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Experimental study on freezing-based methods in treating simulated high salt organic wastewater

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ABSTRACT

Simulated high salt organic wastewater samples with the chemical oxygen demand (COD) and the salt concentration of 10,000 mg/L were prepared in the experiments. Two combined freezing-based methods were employed to deal with the simulated wastewater, which are the freezing and centrifugal method (FCM), and the freezing, gravity-induced and centrifugal method (FGCM). The salt removal efficiency, the COD removal efficiency and the ice recovery rate of the treated ice samples were investigated. The results showed that for FCM experiments, more than 70% of organic matter and salt content can be removed rapidly under the rotation rate of 2,000 rpm and the centrifugation duration of 2 min. Extending the centrifugation duration or further increasing the rotation rate can't improve COD and salt removal efficiencies greatly. For FGCM experiments, the COD and salt removal efficiencies increase with the concentrated wastewater drainage proportion or increase slightly in lower ambient temperature. The salt concentration and COD of the treated ice samples can meet the requirement of China's wastewater discharge standards under certain gravity-induced wastewater drainage proportion or ambient temperature.

Keywords: Freezing-based method; Chemical oxygen demand removal efficiency; Salt removal efficiency; Centrifugal separation; Gravity-induced melting process

1. Introduction

In some industrial processes, such as chemical industrial processes or power generation processes, wastewater with chemical oxygen demand (COD) and salinity higher than 1% may be drained [1]. High salinity affects the activity of microorganisms, which makes the ordinary biological methods unsuitable in the treatment of salt organic wastewater. To deal with this problem, some scholars tried to domesticate salt-tolerant microorganisms or to use bio-augmentation technology to treat high salt organic wastewater. Panswad and Anan [2] carried out some synthetic wastewater treatment experiments to investigate the effects of inoculating domesticated microorganisms. The results revealed when the salinity increases, the COD removal efficiency decreases from 97% to 60% for the experiments without domesticated microorganism inoculation, and the value decreases from 90% to 71% for the experiments with domesticated microorganism inoculation. Hua [3] used bio-augmentation technology instead of changing the biochemical treatment process and facilities to treat the high salinity wastewater and to stabilize the discharge water quality. The study showed that the effluent COD of biochemical unit can be reduced by 21.9% to be stable at 50–60 mg/L with the application of bio-augmentation technology.

Although the screened or acclimated microorganisms can effectively degrade the organic matters in the high salinity wastewater, they can't discompose salt content.

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Scholars have tried some physical methods, chemical methods or combined methods to separate organic matters and salt in wastewater simultaneously. Zhang et al. [4] used a composite process based on membrane distillation to treat the petrochemical high salinity wastewater. Through the treatment of acid modulation, membrane distillation and reverse osmosis, the salt removal efficiency, the total organic carbon (TOC) removal efficiency and the water recovery rate arrived at 99.9%, 90% and 90%, respectively. Liu et al. [5] designed a process combining liquid–liquid extraction and membrane bioreactor to treat synthetic wastewater containing chlorophenol concentration of 1,000 mg/L and NaCl concentration of 5% w/w. The result indicated that the chlorophenol concentration in wastewater can be reduced to lower than 100 mg/L.

Freezing method as a theoretical separation method, its applications in food industry [6–9], pharmaceutical industry [10,11], wastewater treatment [12–14], and desalination [15–18], etc. have been studied widely. Freezing desalination bases on the phenomenon that during freezing process, pure water molecules crystallize to be separated from salt solution. But, in suspension crystalizing process, some concentrated brine is always adhered to ice crystals [19], and in progressive freezing process, some concentrated brine is inevitably trapped inside ice layer to form so-called "brine pockets" [20,21]. Low salinity water will be obtained if the concentrated brine can be separated from ice and the remaining ice is melted [22]. Badawy [23] conducted seawater desalination experiments using multistage freezing-melting to obtain potable water. They found that the water with the salinity of total dissolved solids (TDS) of 610 mg/L can be produced with eight cycles of freezing-melting process, which is equivalent to 98.5% of the salt being removed. Theoretically, freezing desalination method is more energy efficient than distillation desalination because the ice melting heat of 334.7 kJ/kg is much less than the water vaporization heat of 2,259.4 kJ/kg under 1 atm [13,21]. Besides that, freezing process can be a simple physical process without chemical material being added or chemical by-products being produced. Low operational temperature also reduces equipment corrosion risk. In practice, pure water can be produced directly using distillation method but single-stage freezing method. Freezing desalination method can just yield low salinity water since brine is difficult to be separated from ice totally. It means that desalination effect of freezing method is not as good as that of distillation method.

Researchers have explored the application of freezing method in wastewater treatment. When the wastewater is gradually frozen, ice crystals grow from pure water and the contaminants are concentrated with some of them being captured to form "concentrated solution pockets" [20,21,24]. Consequently, the quality of the treated wastewater depends on how much concentrated solution can be separated from the ice. Chen et al. [25] conducted multi-stage freeze-melt experiments to recover olaquindox from wastewater and to reduce the COD and salinity of the discharge water. After three-stage freeze-melt process with the ice formation rate from 45% to 59%, the average removal efficiencies of COD, electric conductivity, ammonia nitrogen and total nitrogen of the discharge water were 99.4%, 98.2%, 98.7% and 98.5%, respectively. Feng et al. [26] used suspension crystallization and freeze-melt technology to recover oil from waste cutting fluid and studied the effects of freezing temperature, stirring speed, pH and other factors. The results showed that the optimal operational conditions were the freezing temperature of –8°C and the stirring speed of 300 rpm for the experiments. Under this experimental condition, the COD removal efficiency and oil recovery rate reached 90% and 95%, respectively. Liu et al. [27] carried out progressive freezing experiments under unidirectional heat transfer condition to treat wastewater containing high Ca^{2+} concentration. They investigated the effects of ice thickness, initial Ca^{2+} concentration, freezing temperature and initial pH of wastewater on Ca^{2+} removal rate. The results proved that during the progressive freezing process, Ca^{2+} migrates downwards from ice to water, and the ice can be purified. Li et al. [28] studied the factors in multi-stage freezing process to treat high salt organic wastewater. The results showed that low freezing temperature and small heat-exchanging area result in low salt and COD removal efficiencies. For the actual chemical wastewater with the initial salinity of 56,448.9 mg/L and COD of 55,690.0 mg/L, the COD and salt removal efficiencies achieved 99.1% and 98.2%, respectively after six-stage freezing treatment.

