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Complex treatment of the ammonium nitrogen wastewater from rare-earth separation plant

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ABSTRACT

In order to treat rare-earth wastewater to the requisite discharge standard, a complex treatment system consisting essentially of evaporation crystallization, ammonia stripping and breakpoint chlorination was studied. The results indicated that the complex treatment system offered a suitable treatment alternative for rare-earth wastewater. This system enabled high rates of removal of heavy metals, TOC and ammonium nitrogen. For high concentrations of ammonium nitrogen wastewater (ammonium chloride content of 130 g/L), evaporation crystallization was employed at a pressure between 22 kPa and 55 kPa and an approximate pH value of 4. The quality of crystalline ammonium chloride from the pretreated wastewater reached industry-level standards, and the condensate with NH_4^+-N content of around 12 mg/L could be returned to the reverse osmosis (RO) system in the plant to produce pure water for use in the production process. For middle level concentrations of ammonium nitrogen wastewater (1556 mg/L), NH_4^+-N removal reached a level of about 95% by employing the ammonia stripping method at a temperature in the range of 35–45°C, aeration flow of 27 L/min and a pH value of 12 for 2 h of aeration. The NH_4^+-N content in the effluent was restricted to around 80 mg/L. For low concentrations of ammonium nitrogen wastewater (68 mg/L), maximum NH_4^+-N removal was observed to be 97.4% by breakpoint chlorination at a pH of 7 and Cl/NH_4^+ ratio of 8:1. TN was measured to be 3.4 mg/L and TOC was reduced from 140 mg/L to 14.7 mg/L. An economic appraisal was performed. It shows that an attractive economic benefit could be obtained.

Keywords: Rare-earth; Ammonium nitrogen; Evaporation crystallization; Ammonia stripping; Breakpoint chlorination

1. Introduction

A rare-earth separation plant with annual production capacity of 5000 tons of rare-earth minerals was newly established in Guangdong (a province of China). It generates large volumes of wastewater containing oil, hydrochloric acid, fluoride, heavy metals, radioelement, ammonium nitrogen (NH_4^+-N), etc. These wastewaters are produced during the manufacturing process involving extracting, precipitating and separating the raw materials used. The average values of the contents of NH_4^+-N, COD and BOD in the wastewater were about 9333 mg/L, 403 mg/L and 58 mg/L, respectively. The responsibility to prevent pollution of the environment being that of the Guangzhou Institute of Geochemistry of the Chinese Academy of Sciences,

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in the spring of 2007 they measured wastewater quality in the plant. They obtained diverse information of a basic nature (as shown in Table 1) and found NH_4^+-N present among these pollutants. Its concentration in the wastewater was so high that it became the cause of major concern as such levels could not be treated to the local discharging standards for NH_4^+-N ($\leq$10 mg/L) by means of individual treatment technology. As a result, a combination of a few techniques was considered to reduce this concentration gradually.

Ammonia stripping, reverse osmosis (RO), and struvite precipitation are usually utilized to pretreat wastewaters to lower NH_4^+-N content. Although RO [1–3] and struvite precipitation [4–7] have high NH_4^+-N removal capabilities, their operating costs are high compared to that of ammonia stripping [8,9]. So, from the viewpoint of economy, ammonia stripping appeared attractive; in addition, ammonia stripping was previously successfully used to pretreat wastewaters such as landfill leachate [10], urea fertilizer plant wastewater [11], swine manure wastewater [12,13], etc., with lower treatment costs and high rates of removal of NH_4^+-N [8,14]. However, although these pretreatments are very effective treatment methods for high strength NH_4^+-N wastewater with high levels of NH_4^+-N removal, the NH_4^+-N content of the effluents still fails to meet the discharge standard. The concentration of NH_4^+-N in effluent therefore needed to be lowered by advanced treatment methods.

Bio-chemical methods [15,16] have been used to treat low concentration of NH_4^+-N wastewater are lower cost and without generating hazardous residues. However, it is difficult to introduce biochemical process into the treatment due to the lack of organics, low biodegradability and heavy salt concentrations characteristically present in rare-earth wastewater [17]. As a result, some other alternatives such as ion exchange and breakpoint chlorination had to be considered. Ion exchange has high NH_4^+-N removal capability [18,19], but requires back washing and regeneration to be carried out frequently making the treatment expensive [20,21]. Breakpoint chlorination is widely practiced as a disinfection process in water and wastewater; it can react with ammonium and has many advantages [22–24] such as high removal rates, low cost of chlorine, is not disrupted by high salt content, does not produce sludge, and an added advantage, namely, the lower the level of organic contents the higher the level of NH_4^+-N removal. In this article, a complex treatment system with low investments costs, using mature techniques and low treatment cost is described. Lab-scale experimental studies were carried out based on discharge alternatives from pretreated wastewater. Additionally, an economic appraisal is also presented.

