplating sludge is discharged per year in China [9]. Electroplating sludge has the characteristics of a large discharge volume and high harmfulness. If not treated properly, such sludge will cause serious secondary pollution to the environment [10]. Therefore, it is urgent to seek a scientific, green and safe electroplating sludge treatment technology to realize the recovery and utilization of resources. Such technology is highly significant for protecting the environment, improving the level of environmental governance and promoting the sustainable development of the electroplating industry [11].

At present, safe landfilling after stabilization/solidification is the main method used to treat electroplating sludge [12, 13]. However, the cost of this method is high (200-500 EUR/ton), which undoubtedly increases the economic burden of electroplating enterprises [14, 15]. In addition, safe landfilling not only leads to certain environmental risks but also causes the loss of metal resources. Therefore, the recovery of valuable metals from electroplating sludge is the goal of electroplating enterprises; such recovery can reduce the environmental risk and effectively mitigate the loss of valuable metal resources. Hydrometallurgy and pyrometallurgy are two

primary metal recovery processes [16, 17]. The principle of hydrometallurgy is based on the feature that metals are easily soluble in acids. After strong acid extraction, metal ions can be separated and purified by different methods. However, this method uses strong acid as the medium, has high requirements in terms of materials and has a high safety risk. The principle of pyrometallurgy is that under high-temperature conditions, metals are separated through oxidation, reduction, decomposition, volatilization, and condensation to achieve the separation of different components. However, this method requires high energy consumption and a large investment and produces substantial secondary pollution.

Our previous research [18] showed that a mixed bacterial system consisting of *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, and *Leptospirillum ferriphilum* can use inexpensive sulfur and pyrite (FeS_2) as a mixed energy substrate to produce dilute sulfuric acid with a pH of 1.0. The dilute sulfuric acid produced by leaching strains can be used instead of sulfuric acid produced by the chemical industry for the recovery of heavy metal ions in electroplating sludge. However, the long cultivation period of leaching strains and the low productivity of dilute sulfuric acid lead to the low efficiency of biosulfuric acid treatment of electroplating sludge. This research focuses on shortening the acid production period through a self-designed MBR and improving the pulp density of leaching electroplating sludge through designing the circulation parameters. Additionally, in this study, a combination of MBR and bioleaching technology is first used for the disposal of electroplating sludge to obtain the key technology of "acid production - electroplating

sludge leaching - leachate regeneration - repeated electroplating sludge leaching - achievement of valuable metal enrichment". Furthermore, this research can provide a demonstration project for the industrial application of MBR-bioleaching technology in electroplating sludge, with a view to applying this technology to the disposal of more types of hazardous waste.

Materials and Methods

Analysis of the electroplating sludge sample

Sample digestion

In this research, the electroplating sludge came from an electroplating factory in Taizhou, Zhejiang Province. The samples were dried and crushed for analysis. A suitable amount of sample was put into the digestion instrument (SH230N, Haineng Instrument, china), and the electroplating sludge sample was digested by the “hydrofluoric acid and nitric acid and hydrochloric acid method”[19, 20]. The concentrations of heavy metals in the samples were analysed by inductively coupled plasma-atomic emission spectrometry (TCAP6300 SERICS, Thermo Scientific, US).

X-ray fluorescence analysis (XRF) of samples

XRF (XRF-1800, Shimadzu, Japan) can analyse the kinds and contents of elements in a sample. X-rays produce fluorescence and excite the tested sample, and different elements in the sample will emit secondary X-rays with different energy characteristics or wavelength characteristics. The secondary X-rays are used in the detection system for energy and quantity analysis, and the analytical information is transformed by the instrumental software to obtain the kinds and contents of different

elements in the samples. In this research, the analytical conditions were as follows: X-ray tube pressure: 60 kV max, 150 ma max; X-ray tube target: Rh target; detection range of elements: 4 Be-92 U; and maximum scanning speed: 300/min.