In order separate the concentrated solution pockets from ice to improve the ice purity, the methods including multistage freezing-melting, centrifugation, gravity-induced melting drainage, etc. have been studied [15,23,29–31]. Zhang [30] used crushing and centrifugation method to process sea ice. The effects of the rotation rate, the centrifugation time and the ambient temperature on sea ice desalination were studied. Under the centrifugal rotation rate of 2,000 rpm, the centrifugal time of 12 min and the ambient temperature of –2°C, the salt removal efficiency reached 72.80%. Xu et al. [31] carried out the gravity-induced desalination experiments to improve the purity of Bohai Sea ice and used blue tracer to observe the concentrated solution flowing downwards together with the ice melting water induced by gravity. With the ambient temperature varying from 2°C to 6°C and the sea ice temperature ranging from –1.5°C to 2°C, the ice salinity approached 0.1% and the water yield rate was nearly 60% after 5 to 7 d.

Our research team has conducted some studies to desalt saline water using combined freezing-based desalination methods [32,33]. Based on our previous work, the freezing and centrifugal method (FCM) and the freezing, gravity-induced and centrifugal method (FGCM) were employed in the experiments of this study to treat the simulated high salt organic wastewater. Taking the removal efficiencies of salt and COD and the ice recovery rate as indicators, the effects of rotation rate and the centrifugation duration in FCM experiments, and the influence of gravity-induced wastewater drainage proportion and ambient temperature in FGCM experiments were investigated.

2. Materials and methods

In the experiments, the analytical reagent glucose and NaCl were dissolved in pure water to form the simulated high salt organic wastewater with both initial COD and salinity of 10,000 mg/L. In order to investigate the mutual effects of salt and organic matter on the removal effect to each other, the simulated salt wastewater with the salinity of 10,000 mg/L as well as the simulated organic wastewater with the COD of 10,000 mg/L were also prepared. FCM and FGCM were utilized to treat the simulated wastewater samples and the flow diagrams of them are shown in Fig. 1. In both FCM and FGCM experiments, each sample consists of nearly 500 g simulated wastewater that was put in a beaker. The samples were placed in the refrigerator set at –24°C for 15 h till the wastewater frozen into ice thoroughly. In the FCM experiments, the ice samples were crushed and then centrifuged. The crushed and centrifuged ice samples are shown in Fig. 2. The centrifugation duration was regulated from 1 to 5 min and the rotation rate of the centrifuge varied from 500 to 3,000 rpm. In the FGCM experiments, after freezing process, each ice sample was taken out from the beaker and placed on a funnel as shown in Fig. 3 to melt a part of the ice. The gravity-induced melting process happened in a constant temperature chamber. The chamber temperature was set at 4°C, 18°C or 28°C, respectively according to the average air temperature of summer, transition seasons and winter in Beijing area. A beaker was placed below each funnel to collect the ice melting water together with the concentrated wastewater. The drainage mass increases with the gravity-induced melting duration. Once the drainage proportion approached the set value, the remaining ice sample

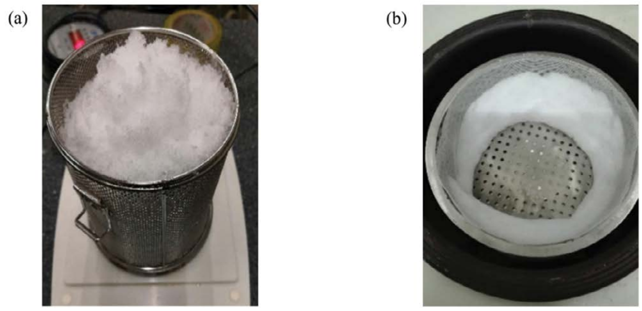

Fig. 2. (a) Crushed and (b) centrifuged ice sample.

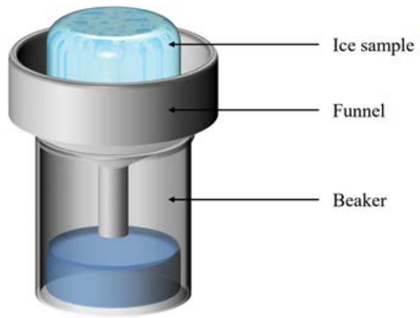

Fig. 3. Schematic of the gravity-induced ice melting process.

