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Development of an evaporation crystallizer for desalination of alkaline organic wastewater before incineration*

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Abstract: A wastewater evaporation-desalination pretreatment method was introduced to remove the Na^+ and K^+ salts in volatile organic compounds (VOCs) wastewater before it was fed into the incinerator. VOCs in the wastewater were volatilized in the evaporation system and then the vapor was combusted in an incinerator. Simulated phenol wastewater containing sodium chloride was evaporated and concentrated and sodium chloride was crystallized in different parameters. The experimental results showed that the higher initial concentration of sodium chloride increases the ratio of volatilization of VOCs, which was due to the effect of "salting out" (a decrease in the solubility of the nonelectrolyte in the solution, or more rigorously, an increase in its activity coefficient, caused by the salt addition (Furter and Cook, 1967)). When evaporation speed was increased from 1.67 ml/min to 2.73 ml/min, the total removal coefficient of sodium chloride was about 99.88%~99.99%. This pretreatment procedure eliminates the slag phenomenon caused by Na^+ and K^+ salts during wastewater incineration, so the incinerator could operate continuously, and the wastewater evaporation could increase the heat value of wastewater, and the operation cost would be reduced.

Key words: Salty wastewater, Volatile organic compounds (VOCs), Sodium chloride, Evaporation, Crystallization, Desalination
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INTRODUCTION

Toxic salty organic wastewater is found in many industries, such as oil refineries, coke plants and chemical plants. Wastewater has the common characteristics of high chemical oxygen demand (COD) (up to 100000 mg/L) and difficult biodegradation (Gulyas, 1997). Because of their resistance to common microorganisms, they cannot be effectively treated by traditional techniques. Improper disposal of wastewater leads to pollution of drinking water sources and agricultural land, then directly harming human health and the environment.

Incineration widely employed over the years for destruction of hazardous solid wastes (Oppelt, 1987; Werther and Ogada, 1999) has also been used for disposal of toxic wastewater with high-level organic pollutants (Sevon and Cooper, 1991; Bie *et al*., 2002; Kaul *et al*., 1998; Grubor *et al*., 1999). To improve the caloric capacity and decrease the cost of incineration, concentration is normally essential, such as evaporation, freeze concentration, ultrafiltration and extraction (Li, 1993; Lemmer *et al*., 2001; Roos *et al*., 2003; Yasuhiro and Takio, 2000). However, in a high temperature incinerator (>900 °C), high content of alkali and alkaline-earth metals in the waste can form compounds with low melting point, which induce agglomeration, fouling, sintering and defluidization (Lin *et al*., 2003; Latva-Somppi *et al*., 1998; Wu *et al*.,

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1999; Arvekakis *et al*., 2001). The technique of adding additives to raise the melting point of ash (Bie *et al*., 2002) was put forward, but universal additives for all alkali and alkaline-earth metal salts have not been found. Controlling temperature below the melting point of these inorganic salts can avoid bed sintering (Grubor *et al*., 1999), but incineration at low temperature can lead to deficient decomposing of organic compounds. Removal of inorganic materials is another method to solve the problems (Kaul *et al*., 1998; Arvekakis *et al*., 2001). Kaul *et al*.(1998) used a four-effect forced circulation evaporator as a pretreatment method. Sodium sulphate was crystallized and condensed wastewater was incinerated. Nevertheless, efficiency of desalination and its effect on incineration was not researched in their study. The objective of our group was to study the desalination efficiency of evaporation and its effect on incineration during treatment of salty wastewater.

Evaporation crystallization is a well-known separation and desalination process that utilizes different volatility of every material (Hisham and Ettouney, 1999). As shown in Fig.1, a new wastewater incineration system with evaporation-desalination pretreatment equipment was put forward to treat salty wastewater in our group. VOCs can be volatilized into steam as the wastewater is heated. The water vapor with VOCs is fed into the incinerator, where VOCs transform into CO_2 and H_2O with high temperature combustion. With water vaporizing, the concentration of dissolved inorganic salts, such as sulphate and chloride of alkali and alkaline-earth metals increase and then begin to crystallize. Remnant water is recirculated to the wastewater tank. This system can be used for incineration of salty wastewater with high concentration of volatile organic compounds.

