Research on Treating Acid Wastewater Containing Heavy Metals by Sulfate-Reducing Bacteria

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Abstract—**Biological treatment with sulfate-reducing bacteria (SRB) has been considered as the most attractive alternative for heavy-metals-containing effluents decontamination. Ordinarily, these wastewaters contain high concentrations of sulfate and heavy metals, it is extremely essential for the development of a bioremediation technology to prevent its harm. Mechanism of SRB for wastewater treatment had been introduced in the paper, together with the application of treating wastewater containing several typical heavy metals. At last, current problems in engineering application of SRB are explained in the paper.**

Keywords-sulfate-reducing bacteria; mechanism; heavy metal; wastewater

I. INTRODUCTION

Anthropogenic release of heavy metals in the environment is principally related to effluents discharged from mine (drainage), metallurgy, electroplating, dye and other industrial activities. It contains high concentration of sulfate and a large number of soluble heavy metal ions. Receiving water will be acidic and produce potential corrosion. Heavy metals such as zinc, copper, lead and thallium, etc. can be accumulated through food chain and result in chronic poisoning which is increasingly harmful to human being and environment [1-5]. Hence, it is a significant and urgent study field about these effluents' treatments to people's health and ecology environment.

Several methods could be applied to remove heavy metals from acid wastewaters, such as chemical precipitation, ion-exchange, reverse osmosis, and electrolysis process, etc. Despite effective treatment, these methods are extravagant and generate large amounts of residual sludge. Therefore, Biological treatment, as a promising alternative over physical-chemical and other methods for heavy metals removal, is now of considerable interest due to its running costs, strong adaptability and no secondary pollution. It obtains widespread concern by the domestic and international environmental scientists [2].

Anaerobic reduction of sulfate by Sulfate-reducing bacteria (SRB) has been reported to be used for the treatment of a multitude of sulfate-containing industrial effluents. SRB are a kind of anaerobic bacteria with various nutrition types and different shapes, which can dissimilate organisms by using sulfate or other oxidation state sulfides as electron acceptors [6, 7]. SRB have the capabilities to reduce sulfate to sulfide which reacts with certain metals dissolved, such as copper, iron and zinc, forming insoluble precipitates. More and more attention should be gotten for their particular dominances.

II. SRB AND TREATMENT MECHANISM

A. Sulfate-Reducing Bacteria

SRB can universally exist in a variety of environments such as lakes, marshes, paddy fields, petroleum deposits, underground pipelines, some industry wastewaters, and some ruminants' first stomach, etc. SRB have strong survival ability because of the enzymes that won't poisoned by oxygen-containing. SRB are included in a group of chemoorganotrophic and anaerobic bacteria, which contains representatives of the genera *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum*, among others [8]. New genus can be separated and named due to the improvements of technology. There are nearly more than 40 species, 12 genera of SRB now [9].

B. Treatment Mechanism

The mechanism of wastewater treatment by SRB involves two stages: (i) Sulfate-reducing bacteria oxidize simple organic compounds (e.g. acetate, lactate, butyrate, propionate etc.) by utilizing sulfate as an electron acceptor and generating hydrogen sulfide and bicarbonate ion under anaerobic conditions (1)), and (ii) the biologically produced hydrogen sulfide reacts with dissolved heavy metals such as Cu, Zn, and Ni to form insoluble metal sulfide precipitates (2)) [10].

$$2CH_2O+SO_4^{2-}\rightarrow H_2S+2HCO_3^- \quad (1)$$

$$Me^{2+}+H_2S\rightarrow MeS\downarrow+2H^+ \text{ (Me=Metal)} \quad (2)$$

III. ENGINEERING APPLICATION

Physiological and biochemical characteristics of SRB make them have great potential and application space in wastewater treatment. Some successes in wastewater containing heavy metal ions treatment has recently been achieved by SRB. And it has become a hot point and front line gambit among the field of relevant wastewater treatment.