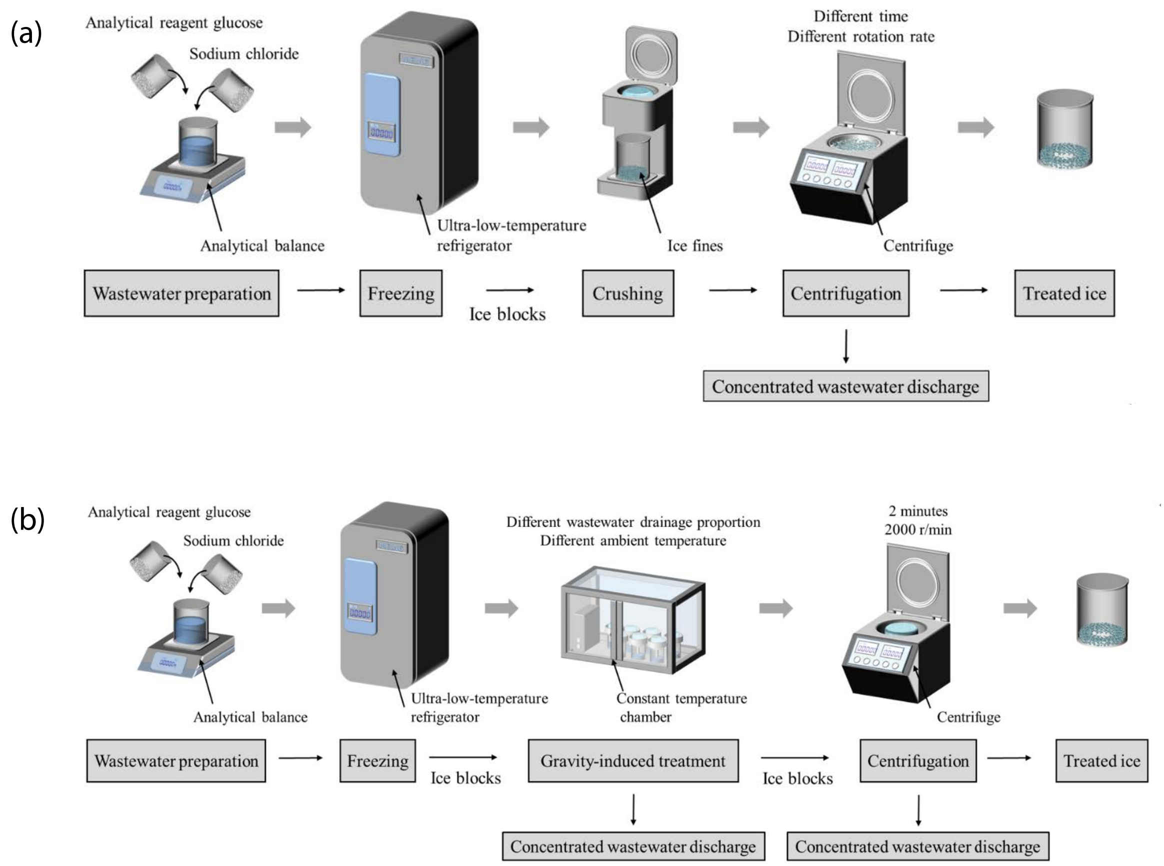

Fig. 1. Flow diagram of (a) FCM and (b) FGCM.

was taken out to measure the mass and then was centrifuged for 2 min at the rotation rate of 2,000 rpm to further separate the concentrated wastewater from ice. Comparing the two freezing-based methods, the ice crushing treatment in FCM was replaced by the ice melting treatment in FGCM. In all of the experiments in this paper, after centrifugation treatment, the treated ice was melted to measure the mass, the salinity and the COD with the analytical balance, the salinity meter and the ultraviolet visible spectrophotometer respectively. The types and technical parameters of the equipment and instruments used in the experiments are listed in Table 1.

According to the test data, the COD removal efficiency, salt removal efficiency and ice recovery rate were calculated using Eqs. (1)–(3) to evaluate the effects of the two kinds of treatments. For FGCM experiments, the gravity-induced wastewater drainage proportion was calculated using Eq. (4).

$$R = \frac{\left(C_0 - C_i\right)}{C_0} \times 100\% \tag{1}$$

$$R_{\text{COD}} = \frac{\left(C_{0\text{COD}} - C_{i\text{COD}}\right)}{C_{0\text{COD}}} \times 100\% \tag{2}$$

$$R_{\text{ir}} = \frac{M_i}{M_0} \times 100\% \tag{3}$$

$$R_{\text{gi}} = \frac{\left(M_0 - M_{\text{gi}}\right)}{M_0} \times 100\% \tag{4}$$

where R is the salt removal efficiency (%), C_0 is the initial salinity of the wastewater sample (mg/L), C_i is the salinity of the treated ice (mg/L), R_{COD} is the COD removal efficiency (%), $C_{0\text{COD}}$ is the initial COD of the wastewater sample (mg/L), $C_{1\text{COD}}$ is the COD of the treated ice (mg/L), R_{ir} is the ice recovery rate (%), M_i is the mass of the treated ice (g), M_0 is the initial mass of the wastewater sample (g), R_{gi} is the gravity-induced concentrated wastewater drainage proportion (%), M_{gi} is the mass of the remaining ice after gravity-induced process (g).

Fast digestion-spectrophotometric method is based on the dichromate method to determine COD in water. Chloride is the primary interference in this method and can be eliminated with mercuric sulfate. In this research, the test vials containing special reagent with mercuric sulfate were used in COD determination and the maximum chloride elimination interference of the vial is 2,000 mg/L Cl^-. The samples with COD higher than 1,000 mg/L Cl^- had been diluted with deionized water according to the national standards on COD determination [34,35].

Table 1
Equipment and instruments used in the experiments

Instrument	Model	Technical parameters
Ultra-low-temperature refrigerator	DW-HL388	–86°C~–10°C
Centrifuge	TD5F	0~4,000 rpm
Constant temperature chamber	–	–20°C~55°C
Analytical balance	TE3102S	0~3,000 g; accuracy: 10 mg
Salinity meter	AZ8371	0~70 g/L; accuracy: ±1%
Ultraviolet–visible spectrophotometer	DR6000	190~1,100 nm; accuracy: ±1 nm
Digester	DRB200	37°C~165°C; accuracy: ±2°C

3. Experiments and results

3.1. FCM experiments

3.1.1. Influence of centrifugation duration

In FCM experiments, the effect of centrifugation duration on the salt and COD removal efficiencies was investigated. Meanwhile, the mutual effects of the salt and organic matter on their removal efficiencies were analyzed. Fifteen simulated wastewater samples were prepared, which include five simulated high salt organic wastewater samples (from Case I-1(1) to Case I-1(5)) with both salt content and COD of 10,000 mg/L, five organic wastewater samples (from Case I-2(1) to Case I-2(5)) with COD of 10,000 mg/L and five salt wastewater samples (from Case I-3(1) to Case I-3(5)) with the salt content of 10,000 mg/L. The experimental conditions and the results are shown in Table 2.

