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Study on leachate treatment for old phosphorous slag

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ABSTRACT

In Yichang, city of Hubei, China, where the famous Three Gorges Project is located, the upstream areas of the reservoir are rich in phosphate rock. During long-term phosphate chemical production, lots of phosphorus slag was buried or dumped in the mountains. Over the past decades, a combination of physical, chemical and microbial processes in the waste transferred pollutants from the waste material to the leachate, the untreated leachate was discharged into Xiangxi River, upstream of the reservoir, worsen the water quality of Three Gorges Reservoir, and resulted in diminishing fish and shrimp in some tributaries. A combined process was employed in this study to treat old phosphorus slag leachate. The results showed that, dispersed aeration reduced yellow phosphorus to 1 ppm, and the addition of sodium hypochlorite accelerated the reaction in 10 min. Besides, coagulation process reduced the leachate turbidity, as well as concentration of F^- and Fe^{2+}, the effluent concentration of turbidity, F^- and Fe^{2+} were below 2 NTU, 0.5 and 1 ppm, respectively. Final process of the combined membranes technology (UF + NF + RO) decreased total phosphorus, COD and Fe^{2+} to below 4, 50 and 0.1 ppm, respectively, and effluent yellow phosphorus was not detected.

Keywords: Phosphate rock; Leachate; Yellow phosphorus; Aeration; Coagulation; Combined membranes treatment

1. Introduction

Statistically, there were about 159 enterprises of yellow phosphorus production in China, 2006 [1]. A large amount of dangerous solid waste (Phosphorous slag and Phosphorous mud) was dumped during yellow phosphorus production, somewhere in Yichang, which was backfilled into the factory area as foundation [2], resulted in large waste accumulation. Consequently, a combination of physical, chemical and microbial processes in the waste transfers pollutants from the waste material to the percolating water [3], generating a highly contaminated liquid called "leachate", that finally flows to the lower reach of Xiangxi River.

Since the nearby mountain body was belong to coal mining area, the surface water and groundwater discharge system were very complicate. Over the long haul, leachate from phosphorous slag containing pollutants such as total phosphorus and fluoride ion (F^-) [4], shaped surface runoff (Fig. 1) and posed a hazard to the receiving water body [5].

During sunny days, leachate generation was about 100 m^3 d^{-1}, while on rainy days, it increased to 1200 m^3 h^{-1} dramatically. As receiving water body of the leachate, Xiangxi River became part of the reservoir since 2003 when the water level of Three Gorges Reservoir was up to 135 m.

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Fig. 1. Picture of leachate outlet.

Yellow phosphorus is a highly toxic compound used in various pyrotechnic products [6]. According to the primary emission standard of yellow phosphorus industrial wastewater, GB 4283–84 (Chinese Environment Protection Agency, 1984), The limit concentration of main pollutant parameters were: $P_4 \leq 0.1$ mg l^{-1}, $F^- \leq$ 20 mg l^{-1}, $COD_{Cr} \leq 100$ mg l^{-1}.

At present few research about leachate from phosphorus slag was reported [3,7,8]. The objectives of this study are to obtain the optimum treatment method of yellow phosphorus, and to offer proper suggestions and parameters to field experiment, engineering design and future actual operation.

2. Materials and methods

2.1. Materials and instrument

All reagents used in this study were analytically pure, and the raw wastewater was derived from leachate outlet somewhere in Yichang. Sample parameters are given in Table 1.

Table 1
Properties of leachate used in this study

	July 14	July 28
Total phosphorus, mg l^{-1}	275.60	332.11
Yellow phosphorus, mg l^{-1}	11.95	3.04
TOC, mg l^{-1}	570.0	371.0
COD_{Cr}, mg l^{-1}	504	320
UV_{254}	0.6404	0.5342
pH	6.34	6.35
Turbidity, NTU	482	276.0
Total iron, mg l^{-1}	2.89	1.08
F^-, mg l^{-1}	2.24	1.78
Cl^-, mg l^{-1}	316	296
NO_3^-, mg l^{-1}	1405	964
PO_4^{3-}, mg l^{-1}	104	167
SO_4^{2-}, mg l^{-1}	1466	1315

Raw wastewater was turbid and in faint yellow, with irritant odor. As shown in Table 1, some parameters like total phosphorus, yellow phosphorus, total iron, COD and turbidity are far beyond the national emission standard.