Analysis of the micromorphology of electroplating sludge (SEM, TEM, EDS)

SEM (scanning electron microscope, FEI-Quanta FEG 250, Shimadzu, Japan) can observe the surface morphology of a sample by electronic signal imaging and analyse the microstructure of the sample, which is of great significance in the microstructure analysis of electroplating sludge. TEM (transmission electron microscope, JEOL-2010F, Shimadzu, Japan) can be used to observe the size and morphology of a sample and is often used to study the appearance and size of the sample. EDS (energy dispersive spectrometer, JEOL-2010F, Shimadzu, Japan) with SEM and TEM is usually used to detect the types and contents of elements in a micro-area of a sample. The analytical conditions were as follows: the acceleration voltage was 20 kV, the initial angle was 40 deg, the magnification was 500-200000; and the operating voltage for TEM and SEM was 200 kV.

H₂SO₄ production and electroplating sludge metal leaching

Optimum pulp density for metal leaching of electroplating sludge

Based on our previous research [18], under the optimized process conditions of 33.6 °C for the temperature, 3.1 m³/min for the aeration rate and 83 rpm for the stirring velocity, a high production efficiency of H₂SO₄ at pH 1.0 (≈850 L/h) was obtained [21]. The sulfuric acid produced by the membrane bioreactor was used for metal leaching experiments in electroplating sludge. To study the effect of different

pulp densities in 10 m³ extraction tanks on the leaching of heavy metals in electroplating sludge, six groups of different pulp densities were designed for comparison. The experimental groups are shown in Table 1. Step 1: The sludge is crushed and collected for leaching. Step 2: All circuits, instruments, and equipment are checked for faults. Step 3: The biological sulfuric acid produced by the membrane bioreactor is pumped into the 10 m³ extraction tanks through an acid-resistant pump. Step 4: The stirring system is turned on, and the crushed electroplating sludge is slowly added according to the pulp density (w/v) in Table 1. Stirring proceeds for 180 min at 120 rpm. Step 5: Every 30 minutes, a sample is collected with a 10 ml pipette and centrifuged, and then the centrifuged supernatant is collected and diluted in a test tube. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, TCAP6300 SERICS, Thermo Scientific) is used to analyse the heavy metal concentration in the leachate and calculate the leaching rate of each metal. Step 6: Solid-liquid separation. After stirring, the sludge in the stirring tank is passed into a filter press through a pump, and the supernatant liquid is collected for use.

Optimum stirring velocity for metal leaching of electroplating sludge

To study the effect of different stirring velocities in the 10 m³ extraction tank on the leaching of heavy metals in electroplating sludge, five groups of comparative experiments with different stirring velocities were designed, as shown in Table 2. Step 1: The sludge is crushed and collected for leaching. Step 2: All circuits, instruments, and equipment are checked for faults. Step 3: The biological sulfuric acid produced by the membrane bioreactor is pumped into the 10 m³ extraction tanks through an

acid-resistant pump. Step 4: The stirring system is turned on, and the crushed electroplating sludge is slowly added at a pulp density (w/v) of 8%. Stirring is performed for 3 min at the experimental stirring velocity specified in Table 2. Step 5: Every 30 minutes, a sample is collected with a 10 ml pipette and centrifuged, and then the centrifuged supernatant is collected and diluted in a test tube. ICP-AES is used to analyse the heavy metal concentration in the leachate and calculate the leaching rate of each metal. Step 6: Solid-liquid separation. After stirring, the sludge in the stirring tank is passed into a filter press through a pump, and the supernatant liquid is collected for use.

Optimum leaching time for metal leaching of electroplating sludge

After determining the optimum pulp density and optimum stirring velocity for the leaching of electroplating sludge, to study the effects of different leaching times on the leaching of heavy metals in electroplating sludge in a 10 m³ extraction tank, the following experiments were designed: Step 1: The sludge is crushed and collected for leaching. Step 2: All circuits, instruments, and equipment are checked for faults. Step 3: The biological sulfuric acid produced by the membrane bioreactor is pumped into the 10 m³ extraction tanks through an acid-resistant pump. Step 4: The stirring system is turned on, and the crushed electroplating sludge is slowly added at a pulp density (w/v) of 8% and stirring velocity of 100 rpm. Step 5: Every 15 minutes, a sample is collected with a 10 ml pipette and centrifuged, and then the centrifuged supernatant is collected and diluted with a test tube. ICP-AES is used to analyse the heavy metal concentration in the leachate and calculate the leaching rate of each metal. Step 6:

Solid-liquid separation. After stirring, the sludge in the stirring tank is passed into a filter press through a pump, and the supernatant liquid is collected for use.