According to the data of Case I-1(1) to Case I-1(5) in Table 2, the effect of centrifugation duration on FCM treatment of the high salt organic wastewater is presented in Fig. 4a. When the centrifugation duration increases from 1 to 5 min, the COD and salt removal efficiencies increase from 71.6% and 70.5% to 76.9% and 75.8% and the ice recovery rate decreases from 67.17% to 62.25%. Whereas, the enhancements of the COD and salt removal efficiencies with the centrifugation duration changing from 1 to 2 min is much bigger than that with the centrifugation duration changing from 2 to 5 min. It implies that under the rotation rate of 2000 rpm, when the centrifugation duration reaches 2 min, continually extending the centrifugation duration has not significant improvement on the COD and salt removal efficiencies. The effect of centrifugation duration on the FCM treatment of organic wastewater and salt water are presented in Fig. 4b according to the data of Cases I-2(1) to I-3(5) in Table 2. It can be observed that the variation tendencies of the COD and salt removal efficiencies as well as ice recovery rate are similar to that of high salt organic wastewater presented in Fig. 4a. The ice recovery rate decreases with the centrifugation duration, and the enhancements of COD and salt removal efficiencies are also slow down when the centrifugation duration is longer than 2 min.

According to the data in Table 2, the changes of COD and salt removal efficiencies with ice recovery rate for the three kinds of simulated wastewater samples are profiled in Fig. 5. It can be found that after FCM treatment, either COD removal efficiency or salt removal efficiency decrease linearly with

Table 2
FCM experiments with different centrifugation duration at rotation rate of 2,000 rpm

Case No.	M_0 (g)	Centrifugation duration (min)	Rotation rate (rpm)	R_{COD} (%)	R (%)	R_{ir} (%)
Case I-1(1)	500.30	1		71.60	70.50	67.17
Case I-1(2)	500.06	2		75.40	74.20	64.20
Case I-1(3)	500.12	3		76.10	75.00	63.26
Case I-1(4)	500.16	4		76.50	75.50	62.98
Case I-1(5)	500.27	5		76.90	75.80	62.25
Case I-2(1)	500.10	1		75.90	–	66.94
Case I-2(2)	500.23	2		79.80	–	64.10
Case I-2(3)	500.07	3	2,000	80.40	–	63.32
Case I-2(4)	500.15	4		80.90	–	62.66
Case I-2(5)	500.30	5		81.30	–	62.13
Case I-3(1)	500.03	1		–	74.20	67.01
Case I-3(2)	500.08	2		–	78.30	64.13
Case I-3(3)	500.16	3		–	79.20	63.31
Case I-3(4)	500.25	4		–	79.80	62.77
Case I-3(5)	500.09	5		–	80.10	62.27

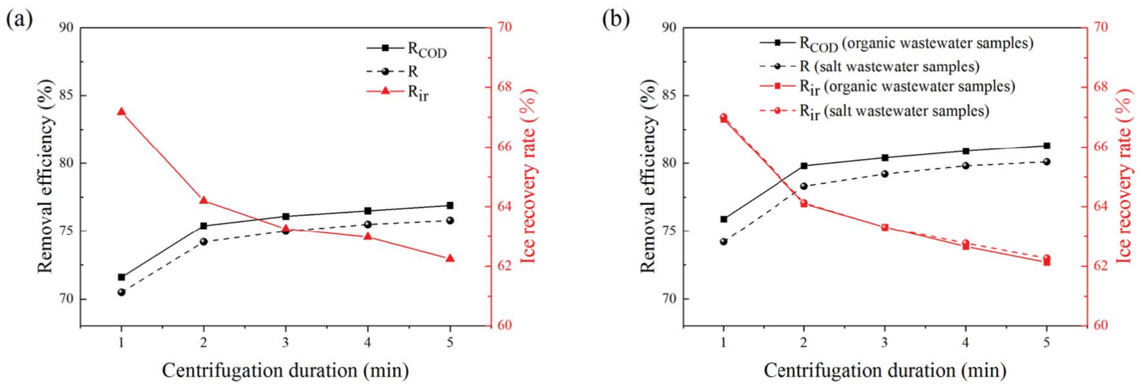

Fig. 4. Change of FCM treatment effect under different centrifugation duration: (a) presents the results with salt organic wastewater samples and (b) presents the results with organic wastewater samples and salt wastewater samples.

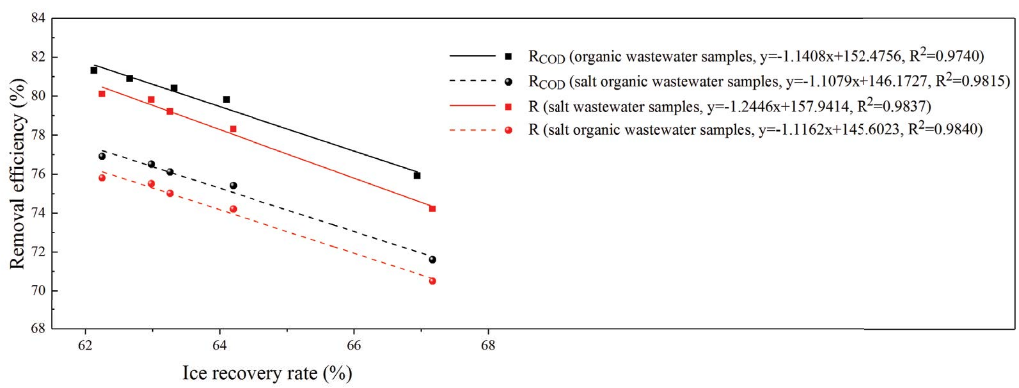

Fig. 5. Variations of salt and COD removal efficiencies with ice recovery rate using FCM treatment for three kinds of wastewater samples under different centrifugation duration.

ice recovery rate. Both the COD removal efficiency and salt removal efficiency for the salt organic wastewater samples are lower than that for the wastewater samples just containing salt or organic matters. This indicates that the organic matter and salt in wastewater affect mutually. The mutual effect leads to about 4% decrease in both COD and salt removal efficiencies for high salt organic wastewater comparing to the wastewater just containing salt or organic matters.