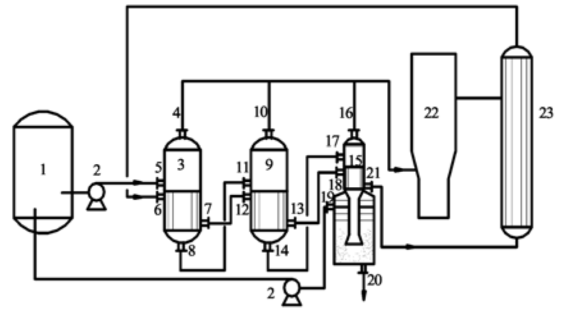

Fig.1 The schematic of wastewater incineration system with evaporation desalination equipment. 1: Wastewater tank; 2: Pump; 3: 1st effect evaporator; 4: Wastewater vapour outlet; 5: Wastewater inlet; 6: Steam inlet; 7: Steam outlet; 8: Wastewater outlet; 9: 2nd effect evaporator; 10: Wastewater vapour outlet; 11: Wastewater inlet; 12: Steam inlet; 13: Steam outlet; 14: Wastewater outlet; 15: 3rd effect evaporating crystallizer; 16: Wastewater vapour outlet; 17: Wastewater inlet; 18: Steam inlet; 19: Condensed water outlet; 20: Crystallized salts exit; 21: Steam outlet; 22: Incinerator; 23: Waste heat oiler

There are some innovative points in this system. Firstly, wastewater vapour (4, 10, 16) produced in evaporator is directly fed into incinerator (22) instead of the next evaporator (9, 15). Secondly, evaporation residue (19) is recycled into the wastewater tank instead of the incinerator. Thirdly, quantity of heat is reutilized by waste heat boiler (23) in evaporation of wastewater. As a result, many advantages can be achieved using this incineration system with evaporation crystallizer. The removal of inorganic salts from wastewater can solve the problem of agglomeration, fouling and sintering, and then, incineration of the wastewater without these salts can operation continuously. Additionally, evaporation increases the heat value of waste fed into incinerator. The heating resource of wastewater evaporation comes from the furnace's waste heat boiler. The heating steam can pass through the multi-effects evaporator out of the heat pipe, and the wastewater's vaporization occurs in the heat pipe.

Evaporation could be affected by some parameters, such as initial content of salts, original concentration of organic compounds and evaporation velocity. Therefore, the influence of operation parameters was studied in this paper, and the efficiency of desalination and volatilization of organic components during vaporization process were analyzed mainly.

EXPERIMENTAL SET-UP AND ANALYSIS METHOD

Phenol was chosen as a model organic pollutant because it is found in many industries, such as refineries, coke plants, paper and pulp industries and chemical plants and has been found to accelerate tumor formation, cancer and mutation (Namasivayam and Kavitha, 2004). Sodium chloride was dissolved in phenol solution to simulate the wastewater. All simulated wastewater were prepared from analytical-reagent grade chemicals, provided by Shanghai Reagent Co., China, in deionized water.

The pilot scale evaporator is shown in Fig.2. To simplify the experimental system, the wastewater was heated by an electric heater. The steam evaporated from wastewater was cooled by a water condenser. Six condensates with equal volume were collected sequentially. Evaporation residue was filtered in nutsch filter to remove crystallized salts.