Instruments used in this experiment are shown in Table 2.

The experimental apparatus used in this study, include specification of membrane module are shown in Figs. 2 and 3, as well as Table 3.

2.2. Aeration experiments

2.2.1. Aeration experiments with different initial yellow phosphorus concentration

Added 10 l wastewater into a plexiglas bucket, and then aerated the wastewater with an air compressor and six aerators. The experiment was employed three times with different initial yellow phosphorus concentration.

Table 2
Instruments used in analytical tests

Names of instruments	Instrument model	Manufacturer
Ultraviolet-visible spectrophotometer	UV-1700	Shimadzu Corporation, Japan
Spectrophotometer	721–100	Shanghai Precision & Scientific Instrument Co., LTD
Turbidimeter	2001P	Hach corporation, America
Multi N/C meter	2100	AnalytikJena AG
pH meter	pHs-3C	Zhiguang Instruments and Measuring Appliance Co., Ltd, Shanghai
Hexa-stirrer	JJ-4	Guohua Electronics Co., Ltd, Changzhou
Electromagnetic air compressor	ACO-001	SenSen Industries Ltd, Zhejiang
Electrothermal/ air-blowing constant-temperature dry box	101-3	Ejiang Instruments Co., Ltd, Shanghai
Electronic alytical balance	AY120	Shimadzu Corporation, Japan
Ultrafiltration/RO system	JCUF-NF-RO-100	Jiecheng Science & Technology Co., Ltd. Wuhan
Ion chromatograph	TCA-2000	DKK Corporation, Japan

Fig. 2. Dispersed aeration equipments.

Fig. 3. Combined membranes treatment system.

2.2.2. Experiments of yellow phosphorus degradation under different aeration manners

During dispersed air aeration, wastewater was aerated by six aerators and an air compressor (ACO-001, SenSen Industries Ltd, Zhejiang), with a displacement of 20 l min^{-1} and working power of 20 W.

During surface agitation, wastewater was aerated with electric agitator (Guohua Electronics Co., Ltd, Changzhou) under rotation speed 300 rpm.

During natural aeration, uncovered vessel was used outdoors under strong sunlight and surface temperature of 40°C.

2.3. Combined aeration and NaClO oxidation experiments

Added NaClO solution to the effluent from dispersed air aeration, agitated for 30 min to make solution fully mixed, then standed the solution for another 30 min before supernatant was sampled. The NaClO solution used in this experiment was analytical pure (the content of activated chlorine and active alkali were above 8.0% and 7.0% ≈ 8.0%, respectively).

2.4. Coagulation experiment

Added 5 g l^{-1} $Al_2(SO_4)_3$ solution to 500 ml effluent from NaClO oxidation, and stirred fast for 1 min, then another slower 15 min. After 30 min standing, supernatant was sampled.

2.5. Combined membrane treatment

Effluent from dispersed air aeration was filtrated through quartz sand, and then it was treated through UF, NF and RO, respectively.

2.6. Analytical method

Analytical methods for major parameters are as follows:

1. Total phosphorus: ammonium molybdate spectrophotometric method (Chinese Environment Protection Agency, 1989)
2. Yellow phosphorus: Spectrophotometric method [9]
3. Fluoride ion: Selective electrode method (Chinese Environment Protection Agency, 1987)
4. Total iron: Phenanthroline spectrophotometric method [10]
5. SiO_2: Silicon-molybdenum yellow spectrophotometry [10]
6. COD_{Cr}: Potassium dichromate method [10]
7. UV_{254}: Spectrophotometric method
8. pH: Glass electrode method (Chinese Environment Protection Agency, 1986)
9. Turbidity: Spectrophotometric method (Chinese Environment Protection Agency, 1991)
10. Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}: Ion chromatography

All parameters were carried out after sample filtration though a 0.45 μm filter membrane, except pH and turbidity.