3.1.2. Influence of rotation rate

Six simulated high salt organic wastewater samples (from Case I-4(1) to Case I-4(6)) with both salt content and COD of 10,000 mg/L were prepared. FCM treatment experiments were carried out to investigate the effect of rotation rate on the salt and COD removal efficiencies as well as the ice recovery rate. The rotation rate varies from 500 to 3,000 rpm and the centrifugation duration was set at 2 min. The experimental conditions and the results are shown in Table 3 and according to the data in it, the variations of salt and COD removal efficiencies as well as the ice recovery rate with the rotation rate are plotted in Fig. 6a. It can be found that when the rotation rate increases from 500 to 2,000 rpm, the COD and salt removal efficiencies increase significantly from 34.2%, 32% to 75.4%, 74.4%, respectively and the ice recovery rate decreases from 85.74% to 60.11%. Whereas, when the rotation rate continuously increases from 2,000 to 3,000 rpm, the COD and salt removal efficiencies increase from 75.4% and 74.4% to 77.9% and 76.2%, meanwhile the ice recovery rate drops slightly from 61.11% to 60.06%. It implies that after 2,000 rpm, further rotation rate increase has not obvious improvement on the FCM treatment effects. The variations of the COD and salt removal efficiencies with the ice recovery rate are plotted in Fig. 6b and the linear negative correlation relationship can be found too.

3.2. FGCM experiments

In above FCM experiments for salt organic wastewater, both the maximum removal efficiencies of COD and salt are less than 80%. In addition, when the centrifugation duration reaches 2 min or the rotation rate reaches 2,000 rpm, extending centrifugation duration or increasing the rotation rate has not significant effects on improving COD or salt removal efficiencies. Based on our previous desalination research work [32,33,36], the freezing, gravity-induced and centrifugal method (FGCM) was tried to treat high salt organic wastewater. In the experiments, the centrifugation duration and rotation rate were set at 2 min and 2,000 rpm respectively according to FCM experimental results.

3.2.1. Influence of gravity-induced concentrated wastewater drainage proportion

Seven salt organic wastewater samples (from Case II-1(1) to Case II-1(7)) with both salt content and COD of 10,000 mg/L were prepared. The thawing time (t_{th}) for each sample was controlled from 60 to 180 min to change the gravity-induced concentrated wastewater drainage proportion. The melting process took place in a constant temperature chamber with the inside ambient temperature (T) set at 28°C. The experimental conditions and results are shown in Table 4.

Table 3
FCM experiments with different rotation rates at centrifugation duration of 2 min

Case No.	M_0 (g)	Centrifugation duration (min)	Rotation rate (rpm)	R_{COD} (%)	R (%)	R_{ir} (%)
Case I-4(1)	500.22		500	34.20	32.00	85.74
Case I-4(2)	500.14		1,000	47.50	46.00	75.55
Case I-4(3)	500.02		1,500	59.70	58.80	68.85
Case I-4(4)	500.01	2	2,000	75.40	74.40	60.11
Case I-4(5)	500.58		2,500	77.10	76.00	60.10
Case I-4(6)	500.05		3,000	77.90	76.20	60.06

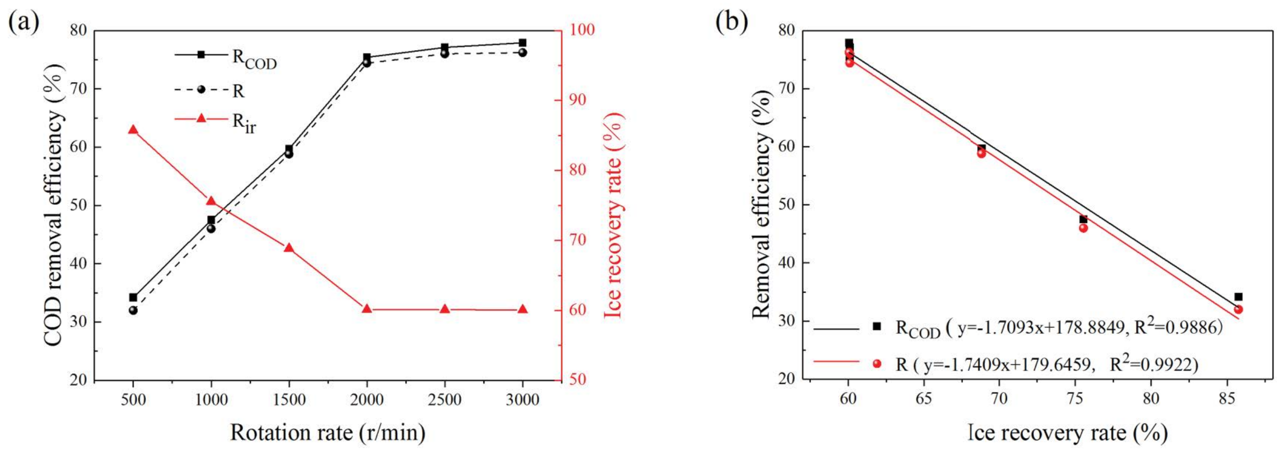

Fig. 6. Change of FCM treatment effect under different centrifuge rotation rate for salt organic wastewater samples: (a) presents the variations of salt and COD removal efficiencies and ice recovery rate with centrifuge rotation rate and (b) presents the variations of salt and COD removal efficiencies with ice recovery rate.