Metal enrichment in electroplating sludge

According to the concentration analysis of heavy metal ions in the leaching supernatant of electroplating sludge by ICP-AES, at 8% pulp density, the target metal concentration in the leaching solution was low after one round of leaching (the $\text{Ni}^+/\text{Cu}^{2+}/\text{Zn}^{2+}$ concentrations were 1401 ppm/1959 ppm/2020 ppm, respectively). It was quite difficult to recover the target metals. To increase the concentrations of the target metals in the leaching solution, a cycle experiment was designed as follows: Step 1: The sludge is crushed and collected for leaching. Step 2: All circuits, instruments, and equipment are checked for faults. Step 3: The biological sulfuric acid produced by the membrane bioreactor is pumped into the 10 m³ extraction tanks through an acid-resistant pump. Step 4: The stirring system is turned on, and the crushed electroplating sludge is slowly added at a pulp density (w/v) of 8%, stirring velocity of 100 rpm, and leaching time of 150 min. Step 5: A sample is collected with a 10 ml pipette and centrifuged, and then the centrifuged supernatant is collected and diluted in a test tube. ICP-AES is used to analyse the heavy metal concentration in the leachate and calculate the leaching rate of each metal. Step 6: Solid-liquid separation. After stirring, the sludge in the stirring tank is passed into a filter press through a pump, and the supernatant liquid is collected for use. Step 7: The separated liquid is returned to the membrane bioreactor through a pump for microbial acid production. Steps 1-7 were repeated. The sample after each cycle of solid-liquid separation was

marked as a raw material for later experiments.

The flow chart of the 10 m³ membrane bioreactor target metal cycle enrichment experiment is shown in Fig. 3:

Criteria for the end of the cycle enrichment experiments: One criteria: When the cell number of microorganisms in the MBR drops sharply (i.e., when the cell number is less than 10⁹ cells/ml) or when the pH of the MBR fluctuates greatly (i.e., when the pH in the MBR is higher than 1.0), the acid production and cycle enrichment experiments should be stopped. The other criteria: When the leaching rate of the target metal in the leaching experiment in the stirred tank is less than 100%, the acid production and cycle enrichment experiments should be stopped.

Results and Discussion

Morphological structure and target metal content of electroplating sludge

Digestion analysis of target metal content in electroplating sludge.

The sample was digested, and it was found that the electroplating sludge mainly contained Ni, Cu and Zn and that the contents of the target metals were 1.75% (Ni), 2.45% (Cu), and 2.53% (Zn), respectively.

X-ray fluorescence spectrometry (XRF) of samples

The XRF analysis results of the composition of the electroplating sludge sample are shown in Fig. 4. From the XRF component analysis chart of the electroplating sludge sample, we can conclude that the main component of this sample was iron oxide but that there were also some valuable metals (Ni, Cu and Zn) and very small amounts of highly toxic metals (Cr and Cd). In addition, the sample contained some

impurity components, but their concentrations were relatively low. The contents of the target metals were basically consistent with the results of the quantitative digestion analysis.

