Academic Education Publishing House

Experimental Study on the Concentrated Filtrate from Membrane Filtration of “Middle-Aged and Aged” Leachate by Coagulation and Micro-Electrolysis

GuicunYue[1], Zhengyang An[2,*], Shaolong Wang[2]
[1]*Kunming Worunte Environmental Engineering Co., Ltd, Kunming, Yunnan, China*
[2]*College of Biological and Agricultural Sciences, Honghe University, Mengzi, Yunnan, China*
**Corresponding Author.*

Abstract: "Middle aged and aged" landfill leachate has the characteristics of high ammonia nitrogen concentration and poor biodegradability. The concentrated liquid of leachate membrane from middle-aged and elderly garbage is a high concentration organic wastewater generated in landfill sites. This type of wastewater usually comes from the decomposition and filtration process of elderly garbage in landfills. Due to the long-term decomposition and stabilization process of organic matter in elderly garbage, the concentration of organic matter in its leachate is high, and it contains some difficult to degrade substances. However, the concentrated liquid after membrane filtration is more difficult to treat because of its own poor biochemical properties. For "middle aged" leachate membrane filtration concentrate, it is advisable to retreat by physicochemical method to reduce organic load and improve biodegradability before returning to the biochemical system for treatment. The combined process of coagulation and enhanced micro-electrolysis was used in this experiment, and the best operating parameters were studied.

Keywords: Landfill Leachate; Membrane Filtration Concentrate; Coagulation; Enhanced Micro-Electrolysis; Membrane Filtration

1. Introduction

The biodegradability of the filtrate from middle-aged and elderly individuals is poor (with a B/C value of around 0.02), and the concentration of ammonia nitrogen is high [1], exhibiting obvious properties of late stage filtrate [2]; After being treated by the MBR system, most of the easily biodegradable organic matter is removed, and the removal effect of ammonia nitrogen is also good [3]; The turbidity of ultrafiltration, nanofiltration effluent, and concentrated solution is very low [4]. The difficult to degrade organic matter that cannot be intercepted by the ultrafiltration membrane is intercepted by the nanofiltration membrane to form a concentrated solution, with a production of about 50 t/d [5].

The concentrated filtrate of "middle-aged and elderly" leachate membrane filtration [6], it is advisable to first use physicochemical pretreatment to reduce organic load and improve biodegradability before returning to the biochemical system for treatment. This experiment adopts a combined process of coagulation and enhanced microelectrolysis, and studies the optimal operating parameters [7].

2. Experimental Materials, Process and Analytical Methods

2.1 Experimental Materials

The COD, TOC and conductivity of nanofiltration concentrate the experimental materials are relatively high; BOD_5 and ammonia nitrogen concentrations are relatively low; The biodegradability of wastewater is extremely poor (B/C value is 0.03). Physicochemical pretreatment should be adopted first to reduce the organic load and improve the biodegradability before returning to the biochemical system for treatment. In this experiment, the combined process of coagulation and enhanced micro electrolysis was used, and the optimal operating parameters were researched.

2.2 Experimental Process

The "middle aged" samples were treated by the combined process of coagulation and microelectrolysis (H_2O_2 strengthening). The test steps of each operating unit are as follows:
(1) Coagulation test: Take 200ml of water sample in a beaker, add coagulant, stir in a six-set mixer, stirring method is rapid stirring (180 r/min) for 1 min, and then slow stirring (60 r/min) for several minutes. After the reaction is over, the water sample is poured into the measuring cylinder for settlement, and the settlement rate is observed. After settling for 60 minutes, take the supernatant and measure the COD, UV_{254} and chroma equivalents.
(2) Micro-electrolysis test: Put the treated waste iron scraps and activated carbon into 1000 ml micro-electrolysis reaction column in a certain proportion, pour 200 ml of water sample with adjusted pH value to be treated, and react with aeration for a certain time. The water sample after the reaction is poured into the beaker to determine the pH value, and then the pH value is adjusted to about 9 with sodium hydroxide solution and stir, after stirring the water sample is poured into the measuring cylinder to settle for 30 min, and the COD, chroma and UV_{254} values, total iron, iron content and sludge settlement ratio of the supernitant are determined.
(3) Combined process test: First adjust the pH value of the water sample, and then add an appropriate amount of coagulant for coagulation settlement. After sedimentation, the supernatant is directly poured into the micro-electrolytic reaction column, after aeration reaction for a certain time, pour into the beaker to determine pH value, and then adjust the pH value to about 9 with sodium hydroxide solution and stir, after stirring, pour the water sample into the measuring cylinder to settle for 30 min.
(4) Parameter selection in the ultraviolet spectrum scanning experiment: the scanning wavelength range is 200~400 nm, the step size is 1 nm, and the scanning speed is very fast.