According to the data in Table 4, the variations of COD removal efficiency, salt removal efficiency and ice recovery rate with the gravity-induced concentrated wastewater drainage proportion using FGCM are shown in Fig. 7a. When the thawing time increases from 60 to 180 min, the wastewater drainage proportion increased from 10.18% to 49.66%, and the COD and salt removal efficiencies increase from 88.92%, 87.6% to 97.47%, 97.2%, respectively. While the ice recovery rate drops from 53.06% to 20.74%. The COD removal efficiency is slightly higher than the salt removal efficiency for all the samples. The variations of COD removal efficiency and salt removal efficiency to ice recovery rate are shown in Fig. 7b. Similar to above FCM experiments, the linear negative relationship between the COD and salt removal efficiencies and ice recovery rate can be found.

3.2.2. Influence of ambient temperature

In order to study the influence of ambient temperature in gravity-induced melting process on salt and COD removal efficiencies, FGCM experiments were conducted under 18°C and 4°C respectively. Fourteen salt organic wastewater samples with both salt content and COD of 10,000 mg/L were prepared and divided into two groups (Cases II-2(1) to II-2(7) under 18°C and Cases II-3(1) to II-3(7) under 4°C). To approach the gravity-induced wastewater drainage proportions in Table 4, the thawing time was regulated from 120 to 280 min under 18°C, and from 380 to 1,083 min under 4°C. The experimental conditions and results are shown in Table 5. It can be found under 18°C ambient condition, when the gravity-induced drainage proportion improves from 10.41% to 48.20%, the removal efficiencies of salt and COD increase from 88.9%, 90.03% to 98.3%, 98.43%, respectively, while the ice recovery rate decreases from 53.73% to 21.69%. Under 4°C ambient condition, when the gravity-induced drainage proportion increases from 10.51% to 49.05%, the salt and COD removal efficiencies increase from 89.4%, 89.98% to 99.3%, 99.4%, respectively, and the ice recovery rate drops from 58.46% to 19.23%. According to the data in Tables 4 and 5, under the ambient temperature of 28°C, 18°C and 4°C, the variations of the COD and salt removal efficiencies and the ice recovery rates with the gravity-induced wastewater drainage proportion are presented in Fig. 8, while the variations of COD removal efficiency and salt removal efficiency to ice recovery rate are shown in Fig. 9. It can be observed from Fig. 8 when the ambient temperature decreases from 28°C to 4°C, the COD and salt removal efficiencies have about 1%–3.5% enhancement and the ice recovery rate doesn't have noticeable change. It's easy to know that 1%–3.5% enhancement of COD and salt removal efficiencies is at the expense of several times of thawing time to reach the same wastewater drainage proportion. The COD removal efficiency is always slightly higher than the salt removal efficiency under different ambient temperatures. From Fig. 9 it can be noticed that both the COD removal efficiency and the salt removal efficiency are linearly negatively correlated with the ice recovery rate. At the same ice recovery, slightly higher COD and salt removal efficiencies correspond to lower ambient temperatures. Whereas, taking the time cost into consideration, it may be more benefit to treat high salt organic wastewater in summer than in winter since the thawing duration can be shortened greatly with only slight decrease of COD and salt removal efficiencies.

Table 4
FGCM experiments with different thawing time (T = 28°C)

Case No.	M_0 (g)	t_{th} (min)	R_{gi} (%)	R_{COD} (%)	R (%)	R_{ir} (%)
Case II-1(1)	500.24	60	10.18	88.92	87.60	53.06
Case II-1(2)	500.20	80	13.35	89.73	88.30	50.70
Case II-1(3)	500.28	100	21.72	92.40	91.60	41.54
Case II-1(4)	500.18	120	24.38	93.10	92.40	36.70
Case II-1(5)	500.16	140	31.33	94.24	93.50	35.42
Case II-1(6)	500.12	160	41.31	97.16	96.80	26.44
Case II-1(7)	500.25	180	49.66	97.47	97.20	20.74

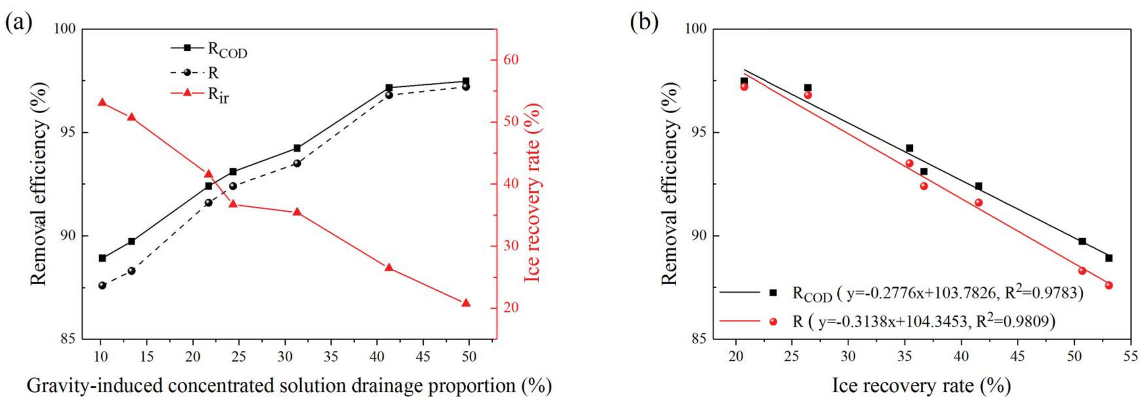

Fig. 7. Change of FGCM treatment effect under different gravity-induced concentrated wastewater drainage proportion (salt organic wastewater samples, ambient temperature at 28°C): (a) presents the variations of salt and COD removal efficiencies and ice recovery rate with gravity-induced concentrated wastewater drainage proportion and (b) presents the variations of salt and COD removal efficiencies with ice recovery rate.