2. Wastewater characteristics and project design

2.1. Wastewater characteristics

Abbreviations employed for wastewater from extracted rare-earth, wastewater from saponification reaction, wastewater from deposited ammonium carbonate, washing water from deposited ammonium carbonate, wastewater from deposited oxalic acid and washing water from deposited oxalic acid are WERE, WSR, WDAC, WWDAC, WDOA and WWDOA, respectively.

From the wastewater characteristics (Table 1), it is found that while the main pollutant is NH_4^+-N, it also contains heavy metals, chemical oxygen demand (COD), acid, etc., but as these contents are low, they are easily removed. Based on the level of NH_4^+-N contained in the rare-earth plant's wastewater, it can be categorized into three types: (1) wastewater of high level of NH_4^+-N of concentration greater than 10,000 mg/L (WERE and WDAC), (2) wastewater of middle level NH_4^+-N with concentration ranging from 500 mg/L to 10,000 mg/L (WSR and WWDAC), and (3) wastewater of low level NH_4^+-N with concentration of less than 500 mg/L (WDOA and WWDOA).

2.2. Project design

In view of the characteristics of wastewater as shown in Table 1 and according to the principle that valuable resources should be recovered as far as possible, and wastewaters of different characteristics are treated to be separately, a project was designed for treatment of rare-earth wastewater. Corresponding to the above classification of wastewater, the treatment processes are divided into three main sections (as shown Fig. 1).

2.2.1. Pretreatment in section 1

According to the process flow (Fig. 1), WERE was pretreated in a dissolved air-floating device with appropriate dosage of organic high polymer (PAM) that was added as flocculating agent after pH was adjusted to 3–4 by addition of ammonia of 30%. The oil content of the pretreated effluent was less than 20 mg/L. Subsequently, the effluent was mixed with WDAC. Suitable dosage of chelating precipitating agent (DTCR) for heavy metals was added into the mixture to precipitate heavy metals after the ammonia of 30% was used to precipitate part of the heavy metals at pH 8–9. PAM was the flocculation agent. Finally, the residual heavy metals and oil of the wastewater were adsorbed and filtered out using granular activated

Table 1
Characteristics of rare-earth wastewater in different sectors (units: mg/L, except pH)

Parameters	WERE	WDAC	WSR	WWDAC	WDOA	WWDOA	Maximum discharge standards
Water volume (m^3/d)	226.0	80.5	82.5	112.7	71.0	236.0	–
pH	0.48	6.34	6.48	6.67	0.17	1.46	6–9
NH_4^+-N	39,278	10,229	2424	967	30	0.9	10
TOC	176	10.7	602.4	0.87	165.3	3.7	20
COD	287	–	1032	–	258	–	90
F^-	0.14	0.68	–	–	0.05	–	10
Ca^{2+}	165	1.95	–	–	–	–	–
Mg^{2+}	8	3.04	–	–	–	–	–
Total Fe	10.7	16.94	–	–	–	–	–
Total Cu	3.69	2.74	5.19	0.38	26.45	0.75	0.5
Total Zn	16.55	55.94	24.39	1.44	152.1	1.87	2.0
Total Pb	67.82	0.13	1.21	0.04	1.31	–	1.0
Total Mn	23.91	0.54	2.34	0.61	4.19	0.05	2.0
Total Cd	0.19	0.06	0.15	–	–	–	0.1
Total Ni	2.12	2.07	3.73	0.22	18.44	0.35	1.0
Total Cr	1.64	2.05	–	0.16	16.74	0.21	1.5
Total As	0.15	–	0.08	–	–	–	0.5
Total Hg	0.03	0.01	–	–	–	–	0.05

carbon. The characteristics of the pretreated wastewater before evaporation and crystallization are shown in Table 2.

2.2.2. Pretreatment in section 2

After the oil in WSR was removed in a dissolved air-floating device, the oil content in the effluent was around 20 mg/L. Sodium hydroxide was used to adjust pH and precipitate heavy metals before the mixture of WSR and WWDAC was pumped into a tower for ammonia stripping. The oil content in the influent of the tower for ammonia stripping was less then 15 mg/L, and that of heavy metals was lower than the required discharge standard. The stripped ammonia was absorbed by water, with no atmospheric pollution and the resulting product was ammonia of around 15%. The effluent pretreated by ammonia stripping was transferred to section 3 for further treatment.