2.3 Analytical Method

These detection methods are standard methods for determining different parameters in water quality. These detection methods and instruments play an important role in water quality monitoring and environmental assessment. They can help people understand the pollution status of water bodies and take corresponding treatment measures.

3. Results and Discussion

3.1 Single Coagulation Test Research

Before the micro-electrolysis test, it is necessary to investigate the influence of single coagulation on the removal effect of water samples, and determine the best coagulation conditions through orthogonal experiment and single factor experiment.

3.1.1 Orthogonal experiment analysis

This experiment is a multi-factor experiment, and multi-factor orthogonal experiment is intended to be used to preliminarily determine the primary and secondary relationship and optimal level of each factor. Taking COD removal rate as the index, the effects of four factors such as coagulant type, coagulant dosage, pH value and slow stirring time on COD removal rate were investigated. Four representative levels were selected for each factor in the experiment, and the orthogonal experimental data and processing results is as follows:
(1) According to the range size, the main and secondary order of influence of each index is: pH value > coagulant type > slow stirring time > coagulant dosage.
(2) The optimum coagulant conditions were preliminarily determined as follows: pH value 4, coagulant selected polyaluminum chloride (PAC), slow stirring time was 10 min, coagulant dosage (Al_2O_3) was 600 mg/L.
In order to further determine the test conditions of each factor, on the basis of orthogonal test, adjust the test conditions, the coagulant is selected as PAC, and the influence of each factor on the removal rate of COD, UV_{254} and chroma is investigated by single factor analysis method, so as to obtain more reliable parameters.

3.1.2 Coagulation single factor test analysis

Under the condition of slow stirring (60 r/min) for 10 min and coagulant dosage (Al_2O_3) 600 mg/L, the pH value was changed to investigate the effect of pH value on the coagulation and sedimentation performance is shown in Table 1.
It can be seen from Table 1 that in the acidic and neutral range during coagulation test, the sludge settling ratio basically increases with the increase of pH value, and the settling

performance deteriorates. When pH value is 4, although the removal rate of chroma and UV_{254} value reaches the highest, at this time the sludge sedimentation ratio has increased from 32 when pH value is 3 to 55, and the sedimentation performance deteriorates rapidly. Taking into consideration, the optimum pH value of 3 was selected in the coagulation test.

Table 1. The Effect of Different pH Value on Coagulation and Sedimentation Performance (%)

pH	2	3	4	5	6	7	8	9
Rate	20	32	55	52	48	90	95	58

3.1.3 Influence of coagulant dosage on coagulation performance

Under the condition of rapid agitation (180 r/min) for 1min and slow agitation (60 r/min) for 12 min at pH 3, the dosage of coagulant polyaluminum chloride (PAC) was changed to investigate the effects of coagulant dosage (Al_2O_3) on the influence of the dosage of coagulant on the coagulation and sedimentation performance is shown in Table 2.

Table 2. The effect of Flocculation Dosage on the Influence of the Dosage of Coagulant on the Coagulation and Sedimentation

Dosag	0.075	0.15	0.22	0.3	0.37	0.45	0.52	0.6
Rate	75	64	60	51	46	40	38	35

when the dosage of coagulant (Al_2O_3) was less than 600 mg/L, with the increase of dosage, the removal efficiency of each index gradually increased; After that, with the increase of coagulant dosage, the removal rate gradually decreased, the sludge sedimentation ratio also gradually increased, and the sedimentation performance became worse. Therefore, under the test conditions, the optimal coagulant dosage (Al_2O_3) was determined to be 600 mg/L.

3.1.4 Best effect test of single coagulation

According to the single factor coagulation test, when PAC is used as coagulant for nanofiltration concentrate of "middle aged" leachate, the optimal coagulation conditions are as follows: pH value is 3, rapid stirring (180 r/min) for 1 min, then slow stirring (60 r/min) for 12 min, and coagulant dosage (Al_2O_3) is 600 mg/L.