Table 5
FGCM experiments with different thawing time (T = 18°C or T = 4°C)

Case No.	M_0 (g)	T (°C)	t_{th} (min)	R_{gi} (%)	R_{COD} (%)	R (%)	R_{ir} (%)
Case II-2(1)	500.08		120	10.41	90.03	88.90	53.73
Case II-2(2)	500.14		140	13.55	91.31	90.40	50.63
Case II-2(3)	500.31		185	21.76	93.22	92.50	41.83
Case II-2(4)	500.29	18	200	23.72	94.11	93.40	37.27
Case II-2(5)	500.36		220	30.36	95.02	94.30	35.45
Case II-2(6)	500.34		254	40.67	98.03	97.90	26.03
Case II-2(7)	500.22		280	48.20	98.43	98.30	21.69
Case II-3(1)	500.13		380	10.51	89.98	89.40	58.46
Case II-3(2)	500.21		470	13.51	92.05	91.50	52.06
Case II-3(3)	500.16		684	22.17	94.53	94.10	40.18
Case II-3(4)	500.09	4	782	24.46	95.18	94.60	37.87
Case II-3(5)	500.22		887	30.93	97.31	97.00	33.13
Case II-3(6)	500.27		968	41.06	98.60	98.40	28.52
Case II-3(7)	500.32		1083	49.05	99.40	99.30	19.23

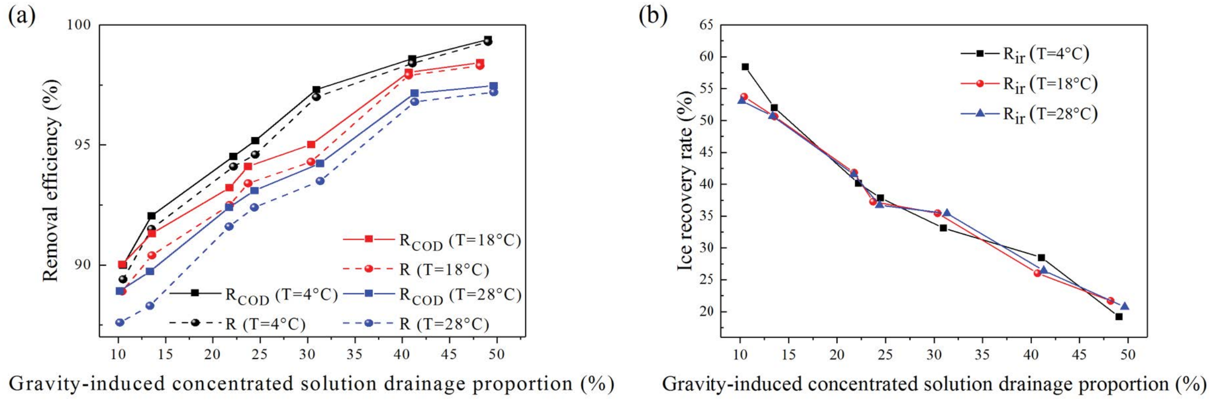

Fig. 8. Comparison of FGCM treatment effect under different ambient temperatures (salt organic wastewater samples, ambient temperature at 28°C, 18°C and 4°C): (a) presents the variations of salt and COD removal efficiencies with gravity-induced concentrated wastewater drainage proportion and (b) presents the variations of ice recovery rates with gravity-induced concentrated wastewater drainage proportion.

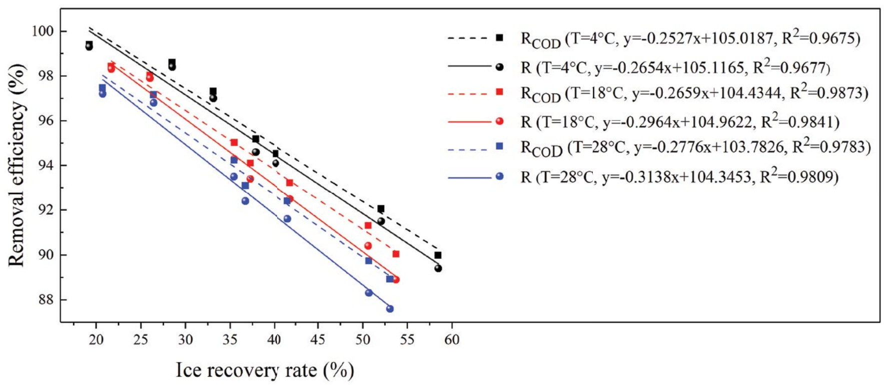

Fig. 9. Variations of salt and COD removal efficiencies with ice recovery rate using FGCM treatment under different ambient temperatures (salt organic wastewater samples, ambient temperature at 28°C, 18°C and 4°C).

3.3. Comparison of FCM and FGCM treatment results

Taking the contents of COD and chloride as the indicators to evaluate FCM and FGCM treatment effect, the experimental results were compared with the limit values required in two national standards on wastewater discharge in China. Table 6 lists the limit values of COD in Integrated Wastewater Discharge Standard (GB 8978-1996) [37] and Table 7 presents the limit values of COD and chloride in Wastewater Quality Standards for Discharge to Municipal Sewers (GB/T 31962-2015) [38]. According to the environmental requirement of the water body, into which the treated wastewater is discharged, the quality limits on discharged wastewater are classified into three grades in GB 8978-1996, as shown in Table 6. Similarly, according to the situation of the wastewater plants connected to the municipal sewers, the discharged wastewater has to respect A grade, B grade or C grade quality limits in GB/T 31962-2015, as shown in Table 7.

Comparing the data in Tables 2–5 with those in Tables 6 and 7, it can be noticed if FCM is used to treat high salt organic wastewater with initial concentration of salt and COD of 10,000 mg/L, neither the COD removal efficiency nor the chloride removal efficiency can meet the wastewater discharge standard requirements. Whereas, if FGCM is used to treat the same high salt organic wastewater, the chloride content of the treated ice in all cases can meet the B-grade and C-grade wastewater discharge standard requirements. If the gravity-induced wastewater drainage proportion is higher than 22%, the chloride content of the treated ice can meet the A-grade wastewater discharge standard requirement. Meanwhile, if the gravity-induced wastewater drainage proportion is higher than 15%, the COD content of the ice being treated under the ambient temperature of 28°C can meet the requirements for the third-grade wastewater discharged in the sugar production with beet, dyestuff industry, organophosphorus pesticide industry, alcohol production, biopharmaceuticals and leather industry, etc. At the ambient temperatures of 28°C, 18°C and 4°C, when the gravity-induced wastewater drainage proportion is increased above 35%, 30% and 24%, respectively, the COD of the treated ice can be decreased further to meet the A-grade and B-grade wastewater discharge requirements. At the ambient temperatures of 4°C, when the gravity-induced wastewater drainage proportion is higher than 49.05%, the COD of the treated ice can even reach 60 mg/L, meeting the requirement for first-grade wastewater discharge.