3. Results and discussions

3.1. Aeration oxidation experiments

3.1.1. Results of different initial yellow phosphorus concentration varying with aeration time

Although the initial yellow phosphorus concentration differed among the three tests, trend variations of three curves were approximately the same (Fig. 4). During the three tests, concentration of the yellow phosphorus decreased rapidly in the first 120 min, and almost linear decrease was observed in the first 30 min.

Results showed that aeration oxidation was an effective method to remove yellow phosphorus, but longer aeration time was proved to be useless, while allow for its cheap cost, the aeration oxidation method was suggested to be pretreatment of deep oxidation process.

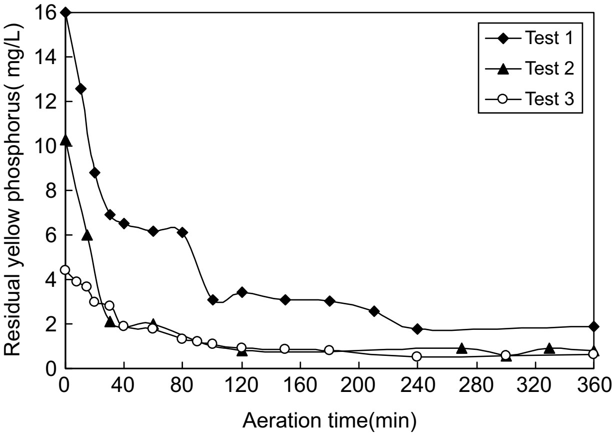

Fig. 4. Change curve of three tests between yellow phosphorus concentration and aeration time.

3.1.2. *Results of yellow phosphorus degradation under different aeration manners*

The above experiments implied that aeration oxidation removed most yellow phosphorus from wastewater. In order to provide evidence for the practical engineering design, three kinds of aeration mode have been employed in this experiment.

As shown in Fig. 5, trend variations of yellow phosphorus was roughly the same in both dispersed air aeration and surface agitation, yellow phosphorus concentration decreased rapidly in the first 120 min, and kept stable in soon afterwards. While in natural aeration experiment, yellow phosphorus showed a slowly descending trend along with time. Considering the operation cost, dispersed air aeration was the best selection.

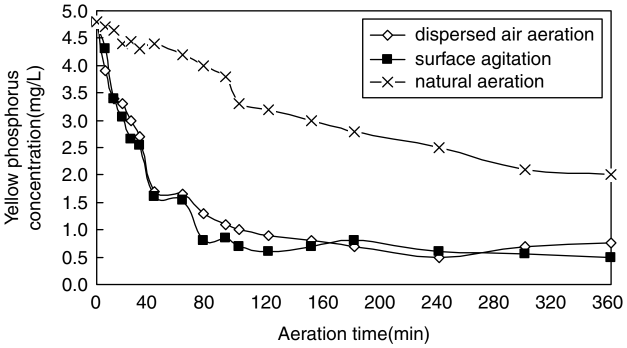

Fig. 5. Change curve between yellow phosphorus concentration and aeration time under different oxidation mode.

Dispersed air aeration increased the yellow phosphorus removal rate up to 89.09% in 4 h, and the turbidity was reduced to an acceptable level (Table 4). However, TOC was almost the same as raw wastewater when COD_{Cr} reduced, which implied that dispersed air oxidation changed the forms of organic substance in wastewater. Considering that the removal rate of total phosphorus was only 3.73%, Primary estimation attributed the low removal rate of total phosphorus and COD to the existence of organophosphorus compounds.

3.2. *Combined aeration and NaClO oxidation*

It was apparent that the addition of NaClO accelerated yellow phosphorus oxidation. Under condition of combined aeration and NaClO oxidation, the yellow phosphorus concentration decreased rapidly to 1 mg l^{-1} in about 10 min (Fig. 6), which cost 120 min to obtain the same efficiency by individual oxidation.

The results suggested that NaClO oxidized yellow phosphorus to orthophosphoric ion, which resulted in lower yellow phosphorus concentration in effluent.