3. Microstructure analysis of electroplating sludge (SEM, TEM, and EDS)

Scanning electron microscopy was applied to analyse the microstructure of the electroplating sludge. The results are shown in Fig. 5. It can be seen from Fig. 5 that the microscopic morphology of the electroplating sludge presented agglomerates with different sizes and irregular shapes. In addition, the light and dark areas in Fig. 5 are uneven. According to the principles of SEM/TEM analysis [22, 23], areas with a small electron scattering angle are bright, indicating that the atom density is low or there are pores in this area. Areas with a large electron scattering angle are dark, indicating that the atom density is higher in this region; the darkest part indicates that the atom density is the highest in this area. Combined with the SEM-EDS data for the electroplated sludge sample in Fig. 6, it can be seen that the contents of the target metals Ni and Cu in the sample were 1.67% and 2.23%, respectively, which is consistent with the XRF results. Zn was not detected in the EDS test, which may be due to the poor uniformity of the target metal distribution in the electroplating sludge and the lack of Zn in the area of the limited energy spectrum sweep.

Optimization of leaching conditions for electroplating sludge in a 10 m³ MBR

Optimum pulp density for metal leaching of electroplating sludge

The variation in the leaching rate of the target metal ions over time in the bioleaching of electroplating sludge with different pulp densities is shown in Fig. 7. It

can be seen from Fig. 7 that the leaching rates of the target metal ions over time in electroplating sludge with different pulp densities show similar trends. In the first 30 minutes of the electroplating sludge leaching reaction, the leaching rate of the target metal ions in the sludge increased rapidly, and then the leaching rate slowed. When the leaching reaction time was 150 min, the leaching rate showed a maximum value. In addition, the target metals could be completely leached when the pulp density was 4%, 6%, and 8%; when the pulp density was 10% or 12%, the target metals could not be fully leached. These results show that the pulp density of bioleaching electroplating sludge has a significant effect on the leaching rate of heavy metal ions in the sludge. The smaller the pulp density was, the higher the leaching rate of heavy metal ions was at a given time. The above results indicate that under the studied conditions, the optimal pulp density of bioleaching electroplating sludge is 8% under the premise of increasing the treatment amount of electroplating sludge as much as possible.

Optimum leaching time for metal leaching of electroplating sludge

The variation in the leaching rate of the target metal ions over time in bioleaching electroplating sludge with different leaching times is shown in Fig. 8. It can be seen from Fig. 8 that the leaching rates of the target metal ions over time in electroplating sludge with different leaching times show similar trends. In the first 30 minutes of the electroplating sludge leaching reaction, the leaching rates of the target metal ions in the sludge increased rapidly, and then the leaching rates of the target metal ions slowed. When the leaching reaction time was 150 min, the leaching rates

showed a maximum value. The above results indicate that under these conditions, the optimal extraction time for bioleaching electroplating sludge is 150 min.

Optimum stirring velocity for metal leaching of electroplating sludge

The variation in the leaching rates of the target metal ions over time in bioleaching electroplating sludge with different stirring velocities is shown in Fig. 9. It can be seen from Fig. 9 that the leaching rates of the target metal ions over time in electroplating sludge with different stirring velocities in the extraction tank show a similar trend. During the first 30 minutes of the electroplating sludge leaching reaction, the leaching rates of the target metal ions in the sludge increased rapidly, and then the leaching rates slowed. When the leaching reaction time was 150 min, the leaching rates showed a maximum value. In addition, the target metals could be completely leached at 100 rpm, 120 rpm, and 140 rpm; at 60 rpm and 80 rpm, the target metals could not be completely leached. This result shows that the stirring velocity of bioleaching electroplating sludge has a significant effect on the leaching rate of heavy metal ions in sludge. The greater the stirring velocity of the leaching tank was, the higher the leaching rate of heavy metal ions was at a given time. The above results indicate that under the studied conditions, the optimal stirring velocity of bioleaching electroplating sludge is 100 rpm.

Maximum cycle number and metal enrichment concentration in the 10 m³ MBR

Under the optimal conditions, we performed a cyclic heavy metal enrichment experiment in accordance with the above experimental steps. The variations in the bacterial count, pH and concentration of heavy metal ions in the MBR during the

cycle process are shown in Fig. 10. It can be seen from Fig. 10 that during the 10 cycles, the cell concentration in the MBR was maintained at $(2.2-2.3) \times 10^9$ cells/ml, and the pH was maintained at approximately 1.0. Combined with Fig. 11, after 10 cycles, the enriched concentrations of three target metal ions (Ni^+ , Cu^{2+} , and Zn^{2+}) in the MBR were 13.867 g/L, 18.118 g/L, and 21.075 g/L, respectively. The results indicate that the activity of the bioleaching strain was not greatly affected by the cycle number within 10 cycles. In other words, the bioleaching strain can tolerate the concentration of heavy metal ions within this timeframe.