3.4. Brief analysis on energy consumption of FCM and FGCM treatment

The energy consumption of FCM and FGCM theoretically consist of freezing energy consumption, partial thawing energy consumption or crushing energy consumption and centrifugation energy consumption. During freezing process, wastewater experiences liquid cooling stage, crystallization stage and ice cooling stage. At 1 atm, the specific heat capacity of water is 4.22 kJ/(kg°C), the latent heat of water solidification is 334.7 kJ/kg and the specific heat capacity of ice is 2.12 kJ/(kg°C). Not considering the thermal characteristic difference between wastewater and water, the heat that needs to be transferred is 462 kJ/kg to freeze wastewater of 20°C into ice of –20°C. If the artificial refrigerating system is taken as cold source with the coefficient of performance (COP) of 1.4 [39], the electricity consumption will be about 0.092 kWh to obtain 1 kg ice. If there is natural cold source or waste industrial cold source that can be used in FCM or FGCM processes to treat wastewater, the freezing energy consumption can be neglected [17,40,41].

In our experiments, the gravity-induced thawing process happened in a constant temperature chamber and its interior temperature was maintained with a mechanical system. Whereas, the process can happen in natural environment too without additional energy consumption for gravity-induced melting process. Consequently, the melting

Table 7
COD and chloride limits in Wastewater Quality Standards for Discharge to Municipal Sewers (GB/T 31962-2015) [38] (mg/L)

Indicator	A-grade	B-grade	C-grade
COD	500 (95%)	500 (95%)	300 (97%)
Chloride	500 (91.8%)	800 (86.8%)	800 (86.8%)

The data in parentheses are the corresponding COD removal efficiencies and salt removal efficiencies to reach the standard limits, which are calculated based on the wastewater with initial COD of 10,000 mg/L and initial salinity of 10,000 mg/L. If the wastewater plant connected to the municipal sewers uses reclamation treatment, the quality of the wastewater discharged to the sewers has to meet the A-grade requirement. If the wastewater plant connected to the municipal sewers uses secondary treatment, the quality of the wastewater discharged to the sewers has to meet the B-grade requirement. If the wastewater plant connected to the municipal sewers uses primary treatment, the quality of the wastewater discharged to the sewers has to meet the C-grade requirement.

Table 6
COD limits in Integrated Wastewater Discharge Standard (GB 8978-1996) [37] (mg/L)

Scope of application	First-grade Standard	Second-grade Standard	Third-grade Standard
Sugar production with beet, dyestuff industry, organophosphorus pesticide industry, etc.	100 (99%)	200 (98%)	1,000 (90%)
Alcohol production, biopharmaceuticals and leather industry, etc.	100 (99%)	300 (97%)	1,000 (90%)
Petrochemical industry (including petroleum refining)	60 (99.4%)	150 (98.5%)	500 (95%)
Urban secondary sewage treatment plant	60 (99.4%)	120 (98.8%)	–
Other sewage discharge industry	100 (99%)	150 (98.5%)	500 (95%)

The data in parentheses are the corresponding COD removal efficiencies to reach the standard limits, which are calculated based on the wastewater with initial COD of 10,000 mg/L.

process duration would be longer in cold climate than that in warm climate. The crushing energy consumption is about 0.023 kWh and the centrifugation energy consumption is about 0.0007 kWh in dealing with 1 kg ice in our experiments. Obviously, FGCM without crushing energy consumption is more energy efficient than FCM. It should be noted that in real wastewater treatment process, much more factors affect the energy consumption. Here is just a brief estimation according to the theoretical calculation or the power of experimental instruments used in the experiments.

4. Conclusion

In this paper, two combined freezing-based methods, that is, FCM and FGCM were employed to treat the simulated high salt organic wastewater. The influences of the centrifugation duration and the rotation rate in FCM experiments and that of the gravity-induced wastewater drainage proportion and the ambient temperature in FGCM experiments, on salt and COD removal efficiencies and ice recovery rate were studied. The experimental results of the two methods were compared and the treatment effects were evaluated with the COD and chloride values required in two China's wastewater discharge standards.

More than 70% of the organic and salt contents can be removed rapidly using FCM treatment at the rotation rate of 2,000 rpm and the centrifugation duration of 2 min. Extending the centrifugation duration or further increasing the rotation rate can't improve COD and salt removal efficiencies greatly. The organic matter and salt in wastewater affect mutually and the mutual effects lead to about 4% decrease in both COD removal efficiency and salt removal efficiency for high salt organic wastewater comparing to the wastewater just containing salt or organic matters.

COD and salt removal efficiencies can be enhanced obviously using FGCM treatment to replace FCM treatment. In FGCM treatment experiments, the COD and salt removal efficiencies increase greatly with the gravity-induced wastewater drainage proportion, while the ice recovery rate decrease. Lower ambient temperature can increase slightly COD and salt removal efficiencies at the expense of several times of thawing time. COD and salt removal efficiencies are always linearly negatively related with ice recovery rate using either FCM treatment or FGCM treatment.

To deal with simulated high salt organic wastewater with both salinity and COD of 10,000 mg/L using FCM process, neither the COD removal efficiency nor the chloride removal efficiency can meet the requirement of China's national wastewater discharge standards. Whereas, to deal with the simulated wastewater with the same content of salt and organic matter, both COD and chloride content can reach the requirements of the standards using FGCM process under certain gravity-induced wastewater drainage proportion or ambient temperature.

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