A. Chromium-Containing Wastewater

Acidic wastewater from electroplating, tanning, mining and other industrial wastewater contains a lot of SO_4^{2-}.

Chromium mainly exists in wastewater by Cr (III) and Cr (VI). Cr (VI) is easy to accumulate in organisms and water because of its solubility, strong oxidation, toxicity and other characteristics [4]. Chromium- containing wastewater treatment is particularly important and must be treated before discharged.

Biological treatment of Cr (VI) contaminated waters was performed in fixed bed reactors inoculated with SRB growing on ethanol. At steady state the column inoculated with SRB removed 65±5% of sulfate and 95±5% of chromium [11]. A new reduction-regeneration circulation process for treating chromium-containing wastewater and reclaiming chromium was developed with the regeneration character of the composites which consisted of SRB and nanosized iron sulfide produced by SRB in 2009. The results indicated that the concentration of total chromium was less than 0.929mg/L in the effluent; Cr (VI) was less than 0.019mg/L simultaneously [12]. The results of treatment of real chromium-containing wastewater by SRB in 2011 showed that the maximum removal of chromium was found to be 82.6% in chromium amended wastewater [13]. The effect of chromium-containing wastewater treatment by SRB with static test point out that when the concentration of chromium wastewater was 50mg/L to 100mg/L, the processing efficiency could reach 99.62% and 99.74%, and the best economical deal time was 1h[14].

B. Zinc-Containing Wastewater

Zinc as the ‘Flower of Life’, is an important material to maintain body’s normal growth and metabolism. It can be widely found in human muscles and bones. High levels of Zinc in the human body will inhibit the activity of phagocytic cells, bactericidal and reduce the body’s immune function, thus increase the susceptibility to diseases [15, 16]. Nowadays, some industrial projects such as bridges, roads, electricity transmission network, etc. requires a lot of galvanized steel. Therefore, they will produce a large number of zinc-containing wastewater which do harm for the environment and human health.

A process for the treatment of Zn^{2+} containing wastewater by SRB in an UASB reactor had been studied in 1995. When the concentration of Zn^{2+} in influent was 100mg/L, the reactor could be successfully operated and removed 99.63% of Zn^{2+}. And when the HRT reduced to 6h, the removal rate was 94.55% [17]. In 2006, according to the research about zinc removal mechanism by sieved SRB, it indicated that the efficiency of zinc removal coincides with the amount of sulfide generated by SRB and the efficiency was about 72% [18]. Compared with the treatment efficiencies of SRB system and SRB+Fe^0 system, the acclimation period of SRB reduced more than 20% under high Zn^{2+} concentration by SRB+Fe^0 system; the inhibiting concentration of Zn^{2+} to SRB increased by approximately 20% by the latter system as well; the reduction velocity of sulfate was fastened apparently [19]. Samia indicated in 2007 that zinc concentrations more than 150mg/L were lethal to SRB and zinc was removed effectively by SRB to less than 5% from medium containing 150mg/L initial zinc concentrations or less [20]. In 2012, when initial Zn^{2+} concentrations were in the range of 73.7 to 196.8 mg/L via anaerobic batch experiments, SRB had high cultivability. But when the concentration was 262.97 mg/L, the activity of SRB significantly inhibited [21].

C. Uranium-Containing Wastewater

Tailings and waste rock from uranium mining and smelting is the major source of uranium-containing wastewater. It will separate out a great deal of radon and pollute the surrounding environments [22]. So the wastewater need to be treated before discharged. U (VI) can be reduced by SRB to U (IV) precipitation thus prevent the migration and proliferation of radioactive uranium [23].

When pH value was 8.0, the treatment effect of uranium by SRB was the best. Cu^{2+} concentration plays an important role in the reduction of U (VI) as well [24, 25]. It inhibited the removal of U (VI) significantly when the concentration was 15mg/L [23]. What’s more, the U (VI) reductive precipitation would not commence until NO_3^- was completely eliminated [26]. Reduced uranium and sulfate by the coordination of SRB and zero-valent iron, the reductive rate of U (VI) could reach 99.4% [22].