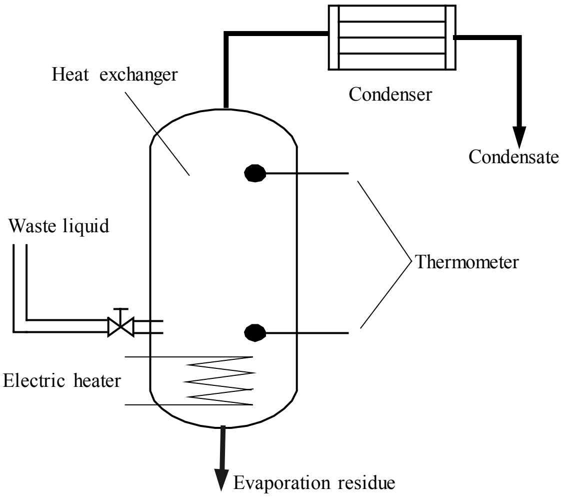

Fig.2 Sketch of the pilot evaporation desalination system

The concentration of Na^+ and phenol in each condensate and the filtrate can illustrate the efficiency of desalination and volatilization in different time and different condition. The concentration of Na^+ in the condensates or the filtrate of the residue was analyzed by ion chromatography (DX-120, Dionex) equipped with an IonPac CS12A column (Dionex) and a 4 mm CSRS-ULTRA suppressor (Dionex). The eluent was 20 mmol/L methanesulfonic acid. The value of COD, instead of phenol concentration was used to denote the total concentration of organic compounds in the condensate and the filtrate considering phenol is oxidable during evaporation. The COD value of the original wastewater, the condensates and the filtrate was measured by a COD measurement system (Model5B-3, Lianhua Environmental Protection Ltd., Lanzhou). The temperature of the wastewater and the steam in the heat exchanger was measured with thermometer.

The ratio of volatilization of organic compounds in each condensate (η_{ci}) is defined below:

$$\eta_{ci}=\frac{C_i\times V_i}{C_0\times V_0}\times 100\%, \tag{1}$$

where C_0 is the original COD of the simulated wastewater; C_i (i=1, 2, …, 6) is the COD value of the sequential condensate, i is number of condensate; C_7 is the COD value of the filtrate of the residue; V_0 is the volume of the original wastewater; V_i (i=1, 2, …, 6) is the volume of the condensate and V_7 is the volume of the filtrate. Therefore, η_{ci} represents the ratio of volatilization of organic components in different time.

The total efficiency Na removal η_s is defined below:

$$\eta_s=\frac{[Na^+]_0V_0-\sum_{i=1}^{6}([Na^+]_iV_i)}{[Na^+]_0V_0}\times 100\%, \tag{2}$$

where $[Na^+]_0$ denotes the Na^+ concentration of the original simulated wastewater, $[Na^+]_i$ (i=1, 2, …, 6) denotes the Na^+ concentration of the condensate. The average evaporation velocity is defined as the total quantity of the steam divided by evaporation time. The rate of vaporization is defined as the volume of the initial wastewater divided by the volume of steam.

RESULTS AND DISCUSSION

Phenol volatilization and desalination result of evaporation method

Twenty g phenol and 10 g sodium chloride were dissolved in deionized water to produce 1 L simulated wastewater. The COD value of the original wastewater was 47670 mg/L, which fits the theoretical value. The content of Na^+ cation was 4090 mg/L, which is close to the calculated value. Three-hundred and fifteen ml wastewater was vaporized, with the final residue being about 10 ml. Evaporation velocity was about 1.67 ml/min.

As shown in Fig.3, the ratio of volatilization of organic compounds in the former condensate is higher than that in the latter. η_{c1} and η_{c2} is 23.89% and 21.09%, while η_{c5} and η_{c6} is 8.28% and 2.53% respectively. The results are due to the fact that phenol is a highly volatile organic compound. At the same time, a small quantity of organic compounds, 2.13%, remained in the filtrate. The total ratio of volatilization of organic materials reached 97.66%.