Table 3
Specification of membrane module

	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)
Origin	Jiecheng, China	DOW, America	GE, America [9]
Module model	UEOS805	NF270-400	AK4040
Exterior size, mm	Φ80 × 615	Φ101.6 × 1000	Φ101.6 × 1000
Molecular weight cutoffs	6000 ≈ 10,000	200 ≈ 1000	<200
Membrane area, m^2	3.0	37	8.4
Water yield,l h^{-1}	120 ≈ 1.50	450 (40% ≈ 60% salt permeation)	250
Membrane material	PS	Polyamide composite membrane	Polyamide composite membrane
pH	2 ≈ 13	1 ≈ 14	2 ≈ 14
Inner/Exterior diameter of fiber, mm	0.4 ≈ 0.6		
Operation mode	External pressure		

Table 4
Water quality comparison between influent and effluent under dispersed air aeration (4 h)

Parameter	Influent	Effluent	Removal rate (%)
Yellow phosphorus, mg l^{-1}	15.86	1.73	89.09
Total phosphorus, mg l^{-1}	272.70	262.52	3.73
pH	6.50	6.71	
Turbidity, NTU	222	86	61.26
COD_{Cr}, mg l^{-1}	520	460	11.5
TOC, mg l^{-1}	544.2	547.8	0
UV_{254}	0.6890	0.6404	7.05

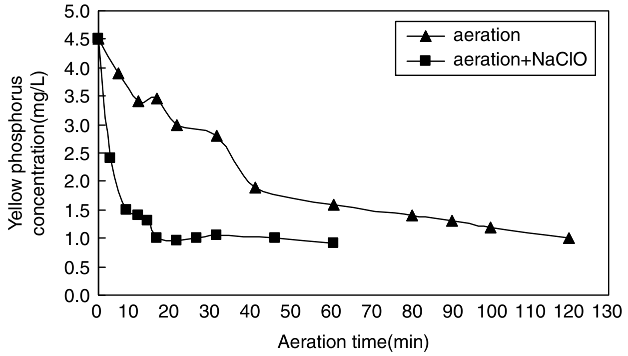

Fig. 6. Comparison of oxidation efficiency between individual oxidation and combined aeration and NaClO oxidation.

However, when the addition of NaClO was beyond 2 ml l^{-1}, removal rate of yellow phosphorus slowed down.

3.3. Coagulation experiment

It is clear that the addition of $Al_2(SO4)_3$ had great influence on pH value (Table 5). Plenty of H^+ produced when $Al(OH)_3$ formed by hydrolysis, and the more $Al_2(SO4)_3$ dosage, the lower pH value. Coagulation technique removed more total iron and F^-, but less TP and TOC, the possible reason was that there only little phosphorus in raw wastewater was orthophosphoric ion, while most phosphorus existed in organic form.

3.4. Combined membrane treatment

Combined membrane treatment was employed in this study [11–14], since yellow phosphorus concentration didn't reach discharge standard after strengthening aeration and coagulation.

UF was not ideal in controlling water quality, the possible reason was limited experiment condition and newly UF membrane which operated not so long enough to attain stable operation. While NF improved water quality greatly (Table 6), total phosphorus removal rate achieved 78.03% and the effluent total phosphorus was reduced to 54.43 mg l^{-1}. Meanwhile, removal rate of yellow phosphorus and COD were 34.59% and 72.41% (effluent COD was below 80 mg l^{-1}), respectively. Since concentration of chlorine in raw wastewater was above 1.0 mg l^{-1}, in order to prevent RO oxidation, reducing agent $NaHSO_3$ was used to decrease influent chlorine concentration to about 0.05 mg l^{-1}. As final process of membrane treatment, RO membrane was so effective that effluent water quality had reached the national standards. Almost complete removal of yellow phosphorus was accomplished, and electric conductivity declined from 1968 to 340 μs cm^{-1}, the concentration of anion-cation and organic compounds also decreased. However, when tap water was used as contrast test in the RO membrane process, sample recovery rate of wastewater was lower than that of tap water, which illustrated that large quantity of organic compounds in wastewater resulted in higher permeation resistance under the same membrane pressure. Further research on membrane fouling and damaging caused by organic compounds in long-term operation will also be tested.