3.2 Single Microelectrolysis Experiment Research

As the turbidity of the water sample is very small, the SS content is very low, and the main pollutants are soluble and difficult to degrade organic pollutants, it is difficult to effectively remove the pollutants by a single coagulation process, so the test design adopts the coagulation + micro-electrolysis process. Before using the combined process, the experiment first carried out a single micro-electrolysis process on the "aging" leachate nanofiltration concentrate removal effect of the study, through orthogonal experiment and single factor experiment to determine the best micro-electrolysis conditions, to provide reference parameters for the combined process.

3.2.1 Orthogonal experimental analysis

It is intended to use multi-factor orthogonal test to determine the conditions of each factor of micro-electrolysis. Since ferrous ions produced by micro-electrolysis may affect the determination of COD value without complete precipitation, it is appropriate to take UV_{254} value or chroma removal rate as an indicator during the orthogonal experiment. This orthogonal experiment takes UV_{254} value as the index to investigate the effects of four factors, such as iron-carbon mass ratio, aeration volume, residence time and initial pH value, on the removal rate of UV_{254} value.

According to the results, the analysis is as follows:

(1) According to the range, the main order of influence of each factor on the removal rate of UV_{254} value is: initial pH value > iron-carbon mass ratio > aeration volume > residence time.

(2) The optimum micro-electrolysis conditions were preliminarily determined as follows: pH value 2, iron-carbon mass ratio 3, aeration volume 20L/h and residence time 4h.

3.2.2 Effect of initial pH value on microelectrolysis performance

Under the conditions of iron-carbon mass ratio of 3, aeration rate of 20 L/h and residence time of 4h. The influence of initial pH value of water sample on E_2/E_4 value is shown Table 3.

Table 3. Effects of Different Initial pH Values on E_2/E_4 Values (%)

pH	2	3	4		5	6	7
Rate	22.6	21.9	23.2		22.3	18.3	16

As can be seen from Table 3., when the initial pH value of the water sample is 4, the E_2/E_4 value reaches the maximum, which is 23.2, and the average molecular weight of the water sample drops to the lowest.

3.2.3 Influence of iron-carbon mass ratio on microelectrolysis performance

Under the conditions of initial pH value of 4, aeration volume of 20 L/h and residence time of 4 h, the mass ratio of iron to carbon in the reaction column was changed, and the effects of the mass ratio of iron to carbon on the iron-carbon mass ratio in water samples were investigated. The influence of iron-carbon mass ratio on E_2/E_4 value is shown in Table 4.

Table 4. Effects of Different Iron-carbon(I-C) Mass Ratios on E_2/E_4 Values

I-C	0	1	2	3	4	5
E2/E4	16.8	19.7	21.6	23.9	23.1	21.6

As can be seen from Table 4., when the iron-carbon mass ratio is 3, the E_2/E_4 value reaches the maximum, which is 23.9.

3.2.4 Influence of aeration rate on microelectrolysis performance

Under the conditions of initial pH value of 4, residence time of 4 h and iron-carbon mass ratio of 3, the aeration rate was adjusted to investigatet aeration rate on E_2/E_4 value of water samples, as shown in Table 5.

Table 5. Effects of Aeration on E_2/E_4

A-A	0	50	100	150	200	250
E2/E4	20.3	24.1	25.6	23.0	26.6	26.1

As can be seen from Table 5., when the aeration rate is 200 L air / (L water sample ·h), the E_2/E_4 value reaches the maximum, which is 26.6.

3.2.5 Influence of reaction time on microelectrolysis performance

Under the conditions of initial pH value of 4, iron-carbon mass ratio of 3 and aeration volume of 200 L air / (L water sample ·h), the effects of micro-electrolysis reaction time on the influence of reaction time on E_2/E_4 value is shown in Table 6.

Table 6. Effects of Reaction Time on E_2/E_4

Time(h)	0.5	1	1.5	2	2.5	3	3.5
E2/E4	21.4	23.1	23.6	24.1	24.5	25.4	25.7

As can be seen from Table 6., the E_2/E_4 value also gradually increased. The dissolved iron ions may have precipitated and accumulated on the surface of the iron filings instead of flowing out of the reaction column with the water sample, resulting in the decrease of the total iron concentration in the effluent and the slowing down of the reaction rate. It may even block the reactor and interrupt the operation of the system.

Considering the above considerations, the reaction time is chosen as 2h.