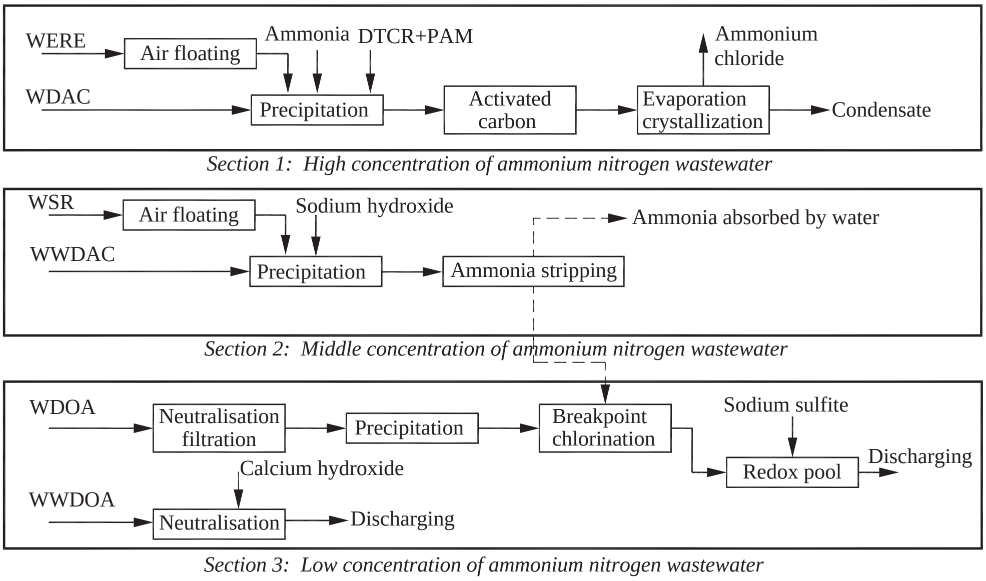

Fig. 1. Process flow of wastewater treatment.

Table 2
Characteristics of the influent before evaporated (units: mg/L)

Pretreatment	Total Cu	Total Zn	Total Pb	Total Mn	Total Cd	Total Ni	Total Cr	Total Fe	Total Hg	Oil
DTCR pretreatment	0.12	0.25	0.35	0.47	0.08	0.17	0.03	0.38	0.01	6.8
Activated carbon pretreatment	0.08	0.186	0.013	0.264	0.07	0.13	0.019	0.18	0.008	<0.1

2.2.3. Pretreatment in section 3

WDOA was neutralized by neutralization and filtration and the pH adjusted to 6. Subsequently, lime was added as a precipitator, causing heavy metals sedimentation and adsorption of the residual oil in the wastewater. Finally, the pretreated wastewater from WDOA and the effluent from ammonia stripping were pumped into a breakpoint chlorination pool for advanced treatment. WWDOA with minimum ammonium nitrogen was discharged directly after neutralization with lime.

By this complex treatment, the main products of value such as ammonium chloride, ammonia, condensate, oil and extractant for industrial use were obtained. The sludge of heavy metals was filter pressed before delivery to a burying mill of hazardous waste for disposal. The effluents of high salinity content from the treated wastewaters of middle and low concentrations of NH_4^+-N were discharged directly because initial capital for investment in downstream treatment equipment was inadequate. In the second phase of the engineering project, RO and evaporation crystallization equipment are to be added for zero discharge of wastewater and recovery of salts such as sodium chloride and calcium chloride.

The lab-scale experiments for evaporation and crystallization, ammonia stripping and breakpoint chlorination are described below.

3. Experimental materials and methods

3.1. Evaporation crystallization

The lab-scale vacuum distillation system consisted an evaporation device comprised of a 1 L distillation flask in a thermostatic bath, Y-type tube, distillation column, straight condenser tube, vacuum storage vessel, storage flask for condensate collection, thermometer and capillary, etc., and a vacuum apparatus which was composed of a rotary water vacuum pump, safeguard flask and vacuum meter. Experiments were performed maintained temperature in excess of the boiling point of around 30°C. Ammonia (5M) and HCl (5M) were used to adjust the pH. Pressure was regulated with a vacuum pump. The evaporation process consisted of evaporating 330 mL from 500 mL wastewater sample at the desired pressure and pH, natural dewatering of the concentrated brine and collecting the condensate and crystallized ammonium chloride for analyses.

3.2. Ammonia stripping

In order to control different temperatures required during the experimental runs, ammonia stripping for 1 L of wastewater was conducted in a 2 L beaker with an air-bubbling device in a thermostatic bath. The air-bubbling device was a ceramic porous distributor submerged in the 2 L beaker. Air was supplied from a blower and flow was controlled with a rotameter (rotating-flow meter) and valve. Sodium hydroxide was used for pH adjustment. Optimum pH for constant aeration time (1 h) was investigated while temperature was a room temperature (26 °C) and air-flow rate was a constant 18 L/min. Adjusting pH to the optimum at a temperature of 26°C, the experiments to determine the effect of air-flow rate on NH_4^+-N removal were performed for different aeration times. When pH and air-flow rate were at the optimum, the effect of temperature on NH_4^+-N removal was studied for different aeration times (0.5–3 h). The pH was measured using pHs-25 type acidity meter. NH_4^+-N analysis was performed according to the Monitoring and Analytical Methods of Water and Wastewater [25].

3.3. Breakpoint chlorination

Breakpoint chlorination experiments were carried out in the batch mode in 500 mL beakers using sodium hypochlorite as oxidant following experimental procedure: (1) the wastewater sample was first poured into the beakers and then the sodium hypochlorite of the requisite Cl/NH_4^+ ratio was added; (2) a magnetic stirrer at the bottom of beaker was switched on and the pH of the wastewater sample was monitored using a pH meter; (3) breakpoint chlorination reaction lasted for about 10 min until an equilibrium state was reached as indicated by a stable pH; (4) the treated sample was collected and residual chlorine and NH_4^+-N were analyzed by the standard methods [25].