In addition, it can be seen that the bacterial cell number and pH in the membrane bioreactor fluctuated slightly at the beginning of each cycle. This fluctuation can be attributed to the fact that when leaching solution containing heavy metal ions was returned to the membrane bioreactor, the pH of the leaching solution (1.3-1.5) was higher than the pH (1.0) in the membrane bioreactor, and the leaching solution returned to the membrane bioreactor at a certain speed under the control of the pump. Therefore, the pH slightly fluctuated, but the fluctuation was small. The fluctuation in the cell concentration of the leaching strain was mainly caused by the slow changes in the environment, including the pH of the leaching solution (1.3-1.5) being higher than the pH (1.0) in the membrane bioreactor and the temperature of the leaching solution (room temperature) being lower than that of the membrane reactor (33 °C). During the cycle process, we found that when the cycle experiment was carried out for the 8th, 9th, and 10th cycles, the pH in the membrane bioreactor showed a gradual increase, which was inconsistent with the pH variation during cycles 1th-7th. Accordingly, the

cell concentration of the leaching strain in the membrane bioreactor showed an irreversible decreasing trend at the 8th, 9th, and 10th cycles. These results heralded the end of the cycle enrichment experiment.

Based on the analysis of the above data, we performed leaching toxicity analysis of the electroplating sludge residues after 10 heavy metal cycle enrichment experiments. The results are shown in Fig. 12. It can be seen from Fig. 12 that as the number of heavy metal enrichment cycles increased, the toxic leaching concentrations of the target metals (Ni^+ , Cu^{2+} and Zn^{2+}) gradually approached the national standard limits. Moreover, for the electroplating sludge residues after the 10th cycle of enrichment, the toxic leaching value was higher than the national standard limit. Therefore, based on the above analysis, the maximum number of cycles for the enrichment of heavy metals in electroplating sludge is 10. After 10 cycles, the enrichment concentrations of Ni^+ , Cu^{2+} and Zn^{2+} were 13.867 g/L, 18.118 g/L and 21.075 g/L, respectively.

The mechanism analysis of heavy metals release in electroplating sludge

Consistent with our previous bioleaching experiments at the same experimental conditions[16], the acidophilic microorganism did not directly affect the metal removal efficiencies, but contributed to accelerate the pH decrease and Fe(II/III) ion conversion. The schematic diagram of acidophilic microorganism sulfur metabolic pathway (Fig. 13) depicting the mechanism of H^+ release (Equations (1)-(3)). The mechanism of heavy metals release in electroplating sludge can be describe through the Equations (4) and (5).

Conclusions

In this research, we concluded that the MBR maintained a high cell concentration throughout the entire operational period, providing a stable sulfuric acid production rate (850 L/h), and the acid solution produced by strains was applied to the treatment of electroplating sludge. Under the optimized conditions (8% pulp density, 100 rpm stirring velocity and 150 min leaching time), 100% leaching rates of Ni, Cu and Zn in electroplating sludge were achieved. Based on the excellent interception performance of MBRs for acidophilic microorganisms, we designed a cyclic enrichment experiment for target metals. We repeated the leaching of electroplating sludge through recycling regeneration of acid solution to achieve the enrichment of target metals in the electroplating sludge. Under the optimal leaching conditions for electroplating sludge, the maximum cycle number (10 times) for enrichment of the target metals in the electroplating sludge was obtained. Additionally, after the end of the cycle enrichment experiment, the concentrations of the target metals Ni^+ , Cu^{2+} ,

and Zn^{2+} were 13.867 g/L, 18.118 g/L and 21.075 g/L, respectively. Furthermore, this research can provide a demonstration project for the industrial application of MBR-bioleaching technology in electroplating sludge, with a view to applying this technology to the disposal of more types of hazardous waste.