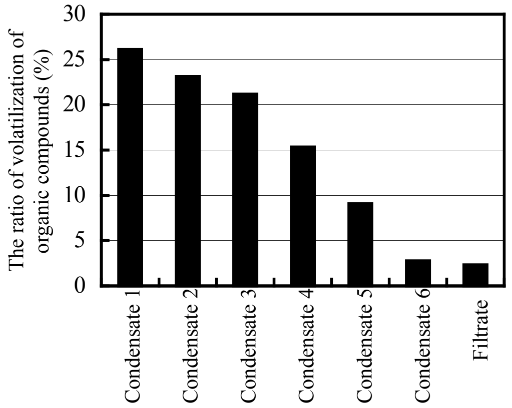

Fig.3 The ratio of volatilization of organic materials

Table 1 shows that the concentration of sodium cation of each condensate is minimal in 10^{-6}, although the value increases slightly in Condensates 5 and 6. The concentration of sodium in the filtrate reaches saturation and some sodium chloride is crystallized. In this evaporation-incineration system, steam is fed into the incinerator and the filtrate is recycled into the evaporator. So, according to Eq.(2), the total efficiency of Na removal for the steam is 99.97%.

Table 1 The Na^+ desalination efficiency

The solution	Volume (ml)	$[Na^+]_i$ (mg/L)	η_S (%)
Condensate 1	50	0.8461	99.97
Condensate 2	50	0.8721	
Condensate 3	50	0.7990	
Condensate 4	50	0.9292	
Condensate 5	50	1.6451	
Condensate 6	50	3.6480	
Filtrate	10 (approx.)	10760	

The above results indicate that the simulated phenol wastewater containing sodium chloride can be desalinated and that organic materials can volatilize with water. Meanwhile, most of organic compounds volatilize when the rate of vaporization reaches 60%.

Effect of initial content of sodium chloride on evaporation process

It was reported that dissolved salts in general tended to enrich the vapour in the component of lower dielectric constant (Furter and Cook, 1967). At the same time, the magnitude of "salting out" depends on the amount of salt presented in solution (Furter, 1993). Fig.4 shows that the initial content of sodium chloride affects evidently the volatilization of phenol, which accords with the theory of salt effect. When the rate of vaporization is 15%, the ratio of volatilization of organic components is increased from 31.75% to 39.82% as the initial content of sodium chloride is increased from 20 g/L to 50 g/L, and the ratio of volatilization is increased from 39.82% to 40.55% as the initial content of sodium chloride is increased from 50 g/L to 70 g/L. The phenomena indicate that the relative volatility increases with increase of the content of sodium chloride, and that the enhancement is weakened when the initial content of sodium chloride exceeds 50 g/L.

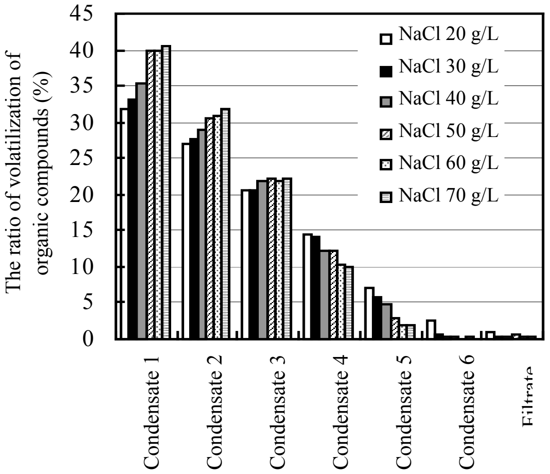

Fig.4 The effect of the initial content of NaCl yield phenol volatilization. The initial concentration of phenol=20 g/L, evaporation velocity=1.67 ml/min

Sodium chloride, being nonvolatile, remains mostly in the residue wastewater. A low quantity of sodium chloride in gas phase comes from mechanical and selective schlepp of vapour (Feng and Shen, 1992). Fig.5 shows that the efficiency of removal of sodium chloride is above 99.9% in spite of its initial concentration. When the initial content of sodium chloride exceeds 30 g/L, η_S is 99.99%. Increasing the initial content of sodium chloride can improve the effect of desalination, which indicates that inorganic salts can be crystallized and removed effectively from wastewater containing high concentration of sodium chloride.