All of the experiments were performed in triplicate.

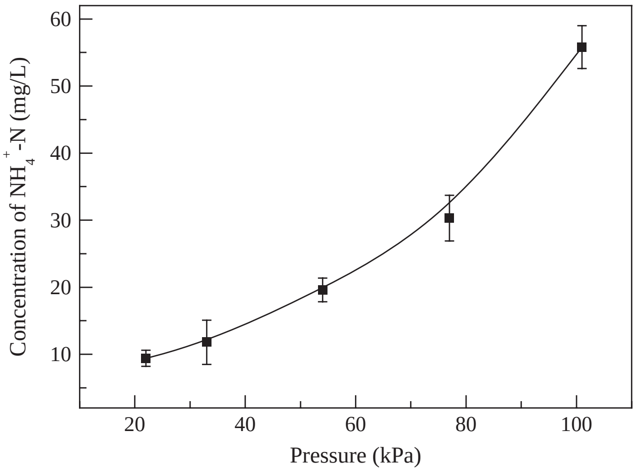

Fig. 2. Effect of pressure on NH_4^+-N content of condensate at pH 4.38. The bars in the presented figure and all subsequently presented figures denote 1 standard deviation ($n = 3$).

4. Results and discussion

4.1. Evaporation crystallization

The concentration of ammonium chloride in the pretreated wastewater from the mixture of WERE and WDAC was 130 g/L. The experimental results with different pressures at an initial pH 4.38 (a pH value of 130 g/L simulated ammonium chloride solution at temperature of 25 °C) are shown in Fig. 2 and illustrate that the lower the pressure the lower the content of NH_4^+-N in the condensate. When pressure was 22 kPa, the NH_4^+-N content of condensate was 9.4 mg/L, reaching a minimum. Since decreasing pressure has the advantage of lowering the boiling point of the solution, according to the reaction formula in the following:

$$NH_4^+ + OH \rightleftharpoons NH_3 \uparrow + H_2O \tag{1}$$

It was seen that the reaction is endothermic; hence, lowering the temperature of boiling point has the advantage of reducing the volatilization of NH_3. Under constant pressure (33 kPa) conditions, the experimental results at different pHs are shown in Fig. 3 and reveal that the concentration of NH_4^+-N in the condensate increased with increasing pH. When the pH value was higher than 4, the increasing trend improved rapidly. The content of NH_4^+-N in the condensate was 43.6 mg/L at pH 6 while the content was 7.3 mg/L at pH 2.5.

In a full-scale wastewater treatment plant, the corrosiveness of high concentrations of chloride ion is intense. Therefore, titanium and graphite, and not stainless steel, should be considered as the material of construction for the evaporator. A triple effect mixed-flow falling film vacuum evaporation technique which produces a high heat transfer coefficient and saves energy [26] should be applied in treating high concentrations of NH_4^+-N wastewater. Based on the above results, the operating parameters were pressure, controlled between 22 kPa and 55 kPa (corresponding to the temperatures of boiling points between 65 °C and 95 °C) and with pH value in the range of 3–4. As a result, the NH_4^+-N content and TDS of condensate would be around 12 mg/L and 70 mg/L, respectively. The quality of crystallized salt obtained by evaporation crystallization is shown in Table 3, proving that the quality of ammonium chloride attained industry-level standards.

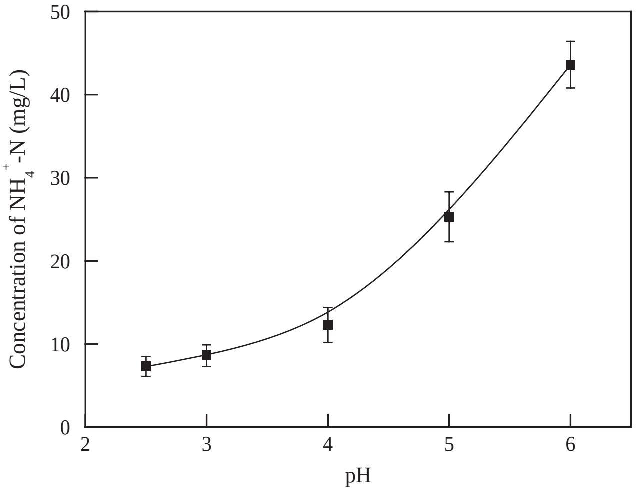

Fig. 3. Effect of pH on NH_4^+-N content of condensate at pressure of 33 kPa.