Abbreviations

MBRs: Membrane bioreactors; FeS_2 : Sulfur and pyrite; SEM: Scanning electron microscope; TEM: Transmission electron microscope; EDS: Energy dispersive spectrometer; ICP-AES: Inductively coupled plasma-atomic emission spectrometry; XRF: X-ray fluorescence spectrometry.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and material

All data generated or analysed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

Funding

This work received financial support from National key research and development program (2018YFC190061), Natural Science Foundation of China (21777007), Beijing Natural Science Foundation (8172042) and Huzhou Sano Environ. Technol. Company, Limited, Zhejiang Province.

Authors' contributions

Yiran Yang and Huichao Chu performed the experiments. Can Qian, Chunyou Jia, Shiyue Qi and Baoping Xin supervised the work. Yiran Yang wrote the manuscript. All the authors edited the manuscript. All authors read and approved the final manuscript.

Acknowledgements

Not applicable.

Authors' information

¹ Department of Energy and Environmental Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

Reference

- [1] Melin T., Jefferson B., Bixio D., et al. Membrane bioreactor technology for waste water treatment and reuse[J]. *Desalination*, 2006, 187(1-3): 271-282.
- [2] Brognaux A., Han S., Sørensen S. J., et al. A low-cost, multiplexable, automated flow cytometry procedure for the characterization of microbial stress dynamics in bioreactors[J]. *Microbial Cell Factories*, 2013, 12: 100.
- [3] Nguyen L. N., Hai F. L., Kang J. G., et al. Coupling granular activated carbon adsorption with membrane bioreactor treatment for trace organic contaminant removal: Breakthrough behavior of persistent and hydrophilic compounds[J]. *Journal of Environmental Management*, 2013, 119: 173-181.
- [4] Dvorak L., Svojitka J., Wanner J., et al. Nitrification performance in a membrane bioreactor treating industrial wastewater[J]. *Water Research*, 2013, 47(13): 4412-4421.
- [5] Wang J. X., Li K., Wei Y. S., et al. Performance and fate of organics in a pilot MBR-NF for treating antibiotic production wastewater with recycling NF concentrate[J]. *Chemosphere*, 2015a, 121: 92-100.
- [6] Yu T., Li D., Qi R., et al. Structure and dynamics of nitrifier populations in a full-scale submerged membrane bioreactor during start-up[J]. *Applied Microbiology and Biotechnology*, 2011, 90(1): 369-376.
- [7] Li C. C., Xie F. C., Ma Y., et al. Multiple heavy metals extraction and recovery from hazardous electroplating sludge waste via ultrasonically enhanced two-stage acid leaching[J]. *Journal of Hazardous Materials*, 2010, 178: 823-833.
- [8] Asavapisit S., Chotklang D.. Solidification of electroplating sludge using alkali-activated