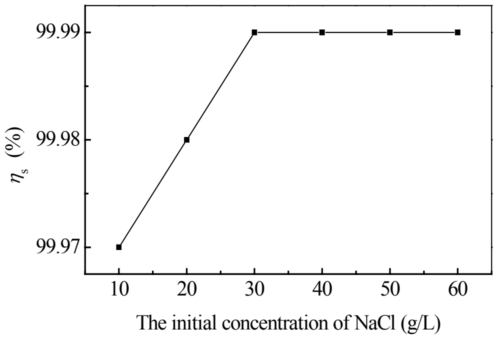

Fig.5 The effect of the initial content of NaCl yield desalination. The initial concentration of phenol=20 g/L, evaporation velocity=1.67 ml/min

Effect of initial content of phenol on the evaporation process

As shown in Fig.6, the ratio of volatilization of organic compounds increases when the initial content of phenol is increased from 10 g/L to 20 g/L, and that the relative volatility decreased when the content exceeds 20 g/L. However, all total ratios of volatilization of organic compounds are larger than 99.3% no matter what the initial concentration of phenol is. Nearly all of the volatile organic components can be evaporated and then incinerated. It indicates that more absolute VOCs removal will be achieved at higher initial phenol concentration.

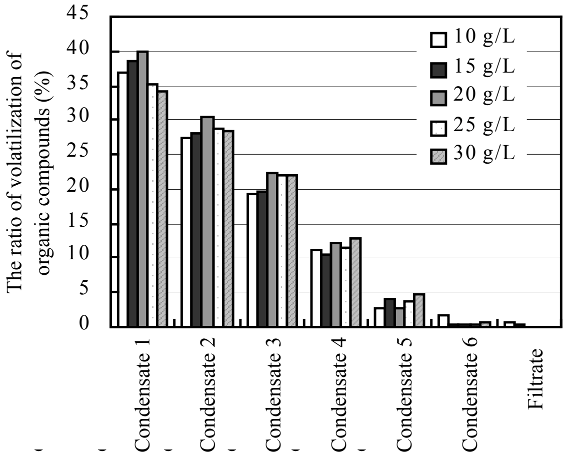

Fig.6 The effect of the initial content of phenol on volatilization. The initial content of NaCl=50 g/L, evaporation velocity=1.67 ml/min

Table 2 shows that η_S is almost not influenced by the initial concentration of phenol. It is concluded that a spot of salts in the steam, as a result of mechanical and selective schlepp of vapour is inevitable.

Table 2 The effect of the initial concentration of phenol on the desalination coefficient of Na$^+$ ([Na$^+$]$_0$ is 19658 mg/L, evaporation velocity=1.67 ml/min)

The initial content of phenol (g/L)	η_S (%)
10	99.98
15	99.98
20	99.99
25	99.99
30	99.99

Effect of evaporation velocity on evaporation process

Evaporation velocity was increased by increasing heating power. Fig.7 shows that η_{ci} is affected distinctly by evaporation velocity when the rate of evaporation is lower than 30%. η_{c1} and η_{c2} decrease at first and then increase when evaporation velocity is increased from 1.67 ml/min to 2.3 ml/min and to 2.73 ml/min. Such results in the volatilization ratio of organic compounds should be possibly attributed to mutual actions: phenol is oxidized into other materials, such as 1,4-benzonquinone, which have different volatility and lower COD. However, the ratio of volatilization differs very little at different velocity when the rate of evaporation is higher than 30%. At the same time, all total ratios of volatilization of organic compounds are larger than 99.9%.