4.2. Ammonia stripping

The NH_4^+-N strength of the mixture of WWDAC and WSR was 1556 mg/L. Optimum pH was determined by a batch experiments using sodium hydroxide adjusted to pH of 8, 9, 10, 11, 12 and 12.5, respectively, at room temperature (26 °C) and air-flow rate of 18 L/min for 1 h of aeration. The results shown in Fig. 4 reveal that the NH_4^+-N removal was highest (66.6%) at pH 12 while the NH_4^+-N removals were 11.3% and 29.2% at pHs of 8 and 9, respectively. Optimal air-flow rate and aeration times were determined by adjusting pH to the optimal value of 12. The results shown in Fig. 5 indicate that an optimal NH_4^+-N removal of 97% was obtained at an air-flow rate of 45 L/min, with an aeration of 3 h. The concentration of residual NH_4^+-N in the effluent was 47 mg/L. However, from the viewpoint of engineering applications

Table 3
Quality of production and the industry-level standard

Index name	First grade	Eligible	Quality of product
Content of ammonium chloride, %, ≥	99.3	99.0	99.2
Moisture, %, ≤	0.7	1.0	–
Burning residue, %, ≤	0.4	0.4	0.38
Content of iron, %, ≤	0.001	0.003	0.003
Content of heavy metals (calculated as lead) %, ≤	0.0005	0.001	0.0008
Content of sulfate (calculated as SO_4^{2-}), %, ≤	0.02	–	0.01
pH (concentration: 200 g/L, temperature: 25 °C)	4.0–5.8	4.0–5.8	4.32

an air-flow rate of 27 L/min for 1 L of wastewater would be preferred because using an air-flow rate of 45 L/min for 1 L of wastewater increases the NH_4^+-N removal efficiency by only about 3% compared with that at 27 L/min. The optimum temperature was determined when the experiments at different temperatures (26 ± 1 °C, 35 ± 1 °C, 45 ± 1 °C, 55 ± 1 °C and 65 ± 1 °C) were performed at a pH of 12 and air-flow rate of 27 L/min. The results displayed in Fig. 6 show that maximum NH_4^+-N removal was greater than 99% when the temperature was higher than 55 °C and aeration time was over 2 h, while the content of NH_4^+-N in effluent was less than 16 mg/L. Although the enhancement of temperature has the advantage of increasing NH_4^+-N removal, the higher the temperature the higher the quantity of water evaporated and the greater the energy consumed. The evaporation rates of water at 45 °C, 55 °C and 65 °C were 20%, 40% and 50%, for 3 h of aeration, respectively, which consumed a large amount of energy. It was determined that the treatment costs and removal efficiency would reach an optimum when ammonia stripping is performed at temperatures in the range of 35–45 °C, pH of 12 and an air-flow rate of 27 L/min for 2 h of aeration. The NH_4^+-N removal and the content of residual NH_4^+-N are around 95% and 80 mg/L, respectively. In these ammonia-stripping experiments, it was determined that COD was not significantly reduced. Although lime can be used to adjust pH and obtain similar removal with sodium hydroxide, scale substances were produced due to presence of calcium ions in wastewater at high pH absorbing CO_2 in the air, affecting the operation of the ammonia stripping facility.

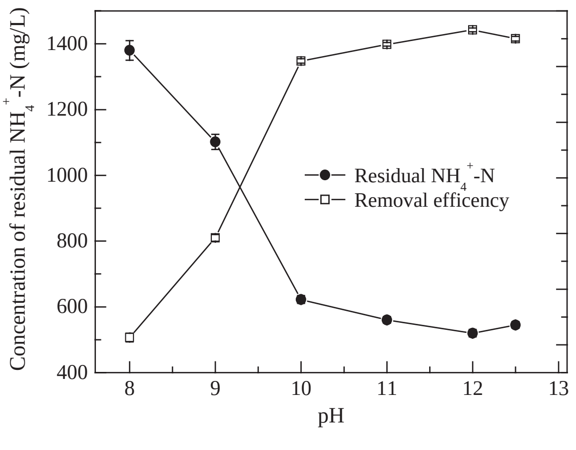

Fig. 4. Effect of pH on NH_4^+-N removal.

4.3. Breakpoint chlorination

The NH_4^+-N concentration of the mixture of WDOA and the effluent from ammonia stripping was 68 mg/L. According to the chlorination reaction expressed as follows:

$$1.5NaOCl + NH_4^+ \rightarrow 0.5N_2 + 1.5NaCl + 1.5H_2O + H^+ \tag{2}$$

the stoichiometric ratio of mass concentration of available chlorine and that of NH_4^+ (Cl/NH_4^+) is 5.91:1.

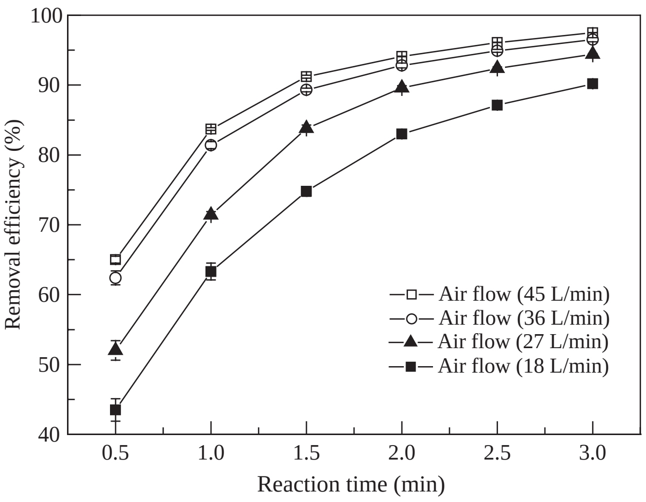

Fig. 5. Effects of aeration flow and aeration time on NH_4^+-N removal.