- pulverized fuel ash as cementitious binder[J]. *Cement and Concrete Research*, 2004, 34(2): 349-353.
- [9] Zhang Z. M., Shi X. S.. Formation and Treatment of Electroplating Sludge [J]. *Sci-Tech Information Development & Economy*, 2003, 13(5): 91-92.
- [10] Peng G. L., Deng S. B., Liu F. L., et al. Superhigh adsorption of nickel from electroplating wastewater by raw and calcined electroplating sludge waste[J]. *Journal of Cleaner Production*, 2020, 246: 118948.
- [11] Li P. P., Peng C. S., Li F. M., et al. Copper and nickel recovery from electroplating sludge by the process of acid-leaching and electrodepositing[J]. *International Journal of Environmental Research*, 2011, 5: 797-804.
- [12] Orescanin V., Mikulic N., Mikelic I. L., et al. The bulk composition and leaching properties of electroplating sludge prior/following the solidification/stabilization by calcium oxide[J]. *Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering*, 2009, 44(12): 1282-1288.
- [13] Wang Q.H., Yang J., Wang Q.. Effects of water-washing pretreatment on bioleaching of heavy metals from municipal solid waste incinerator fly ash[J]. *J. Hazard. Mater.*, 2009, 162:812-818.
- [14] Xin B. P., Jiang W. F., Aslam H.. Bioleaching of zinc and manganese from spent Zn–Mn batteries and mechanism exploration[J]. *Bioresource Technology*, 2012a, 106: 147-153.
- [15] Xin B. P., Jiang W. F., Li X.. Analysis of reasons for decline of bioleaching efficiency of spent Zn-Mn batteries at high pulp densities and exploration measure for improving performance[J]. *Bioresource Technology*, 2012b, 112: 186-192.
- [16] Wang J., Huang Q. F., Li T., et al. Bioleaching mechanism of Zn, Pb, In, Ag, Cd and As from Pb/Zn smelting slag by autotrophic bacteria[J]. *Journal of Environmental Management*, 2015b, 159: 11-17.
- [17] Xin B. P., Chen B., Duan N.. Extraction of manganese from electrolytic manganese residue by bioleaching[J]. *Bioresource Technology*, 2011, 102: 1683-1687.
- [18] Yiran Yang, Can Qian, Xingfu Shi., et al. Efficient and industrial production of H₂SO₄ from sulfur sludge by acidophilic cells in a membrane bioreactor via optimizing process[J]. *Journal of Cleaner Production*, 2019, 119444.
- [19] Potysza A., Lens P. N. L., Vossenberg J., et al. Comparison of Cu, Zn and Fe bioleaching from Cu-metallurgical slags in the presence of *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans*[J]. *Applied. Geochemistry*, 2016, 68: 39-52.
- [20] Zhang X., Feng X., Tao J. M., et al. Comparative Genomics of the Extreme Acidophile *Acidithiobacillus thiooxidans* Reveals Intraspecific Divergence and Niche Adaptation[J]. 2016,17,1355.
- [21] Mesquita T. J. B., Sargo C. R., Neto J. R. F., et al. Metabolic fluxes-oriented control of bioreactors: a novel approach to tune micro-aeration and substrate feeding in fermentations[J]. *Microbial Cell Factories*, 2019, 18: 150.
- [22] Gabal M.A., Al-Angari R.S., Al-Angari Y. M.. Mn-Zn nano-crystalline ferrites synthesized from spent Zn-C batteries using novel gelatin method[J]. *J. Hazard. Mater.*, 2012, 246: 227-233.
- [23] Kiddee P., Naidu R., Wong M. H.. Electronic waste management approaches: an overview[J].

Waste Manag., 2013, 33: 1237-1250.

Figures

Figure 1

Cluster analysis of keywords related to membrane bioreactors

Figure 2

Evolutionary trend analysis of keywords related to membrane bioreactors

Figure 3

Flow chart of the target metal cycle enrichment experiment

Figure 4

XRF composition analysis of electroplating sludge samples

Figure 5

Scanning electron microscope images of electroplating sludge with a magnification of $\times 6000$ (left) and $\times 10000$ (right)

Element	C K	O K	Al K	Si K	S K	Fe K	Ni K	Cu K
Weight (%)	37.63	40.39	10.24	0.70	5.62	1.52	1.67	2.23
Atom (%)	48.08	41.47	5.85	0.38	2.70	0.42	0.45	0.65

Figure 6

The scanning electron microscope-energy spectrum results for the electroplating sludge

Figure 7

The leaching rate of target metals from electroplating sludge under different pulp densities

Figure 8

The leaching rate of target metals from electroplating sludge under different stirring velocity

Figure 9

The leaching rate of target metals from electroplating sludge under different leaching time

Figure 10

Variations of cell concentration and pH with the cycle number during target metal cycle enrichment process

Figure 11

Enrichment concentration of ions during target metal cycle enrichment process

Figure 12

Toxic leaching concentration of electroplating sludge with different cycles enrichment number

Sulfur metabolic pathway of acidophilic microorganism