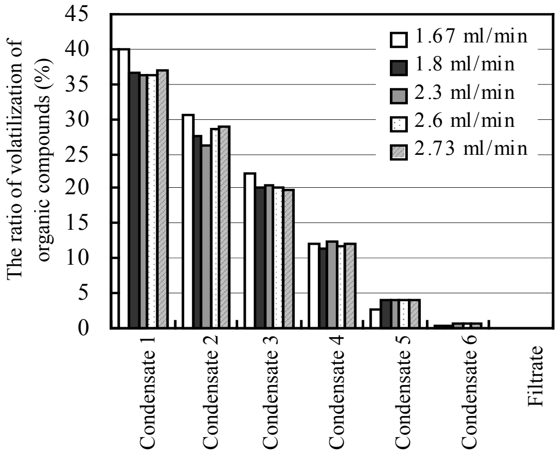

Fig.7 The effect of evaporation velocity on volatilization. The initial concentration of phenol=20 g/L, the initial content of NaCl=50 g/L

Fig.8 shows that the efficiency of desalination decreases from 99.99% to 99.88% with evaporation velocity increasing from 1.67 ml/min to 2.73 ml/min. Such results show the enhancement of mechanical and selective schlepp of vapour at higher evaporation speed. However, sodium chloride in Condensates 1, 2, 3 and 4 is still in very trace amount and the increase of mechanical and selective schlepp of vapour appeared in Condensates 5 and 6. In view of the above results, lower evaporation velocity favors desalination.

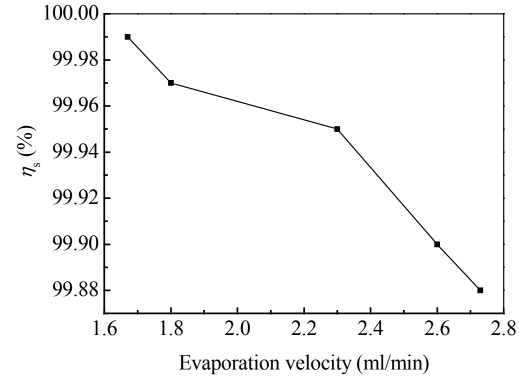

Fig.8 The effect of evaporation velocity on desalination. The initial concentration of phenol=20 g/L, the initial content of NaCl=50 g/L

CONCLUSION

An evaporation-crystallization method to be applied before wastewater incineration was put forward for treating salty organic wastewater. Simulated phenol wastewater containing sodium chloride was researched by using pilot evaporator equipment. Various parameters on volatilization of VOCs and removal of salts were investigated. Higher concentration of sodium chloride is helpful for volatilization of phenol and its oxygenized products due to the effect of "salting out", but when the initial concentration of sodium chloride is increased to 50 g/L, such improvement becomes insignificant. The total efficiency of sodium chloride removal is increased as the initial concentration of sodium chloride increases. The initial concentration of phenol could not obviously affect volatilization of VOCs and desalination. It was observed that the ratio of volatilization of desalination was higher at lower evaporation velocity. For example, η_S decreases from 99.99% to 99.88% when the evaporation velocity is increased from 1.67 ml/min to 2.73 ml/min. Dissolved salts in the steam is ascribed to the mechanical and selective schlep of vapour. In conclusion, evaporation and crystallization can be an effective method for pretreatment of incineration of salty liquid waste.

This research provides theoretical basis for development of a multiple-effect crystallizing evaporator with two main functions: volatilization of organic compounds and removal of inorganic salts. Before incineration, evaporation and crystallization of wastewater containing a lot of VOCs and sodium chloride offer distinct advantages. The desalinated liquid wastes will be incinerated without the accompanying occurrence of agglomeration, fouling, sintering and defluidization. As a result, the incinerator can function continuously, which is a difficulty for many incineration techniques now. Most of the VOCs are evaporated with the vapor to form steam, which will reduce the demand for supplementary fuel in incineration. The filtrate can be reflowed to the waste container and evaporated once again.

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