Table 5
Relation between coagulant addition and water quality

Coagulation dosage, mg l^{-1}	Total phosphorus, mg l^{-1}	pH	F^-, mg l^{-1}	Turbidity, NTU	Total iron, mg l^{-1}	TOC, mg l^{-1}
0	393.53	7.55	1.85	7.31	1.61	544.2
100	388.54	7.02	1.31	1.30	0.89	540.6
200	340.50	6.26	0.66	3.21	0.91	539.4
300	334.71	5.11	0.47	4.15	0.86	526.2
600	317.63	4.05	1.65	5.72	0.95	519.4
1200	223.02	3.77	2.01	17.5	0.88	505.6
2000	328.97	3.68	1.93	30.9	1.03	506.4
The highest removal rate, %	43.33		85.17	82.22	46.58	7.09

Table 6
Results of combined membrane treatment

	UF influent	UF yield	UF concentrated water	NF yield	RO yield	RO concentrated water
Total phosphorus, mg l^{-1}	273.32	256.81	360.70	54.43	4.21	187.94
Yellow phosphorus, mg l^{-1}	1.56	1.33	3.96	0.87	ND	1.63
pH	7.29	7.29	7.27	8.56	8.39	8.50
Turbidity, NTU	0.21	0.13	0.25	0.15	0.09	0.38
TOC, mg l^{-1}	389.3	386.6	424.7	183.7	78.4	251.8
COD$_{Cr}$, mg l^{-1}	300	290	300	80	51	230
UV$_{254}$, Abs	0.2542	0.2518	0.2515	0.0654	0.0157	0.1864
Silicon, mg l^{-1}	52.59	51.03	52.59	8.48	4.09	22.80
Total iron, mg l^{-1}	0.49	0.43	0.54	0.13	0.11	0.35
F^{-}, mg l^{-1}	1.47	1.17	1.47	0.31	0.11	0.77
Cl^{-}, mg l^{-1}	270	266	264	205	9.73	311
NO$_3^{-}$, mg l^{-1}	978	960	955	757	190	850
SO$_4^{2-}$, mg l^{-1}	1119	1116	1147	47	2.31	727
PO$_4^{3-}$, mg l^{-1}	89	77	77	26	1.33	31
Na^{+}, mg l^{-1}	852	842	849	385	47.65	735
K^{+}, mg l^{-1}	645	609	644	224	32.40	451
Ca^{2+}, mg l^{-1}	81	77	138	17	1.25	113
Mg^{2+}, mg l^{-1}	9	6	25	3	0.19	41
electric conductivity, μs cm^{-1}				1968	340	

ND = Not detected.

UF influent, UF effluent, NF effluent and RO effluent were tested with Ultraviolet scanning, to obtain trend variations of organic compounds in wastewater. Results are shown in Fig. 7.

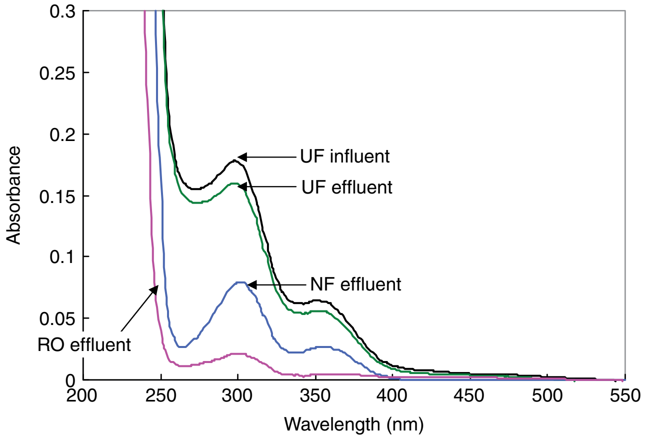

Fig. 7. UV scanning spectrum of membrane treated water samples.

