Reduction and Heavy Metals Removal of Excess Sludge by Radio Frequency Discharge Plasma

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Abstract. Excess sludge is an unavoidable by-product in wastewater treatment. The conventional methods (landfill, incineration etc.) may cause secondary pollution. In this study, both reduction and heavy metals removal of excess sludge by radio frequency discharge plasma (RFDP) were investigated. The experimental results showed that RFDP was an effective removal method on total chemical oxygen demand (TCOD) and mixed liquid suspended solids (MLSS). Discharge process could also damage the cell structure of sludge, so that organic matter and heavy metals within the cell structure could enter the liquid phase. At the same time, combined with spectral diagnosis, the radical reactions was discussed.

1. Introduction
Excess sludge without properly disposed will naturally contaminate the water and air to some extents\textsuperscript{[1]}. The traditional methods for treating excess sludge include composting, landfill and incineration. However, apart from organic matters and secondary clay minerals, as a complex system, sludge includes abundant harmful matters of heavy metal and pathogen etc. for Cd, Cr, Cu, Ni, Zn, Hg, Pb and As etc\textsuperscript{[2]}. Direct landfill or composting will make the concentration of heavy metal in the soil seriously exceeded\textsuperscript{[3]}. Heavy metals enter the human body mainly through the food chain, water and breathing. Recently, the disposal of excess sludge has attracted more interest. \textit{Chironomid Larvae} could be used to treat excess sludge, but the shortcomings of biological methods are slow reaction speed and harsh reaction condition\textsuperscript{[4]}. Nina et al. found that the sludge volume index would rise sharply when ultrasonic worked\textsuperscript{[5]}. Therefore, it is necessary to study other optimal methods for treatment.

Radio Frequency Discharge Plasma (RFDP) technology is a new electrochemical method to remove toxic and harmful organic matter in water. When RFDP working, active substances are generated near the electrodes. The solution around platinum electrode vaporized quickly to form a stable steam sheath and it can generate highly active components such as \textit{H}, \textit{H}_2\textit{O}_2 and \textit{OH}\textsuperscript{[6]-[7]}. These highly active particles are continuously produced and can be easily transferred to the solution, making complex organics in the water completely degraded to simple ones, water and carbon dioxide. It could apply to waste-water disinfection and purification. In conclusion, sludge treatment by radio frequency discharge plasma is innovative and promising.
2. Experimental

Experimental device was mainly consist of a RF power supply(13.56MHz) and a reactor, which is shown in figure 1. Container of sludge was made of glass, and it was installed with an inter-layer of cooling water. Platinum electrode was connected to the high voltage terminal. Sludge in this experiment was collected from a sewage plant and 200ml sludge was poured into container each time. Container bottom was placed with magnetic stir bar in order to make reaction evenly and sufficiently. The whole set of device worked stably and power was controlled at 120W. Maya2000 Pro spectrometer (American Ocean Optics Company) was used to measure spectrogram, and TBS 1052B oscilloscope (American Tektronix Company) was used to measure voltage, current wave form.

During the process of reaction, a few samples were taken for data measurement in a while. The total chemical oxygen demand (TCOD) and supernate chemical oxygen demand (SCOD) 5 min after centrifugation (4000r/min) were measured at the usage of potassium dichromate method. A standard method was used to measure mixed liquid suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). Concentration changes of several kinds of heavy metals in supernate were obtained through detection of inductively coupled plasma spectrometer (ICP-OES OPTIMA 7X00DV, American Perkinelmer Company). In addition, biodegradability of sludge was evaluated by BOD5/COD. Finally, pH and temperature changes during the process were detected.

\[ H_2O + e \rightarrow \cdot OH + H \]  \hspace{1cm} (1)
\[ \cdot OH + \cdot OH \rightarrow H_2O_2 \]  \hspace{1cm} (2)
\[ HO_2 \rightarrow \cdot O_2^- + H^+ \]  \hspace{1cm} (3)
\[ HO_2 + \cdot HO_2 \rightarrow H_2O_2 + O_2 \]  \hspace{1cm} (4)
\[ OH + H_2 \rightarrow \cdot H + H_2O \]  \hspace{1cm} (5)
\[ OH + \cdot OH \rightarrow H_2O + \cdot O \]  \hspace{1cm} (6)

The energetic electrons in the RF plasma region cause a series of complex free radical reactions, as figure 2 shown[8]:

![Radio-frequency power supply](image)

**Figure 1.** RF Discharge Reactor for Sludge Reduction.
The spectrum also detected the yellow light emitted by the sodium (to adjust the conductivity) and the black-body radiation of the platinum.

![Spectrum](image)

**Figure 2.** Spectrum of RF Plasma Reactor in Sodium Chloride Solution (conductivity 600us/cm).

3. Results and discussion

3.1. COD variations and suspended solid degradation

Under the common function of generated high temperature (it can reach 6000K nearby electrode), shock wave, ultraviolet light and chemical active particles, cell structure of sludge was damaged. As is shown in Fig. 3, intracellular matters were released to liquid phase, which made SCOD continuously increasing. Meanwhile, organic matters in sludge reduce constantly, which made TCOD presented the down trend. BOD₅/COD change rules during the process are shown in Fig. 4, the value increased from 0.16 to 0.62, which showed that RF discharge plasma technology can rapidly degrade organic matters and effectively improve the biodegradability.