3.2.6 Effect of addition of H_2O_2 on microelectrolysis performance

At present, many scholars combine Fenton reagent with micro-electrolysis to treat industrial wastewater. That is, a large amount of Fe^{2+} produced in the wastewater after micro-electrolysis is used to catalyze H_2O_2 to form hydroxyl free radical ·OH. Hydroxyl free radical ·OH has higher oxidation activity, which can strengthen the oxidative degradation of organic matter in water, which not only greatly improves the treatment effect, but also strengthens the effect of micro-electrolysis. In addition, Fe^{2+} in wastewater can be fully utilized without adding Fe containing re^{2+}agents. According to literature reports, the pH value of Fenton reagent process is about 3-6; Wang Kai's research shows that for landfill leachate nanofiltration concentrate, the optimal pH value of Fenton reaction is 7.

Under the conditions of initial pH value of 4, mass ratio of iron to carbon of 3, aeration volume of 200 L air / (L water sample ·h) and reaction time of 2h, H_2O_2 (30%) was added to the micro-electrolysis system after 1 h of reaction, and the effects of H_2O_2 dosage (ml/L) on the influence of reaction time on E_2/E_4 values and the sludge sedimentation is shown in Table 7.

Table 7. Effect of H_2O_2 Dosage on the Value of E_2/E_4 and the Sludge Sedimentation

H_2O_2 dosage	0	0.1	0.2	0.3	0.4	0.5
E2/E4	23.6	20.4	21.6	22.3	24.0	24.1
Sludge settling ratio	60	52	44	37	35	31

As can be seen from Table 7., although the addition of H_2O_2 in a single micro-electrolytic reaction process can not effectively improve the E_2/E_4 value, it can effectively improve the sludge settling performance, reduce the settling ratio and accelerate the settlement.

4. Conclusions

(1) In the treatment of aging leachate nanofiltration concentrate by single coagulation method, the removal rate of pollutants is not large The BOD_5/COD value rises from the original 0.03 to 0.085, and the biodegradability is not significantly improved.

(2) The BOD_5/COD value was increased from the original 0.03 to 0.21. The biodegradability of wastewater was improved, but the HO_2 consumption$_2$ was large.

(3) The optimum conditions for the treatment of leachate concentrate in "middle aged" landfill by coagulation-Ho_2 enhanced$_2$

microelectrolysis process are as follows: pH value of water sample 4, PAC dosage (Al_2O_3) of 525 mg/L in coagulation stage, supernatant of supernatant after settlement for micro-electrolysis reaction; In the micro-electrolysis stage, the mass ratio of iron to carbon is controlled to be 3, the aeration rate is 200L air /(L water sample·h), the reaction time is 3h, and 30% H_2O_2 0.2 ml/L is added when the reaction is carried out to 0.5 h. Under the combined process conditions, and the BOD_5/COD value increased from 0.03 to 0.31 of raw water, which greatly improved the biodegradability and was conducive to subsequent biological treatment.

(4) The coagulation-H_2O_2 enhanced micro-electrolysis combined process has remarkable treatment effect, and is an effective treatment method for "middle aged" leachate membrane filtration concentrate. Compared with the single coagulation process, the combined process reduced the optimal coagulant dosage from the original 600 mg/L to 525 mg/L; Compared with the single micro-electrolysis process, the combined process reduced the amount of hydrogen peroxide from the original 0.5 ml/L to 0.2 ml/L.

Acknowledgments

This paper is supported by Master's and doctor's research initiation projects (No. XJ19B06).

References

[1] Jiang Shaojie, Liu Zongyuan. Significance of organic matter control index in water treatment. Journal of Chongqing Jianzhu University, 2002, 24(2): 61-65.

[2] Zhao Yuanyuan, Wang Zhi, Wang Jixiao, et al. Study on ultrafiltration process of simulated wastewater containing humic acids. Membrane science and technology, 2006, 26(1): 42-46

[3] Wu Jun. Preliminary study on characterization of humus and bioavailability of heavy metals in domestic waste landfill. Shanghai: Tongji University, 2005

[4] Wang Baozhen, Wang Lin. Treatment and disposal of municipal solid waste leachate. Beijing: Chemical Industry Press, 2004

[5] Su Hui, Zhao Youcai. Experimental study of oxidant in low concentration refractory landfill leachate Journal of Suzhou Institute of science and technology, 2003,16(6): 30-35

[6] Yasunobu k, Teuu K, Hiroshi N. The prediction of chemical oxygen demand (COD) in waste water By UV - Visible absorption spectrum-neural network. Orientnal Journal of Chemistry, 2001(17): 24-31.

[7] Cao Zhanfeng, He Pingjing, Shao Liming, et al. Experimental study on the treatment of fresh landfill leachate by SBR Environmental pollution control technology and equipment, 2005. 6(2): 33-35. 48