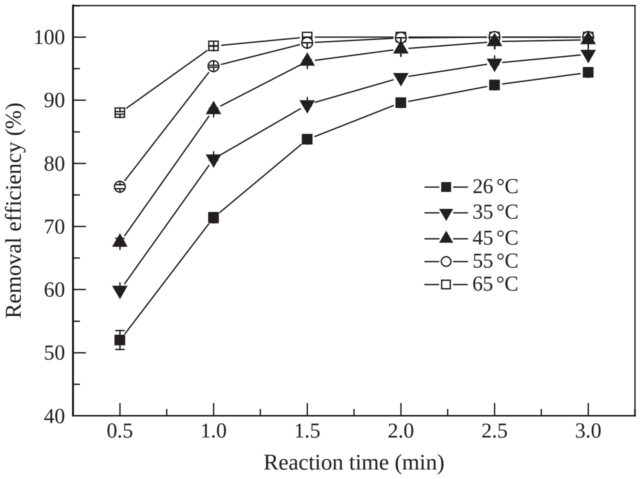

Fig. 6. Effects of different temperatures at different aeration time on NH_4^+-N removal.

Optimum pH was determined by batch chlorination experiments using 10 M NaOH and 1 M HCl to adjust pH when sodium hypochlorite was added into the tested wastewater according to the stoichiometric ratio. The results displayed in Fig. 7 show that pH value has an important effect on NH_4^+-N removal. A maximum NH_4^+-N removal of 66% with a residual chlorine content of 9.8 mg/L was observed when pH value was at 7. The residual chlorine and remaining NH_4^+-N content increased rapidly when pH value was below or over 7, which can be interpreted by the reasons reported by previous authors [27,28]. The removals at different ratios of Cl/NH_4^+ were studied when pH was restricted to 7. As displayed in Fig. 8, the results show that NH_4^+-N removal was the maximum at the Cl/NH_4^+ ratio of 8:1. The contents of residual chlorine and the remaining NH_4^+-N were observed as 5.6 mg/L and 1.8 mg/L, respectively. NH_4^+-N removal reached 97.4%. TN was measured at 3.4 mg/L. TOC was reduced from 140 mg/L to 14.7 mg/L (89.5% removal). Some residual chlorine still existed in the treated wastewater, which it is essential to remove. Sodium sulfite was added to the effluent to remove residual chlorine, reducing the content of residual chlorine to below discharge standard.

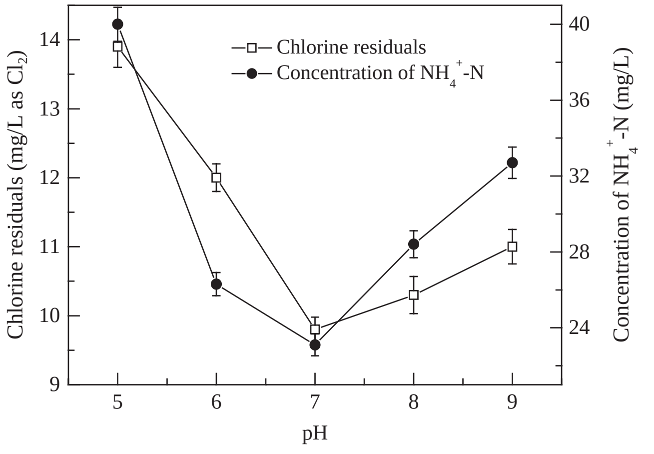

Fig. 7. Effect of pH on NH_4^+-N removal.

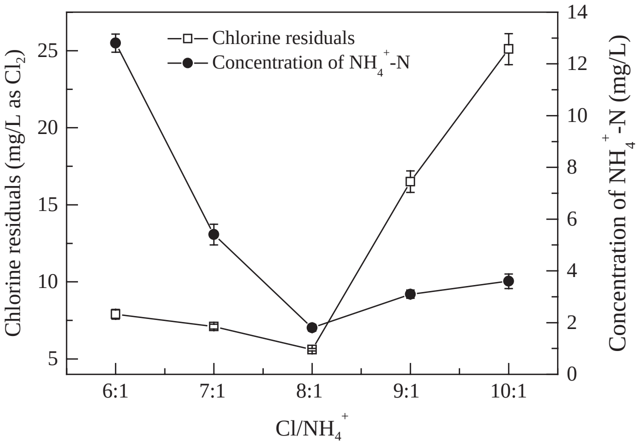

Fig. 8. Effect of Cl/NH_4^+ on NH_4^+-N removal.