D. Copper-Containing Wastewater

Metallurgical industries and electronics industries lead to a large number of generations of copper-containing wastewater. If excess copper is inhaled, the human digestive system will be stimulated and may lead to cirrhosis after a long-term inhalation. Lower organisms and crop will be toxic by copper and appear diseases. So it is particularly important to treat and recycle copper before discharge [27].

Kathy indicated in 2000 that copper was removed effectively by SRB when Cu^{2+} concentration was 150mg/L or less, the removal rate of copper could reach 99%. The association of copper with bacteria cells could promote precipitation rate [28]. By the laboratory intermittent experiment, it was feasible to use SRB to absorb the copper in the mine wastewater diluted. The removal rate of copper ions could reach 99.8% and 100% after operating 24d [29]. Furthermore, some experiments showed that the removal rate of copper ions were 99.9% under the conditions of pH 7, 35 ℃ and the ratio of COD/SO_4^{2-} at 3 [30]. On the bases of analyses of principle and applications of ABR and the culture and acclimatization of SRB granular sludge, the removal rate of Cu^{2+} became stabled over 98% while mass concentration of Cu^{2+} was lower than 35mg/L [31].

E. Other Metal-Ions-Containing Wastewater

Currently, a lot of wastewater containing heavy metals is generated by the mining industries, leather industries and other industries. The contents and components of heavy metals in it are quite different. Except for the metal ions mentioned before, scientists also pay attention to other heavy metal ions, such as Fe, Mn, etc. The effect of this wastewater containing heavy metal ions treatment is significant.

Bradley proved in 1998 that SRB could exist in the solution containing Cr (VI), U (VI), Mn (IV) and Fe (III). And it could use these metal ions as electron acceptors [32].

Adding some metal ions Fe, Zn and Cu which concentrations were respectively 400mg/L, 150mg/L and 80mg/L to AMD was not toxic for the SRB presented in it [33]. What's more, SRB culture solution could effectively precipitate Ni^{2+}, Cu^{2+} and Fe^{3+} while Mg^{2+} remain in the liquid phase [34]. When content of sulfate reduce 50±10%, the metal ions such as As (V), Cd, Cr (VI), Cu, Zn, etc. could be totally removed [35]. The results of the experiment that treating real wastewater containing heavy metals by SRB showed that there was no inhibition of SRB growth while the removal efficiencies of 94-100% for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cr^{6+} existed in the solution [10]. In addition, the removal rate of Fe^{2+} and Mn^{2+} by SRB were respectively 99.37% and 59.18% and the effect was significant [36].

Comparing with the studies above, it shows that it is popular and mature to use SRB to deal with single-heavy-metal-containing wastewater. But the actual wastewater contains not only a single heavy metal ion, but also a variety of heavy metal ions which may also have inhibiting effect to the physiology and biochemistry of SRB. What's more, the treatment of toxic heavy-metal-containing wastewater, such as thallium-containing wastewater, should be further studied and discussed by domestic and international scholars.

IV. CONCLUSION

Nowadays, SRB can be widely used in wastewater treatment because of their advantages, such as simple operation, low processing cost and better treatment effect. But it still has a lot of study to do, including the following aspects:

1) The differences of contents and types of heavy metal ions will lead to differences of toxicity and inhibition of microorganisms like SRB. Single metal effect is different from multi-metals effect, which we need to conduct a comprehensive research.

2) The inhibitions or promotions between different microorganisms have yet to be study.

3) Sulfur in the wastewater can be reduced into H_2S, which can strongly inhibit other microorganisms' growth, such as methanogens. Meanwhile, it can affect the survival environment and the activity of SRB. So it will change the effect of wastewater treatment by SRB. Thus, it also requires further study how to eliminate the reductive products.

4) It is very important to find the technical, feasible and inexpensive carbon source treat the wastewater containing heavy metals. We need to ensure the effluent COD reach standards while reducing processing cost.

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