The most absorption peak and the maximum peak height presented to the UF influent, while UF, NF and RO effluent declined in turn (Fig. 7). Similar absorption peak was seen in UF influent and effluent indicating weak removal rate of organic compounds by UF. While peak height of NF effluent declined sharply with the same peak number, indicating good removal rate of organic compounds by NF. For RO effluent scanning, less peak and lower peak height showed excellent removal effect of refractory organics in wastewater.

4. Conclusions and suggestions

4.1. Conclusions

The highest removal rate of yellow phosphorus attained 89% by dispersed air aeration, and the effluent concentration of yellow phosphorus was 0.30 mg l^{-1}. In the first 2 h, yellow phosphorus concentration decreased rapidly, especially in the first 30 min. So aeration oxidation was an effective method to remove yellow phosphorus, but longer aeration time was proved to be useless. While allow for its cheap cost, the aeration oxidation method was suggested to be pretreatment of deep oxidation process.

The addition of NaClO accelerated oxidation of yellow phosphorus, when the initial yellow phosphorus concentration was 3.8 mg l^{-1}, the effluent concentration decreased rapidly to 1 mg l^{-1} in 10 min by combined aeration and NaClO oxidation, which cost 120 min to obtain the same efficiency by individual oxidation. Therefore the addition of NaClO was suggested to be used in practical engineering to reduce reaction time, as well as hydraulic retention time, especially on rainy days.

Yellow phosphorus could not be detected, while total phosphorus was below 4.21 mg l^{-1} in effluent from RO membrane, which implied that combined membrane process was an effective method to improve water quality, make the effluent meet discharge standards, or even reuse standard. Therefore, combined membrane process was an effective final treatment measure for water quality control. However, the damage caused by refractory organics to membrane should not be ignored. Practicability and feasibility of membrane treatment in practical engineering are needed to be proved through pilot test.

4.2. Suggestion

Aeration oxidation was used as a pretreatment method of leachate from phosphorus slag, due to its cheap cost and high-efficient performance. Meanwhile, considering wastewater quality and quantity varies greatly with rainfall, combined aeration and NaClO oxidation was suggested to prevent heavy rainfall, the specific pretreatment process is as follows (Fig. 8):

The suggested retention time of aeration tank was 2 h, and the suggested retention time of aeration tank with addition of NaClO was 30 min on heavy rainy days.

Results showed that combined membrane treatment was an ideal method to control water quality. If it is used in real leachate from phosphorus slag as final treatment process, the suggested process is as follows (Fig. 9):

Estimating a reliable treatment cost for leachate is complicated due to many cost components such as collection system, pumping equipment and treatment facility. In addition, changes in the quality and quantity of leachate with seasons also contribute to the inconsistency of its treatment cost [15].

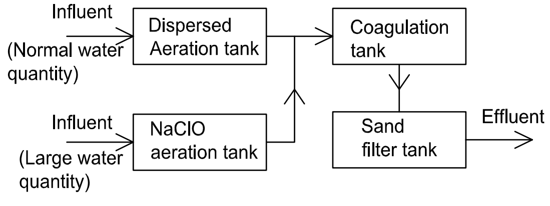

Fig. 8. Pretreatment flow sheet under different quantity.

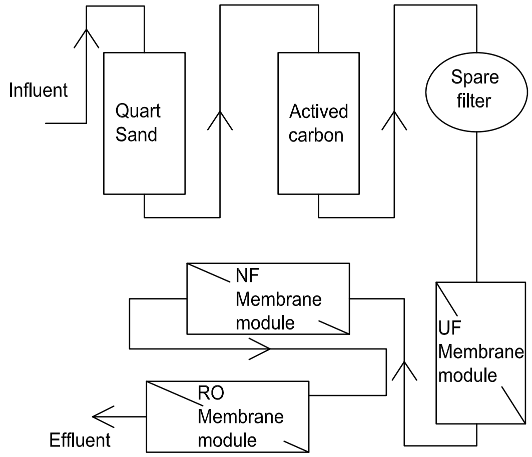

Fig. 9. Suggested flow sheet of combined membrane treatment process.

The technical and economical feasibility of membrane treatment should be obtained through long-term operation, so instead of laboratory experiment, pilot-scale experiment should be further conducted to overcome water quantity restrictions.

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