5. Economic evaluation

In the scope of this study, operating costs (in US$) were analyzed and performance of the wastewater treatment system evaluated. The basic parameters of a variety of used reagents and recovered resources were noted in Table 4 (according to 2007 market prices in China). The total investment for the entire treatment project was about $2.7 million. A payoff of 2049.3 $/d was achieved (Payoff = Throughput × Unit selling price − Dosage × Unit price). The unit operating cost and recovery income are given in Table 5 (Unit operating cost = Unit price × Dosage/Total wastewater per day, the calculation method of the unit recovery income is same.). It is shown that the total operating costs and the total recovery incomes are calculated to be 4.45 $/m^3 and 6.98 $/m^3, respectively. A payoff of 2.53 $/m^3 is achieved. The economy of the treatment system depends on the sale of such valuable products as ammonium chloride and condensates for industrial use. The income from these products, and savings on environmental fees and penalty fines for discharge of NH_4^+-N wastewater, indicates that the time needed to recover investment cost would be less than 5 years. It is concluded that the complex treatment system is a feasible system for the treatment of rare-earth wastewater and an attractive economic benefit can be obtained.

Table 4
Basic parameters of a variety of used reagents and recovered resources (the dosage and unit price of power consumption are kWh/d and $/kWh, respectively)

Process	Investment cost (million$)	Chemicals/energy	Dosage (t/d)	Unit price ($/t)	Recovered resource	Throughput (t/d)	Unit selling price ($/t)
Pretreatment sector 1	0.25	Ammonia (30%)	6.2	40.5	Oil and extractant	0.2	607
		DTCR	0.048	3378			
		Activated carbon	0.73	500			
		Power consumption	324	0.1			
Pretreatment sector 2	0.35	Lime	0.2	40.5			
Evaporation crystallization	1.6	Steam	125	16.2	Ammonium chloride	39.8	136
		Power consumption	405	0.1	Condensate	306	0.27
Air stripping	0.37	NaOH	1.5	270	Ammonia (15%)	2	12.1
		Power consumption	1134	0.1			
Breakpoint chlorination	0.13	NaOCl (12%)	2.2	92	–	–	–

6. Conclusions

The results indicate that the pretreatment process to remove oil in a dissolved air-floating device, adding ammonia to neutralize and DTCR to remove heavy metals, and using activated carbon for absorbing minimal heavy metals and oil in sequence is an appropriate pretreatment alternative for pretreatment of wastewater with high concentration of NH_4^+-N. The process afforded high removal in terms of heavy metals and TOC. Hence, a high quality of ammonium chloride was obtained. The results of evaporation crystallization demonstrated that the quality of ammonium chloride measured up to industry level and the condensate used as tap water could be returned to the RO system in the plant to produce pure water for production purposes.

Results of the ammonia stripping employed for the treatment of middle level concentration of ammonium nitrogen wastewater showed that NH_4^+-N removal as high as 95% could be achieved by stripping conditions of temperature in the range of 35–45°C, air-flow rate of 27 L/min, a pH value of 12 and 2 h of aeration. The NH_4^+-N content in the effluent was restricted to around 80 mg/L. The stripped ammonia was absorbed by water and the resulting ammonia was recovered for reuse, with no atmospheric pollution.

Table 5
Estimated unit operating costs and unit recovery income

Process	Removal efficiency (%)			Chemicals/energy	Unit operating cost ($/m^3)	Recovered resource	Unit recovery income ($/m^3)
	Heavy metals	TOC	NH_4^+-N				
Pretreatment sector 1	>99	>99	–	Ammonia	0.31	Oil and extractant	0.15
				DTCR	0.2		
				Activated carbon	0.45		
				Power consumption	0.04		
Pretreatment sector 2	95	89	–	Lime	0.01		
Evaporation crystallization	100	–	99.98	Steam	2.5	Ammonium chloride	6.7
				Power consumption	0.05	Condensate	0.1
Air stripping	–	–	95	NaOH	0.5	Ammonia	0.03
				Power consumption	0.14		
Breakpoint chlorination	–	89.5	98	NaOCl	0.25	–	–

The mixture of the effluent from ammonia stripping and the pretreated WDOA having NH_4^+-N and TOC concentrations of 68 mg/L and 140 mg/L were reduced to 1.8 mg/L and 14.7 mg/L at Cl/NH_4^+ ratio of 8:1 and pH of 7 by breakpoint chlorination, respectively. Residual chlorine was removed by addition of the appropriate dosage of sodium sulfite. The quality of the effluent was suitable for discharge into receiving waters.

Results of an economic analysis showed that the complex treatment system is a feasible treatment alternative for rare-earth wastewater. The treatment process not only recovers valuable resources, a high economic benefit is also possible.

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References

[1] K. Häyrynen, J. Langwaldt, E. Pongrácz, V. Väisänen, M. Mänttäri and R.L. Keiski, Separation of nutrients from mine water by reverse osmosis for subsequent biological treatment, Miner. Eng., 21 (2008) 2-9.

[2] W.Y. Ahn, M.S. Kang, S.K Yim and K.H. Choi, Advanced landfill leachate treatment using an integrated membrane process, Desalination, 149 (2002) 109-114.