![Evolution of COD](image)

**Figure 3.** Evolution of COD During the Treatment Time (power, 120w; T, 298K; pH₀, 7.4).
Figure 4. Evolution of BOD₅/COD During the Treatment Time (power, 120w; T, 298K; pH₀, 7.4).

Furthermore, the effection of sludge reduction was observed by the concentration change of suspended matters. As is shown in figure 5, two suspended matters parameters declined as the experiment going. The reason is that complex structure matters be gradually decomposed and soluble components be gradually increased under the discharging. High temperature nearby electrodes kept volatile suspended matters in sludge sustainably volatilizing.

Figure 5. Concentration Variations of MLSS and MLVSS with Treatment Time (power, 120w; T, 298K; pH₀, 7.4).

3.2. pH and temperature variations during the discharging process
In order to research water and heat effect of RFDP in sludge treatment, pH and temperature changes during the discharging process were recorded. As shown in figure 6, sludge pH changed from initial 7.40 to 8.45 smoothly, one possible reason is that the death of microorganisms led to the conversion of metabolic method. This condition was beneficial to sludge digestion.
3.3. In supernatant, concentration of partial overproof metals during the discharging

Concentrations of heavy metals Cr, Ni, Zn in supernate after centrifugation at different discharging time were detected by ICP which are shown in figure 7 and figure 8. It was found that concentrations of these three representative heavy metals increased as the experiment going. The total amount of heavy metal in sludge is constant, therefore, only heavy metal in the solid phase leached to liquid phase, and its concentration would increase. Affected by RF discharge plasma, the following changes occurred to metals in sludge:

(1) Metal cation participated in free radical reactions, changed from high valence to low valence[9]:

\[
\cdot\text{O}_2^- + \cdot\text{HO}_2 + \text{M} \rightarrow \text{Products} \quad (7)
\]

\[
\cdot\text{H} + \text{M} \rightarrow \text{Products} \quad (8)
\]

(2) The destruction of the cell structure of sludge caused the intracellular material be released into the liquid phase, therefore, increasing the content of metal elements in the supernatant.

![Figure 6. Temperature and pH Variation With Treatment Time (power, 120w).](image)

![Figure 7. Evolution of Partial Heavy Metal Concentration During the Treatment Time (power, 120w; T, 298K; pH₀, 7.4).](image)
Figure 8. Evolution of Partial Heavy Metal Concentration During the Treatment Time (power, 120w; T, 298K; pH<sub>0</sub>, 7.4).

4. Conclusion
The effect of RFDP treatment of sludge is obvious. The heat generated during discharge is well utilized. The oxidation and reduction of free radicals were used in the reaction. The effect of destroying the cell structure of sludge is remarkable, chemical active matters gradually degrade organic matters in sludge, supernatant COD concentration increased more than 6 times. Heavy metals precipitate from the sludge cells into the supernatant, among them, the zinc content increased 125%, the chromium content increased 600%, the nickel content increased 80%.

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References
[1] Hara K, Mino T 2008 Environmental Assessment of Sewage Sludge Recycling Options and Treatment Processes in Tokyo J. Waste Management 28(12) 2645 -2652
[2] Zhipeng Z, Saeid B, M.T. Munir and Brent R 2017 Variation in Metals During Wet Oxidation of Sewage Sludge J. Bioresource Technology 245(12) 234-241
[3] WanQian G, QingLian W, ShanShan Y, SiMai P and HaiChao L 2014 The Promising Resource Utilization Methods of Excess Sludge: A Review J. Applied Mechanics and Materials 2972 507
[4] Qiong Z 2013 Effect of Chironomid Larvae on Sludge Reduction and Activated Sludge Settling Performance. In Conf. on Materials for Renewable Energy and Environment (Beijing) vol 1 pp 754-758
[5] Nina Van de Moortel, Rob Van den Broeck, Jan Degr Œ ve, Raf Dewil 2017 Comparing glow discharge plasma and ultrasound treatment for improving aerobic respiration of activated sludge J. Water Research 122 109
[6] Igor B, Serhiy I, and Nikolay V 2017 New Combined-Cycle Gas Turbine System for Plasma-Assisted Disposal of Sewage Sludge J. Plasma Sci. 45(12) 3100-3104
[7] Yu G, Yongdi D and Yekun M 2016 Disruption of Microbial Cell Within Waste Activated Sludge by DC Corona Assisted Pulsed Electric Field J. Plasma Sci. 44(11) 2682-2691
[8] Shuangyan S, XingJ and Peng Z 2016 Measurement of Emission Spectroa Air Dielectric Barrier Discharge and Particle Analysis of Discharge Process J. Spectroscopy and Spectral Analysis 36(02) 359-363
[9] HaoJie F 2007 *Study on the Microscopic Reaction Mechanism of Sulfur-containing Compounds with Oxidizing Radicals in the Aqueous Phase* PhD thesis. Fudan University