[3] A.J. Karabelas, S.G. Yiantsios, Z. Metaxiotou, N. Andritsos, A. Akiskalos, G. Vlachopoulos and S. Stavroulias, Water and materials recovery from fertilizer industry acidic effluents by membrane processes, Desalination, 138 (2001) 93-102.

[4] J.M. Chimenos, A.I. Fernández, G. Villalba, M. Segarra, A. Urruticoechea, B. Artaza and F. Espiell, Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product, Water Res., 37 (2003) 1601-1607.

[5] S.A. Lobanov and V.Z. Poilov, Treatment of wastewater to remove ammonium ions by precipitation, Russ. J. Appl. Chem., 79(9) (2006) 1473-1477.

[6] X.Z. Li and Q.L. Zhao, Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer, Ecol. Eng., 20 (2003) 171-181.

[7] G.E. Diwani, S.E. Rafie, N.N.E. Ibiari and H.I. El-Aila, Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer, Desalination, 214 (2007) 200-214.

[8] I. Ozturk, M. Altinbas, I. Koyuncu, O. Arikan and C. Gomec-Yangin, Advanced physico-chemical treatment experiences on young municipal landfill leachates, Waste Manag., 23 (2003) 441-446.

[9] T.A. Kurniawan, W. Lo and G.Y. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, J. Hazard. Mater., B129 (2006) 80-100.

[10] K.C. Cheung, L.M. Chu and M.H. Wong, Ammonia stripping as a pretreatment for landfill leachate, Water. Air Soil Pollut., 94 (1997) 209-220.

[11] V.K. Minocha and A.V.S. Prabhakar, Ammonia removal and recovery from urea fertilizer plant waste, Environ. Technol. Lett., 9 (1988) 655-664.

[12] P.H. Liao, A. Chen and K.V. Lo, Removal of nitrogen from swine manure wastewaters by ammonia stripping, Bioresour. Technol., 54 (1995) 17-20.

[13] A. Bonmati and X. Flotats, Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, Waste Manag., 23 (2003) 261-272.

[14] W. Budzianowski and A. Koziol, Stripping of ammonia from aqueous solutions in the presence of carbon dioxide: effect of negative enhancement of mass transfer, Chem. Eng. Res. Des., 83(A2) (2005) 196-204.

[15] C. Gabaldón, M. Izquierdo, V. Martínez-Soria, P. Marzal, J. Penya-roja and F.J. Alvarez-Hornos, Biological nitrate removal from wastewater of a metal-finishing industry, J. Hazard. Mater., 148 (2007) 485-490.

[16] Y. Ahn, Sustainable nitrogen elimination biotechnologies: a review, Process. Biochem., 41 (2006) 1709-1721.

[17] S. Xia, S. Xia and C. Zhu, Removal of organic pollutants from 2,2′,5,5′-tetrachlorobenzidine (TCB) industrial wastewater by micro-electrochemical oxidation and air-stripping, J. Hazard. Mater., 144 (2007) 159-163.

[18] A. Thornton, P. Pearce and S.A. Parsons, Ammonium removal from digested sludge liquors using ion exchange, Water Res., 41 (2007) 433-439.

[19] A. Ancuta, D. Kaušpėdienė, A. Gefenienė, J. Snukiškis and E. Vasilevičiūtė, Effect of hydroxyl and nitrate ions on the sorption of ammonium ions by sulphonic cation exchangers, Desalination, 175 (2005) 259-268.

[20] O. Lahav and M. Green, Ammonium removal using ion exchange and biological regeneration, Water Res., 32(7) (1998) 2019-2028.

[21] N. Miladinovic and L.R. Weatherley, Intensification of ammonia removal in a combined ion-exchange and nitrification column, Chem. Eng. J., 135 (2008) 15-24.

[22] C. Shang and E.R. Blatchley III, Chlorination of pure bacterial cultures in aqueous solution, Water Res., 35(1) (2001) 244-254.

[23] E. Coro and S. Laha, Color removal in groundwater through the enhanced softening process, Water Res., 35(7) (2001) 1851-1854.

[24] X. Yang, C. Shang and J. Huang, DBP formation in breakpoint chlorination of wastewater, Water Res., 39 (2005) 4755-4767.

[25] The State Environmental Protection Administration of China (SEPA), Editorial Committee of ''Monitoring and Analytical Methods of Water and Wastewater'', Monitoring and Analytical Methods of Water and Wastewater (4th ed.), China Environmental Science Press, Beijing, 2002.

[26] B. Zhao, S. Zhang, J. Li and J. Zhao, The technology of waster water including low concentration ammonia chloride by three effect mixed–flow falling film vacuum evaporation, Inorg. Chem. Industry, 38(8) (2006) 35-37 (in Chinese).

[27] C. Lu, P. Biswas and R.M. Clark, Modeling of breakpoint reaction in drinking water distribution pipes, Environ. Int., 19 (1993) 543-560.

[28] W.J. Eilbeck, Redox control in breakpoint chlorination of ammonia and metal ammine complexes, Water Res., 18(1) (1984) 21-24.