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Treatment of electroplating wastewater using the freezing method

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ABSTRACT

Wastewater produced from washing can be concentrated and reused in an electroplating bath to produce a cleaner product. Predominant methods of concentrating wastewater from electroplating washing include reverse osmosis and evaporation concentration. However, reverse osmosis cannot treat strongly acidic (pH < 2) or strongly alkaline (pH > 12) wastewaters, and the scope of its application is narrow, while evaporation uses high quantities of energy and is costly. In contrast, freezing electroplating washing wastewater incurs low cost and can be used for treating washing wastewater from various electroplating processes. In this study, supercooled water dynamic ice making (SWDIM) technology was applied for the first time to freeze and crystalize electroplating washing wastewater, followed by centrifugal separation to separate solid and liquid phases. Freezing treatment was performed on the washing water from the acid copper process (pH = 1.15), nickel plating process (pH = 5.1), and zincate zinc plating process (pH = 13.2). The results show that after primary freezing and centrifugal dehydration, the solute removal rate of ice melt water exceeded 90%, which can meet the requirements of the primary washing tank to supplement the washing water. After secondary freezing and centrifugal dehydration, the concentrated wastewater (approximately 0.14 vol of the original wastewater) can be produced, further evaporated and concentrated 2.8 times, and reused for the electroplating bath.

1. Introduction

Electroplating wastewater contains significant quantities of heavy metals. These metals are harmful to the environment, as well as pose adverse effects on human health. However, the recovery value of these heavy metals is very high; thus, cleaner production is the key research direction of electroplating wastewater treatment technology for efficient recovery of these metals.

In the current electroplating technique, plated parts that have undergone an electroplating bath are sent to a countercurrent multi-stage washing tank. These are washed to remove electroplating solution from the plated parts, in a step-by-step manner, before entering the next electroplating cycle. Washing wastewater from plated parts generally accounts for more than 85% of the total wastewater from plating plants and is the biggest target for the treatment [1].

The developing trend of treating electroplating wastewater is based on the idea of cleaner production. Cleaner production refers to the use of advanced technology and equipment to reduce pollution from its source, improve the efficiency of resource utilization, and reduce or avoid the generation and discharge of pollutants in the process of product creation servicing and use [2]. One approach towards achieving cleaner production involves the concentration and reuse of electroplating washing wastewater. There are two methods commonly used to concentrate electroplating wastewater: reverse osmosis and evaporation.

Reverse osmosis has been used to concentrate nickel plating washing wastewater for reuse in an electroplating bath and has achieved good economic returns [3–5]. Hu et al. [6] reported that reverse osmosis treatment of nickel electroplating wastewater achieved a 438% annual operating return rate in an engineering application. However, the washing wastewater from the frequently used acid copper, pyrophosphate copper, and chromium electroplating are strongly acidic, having a pH less than 2, while that from alkali copper process and zincate zinc plating are strongly alkaline, with pH greater than 12. These are both beyond the allowable pH value range of existing reverse osmosis membranes.

The evaporation concentration method involves concentrating the wastewater by heating it under normal or lower than normal pressures to evaporate the solvent moisture. The concentrated solution can then be returned to the electroplating bath, and the water vapor from the process can be used as cleaning water after it is condensed and recovered [7]. However, this method consumes high amounts of energy and is expensive. At present, it is seldom used alone to treat electroplating wastewater; it is generally one of the steps employed in a

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combined treatment plan, such as for treating the concentrated liquid produced by reverse osmosis [6].

Ice is a monomineralic solid that cannot coexist with other substances because water automatically removes impurities in the crystallization process to keep itself pure. The freezing water treatment technology is based precisely on this basic principle [8–11]. This treatment method has been applied widely, has almost no selectivity for wastewater, and has significant advantages in treating refractory wastewater, particularly that which is toxic and has a heavy metal content [12–14]. Its energy consumption is much lower than that of evaporation concentration [11–12]. The latent heat of vaporization of water at 100 °C is 0.63 kWh/kg, and the latent heat of solidification of water at 0 °C is 0.093 kWh/kg. The theoretical energy consumption of evaporation concentration is 7 times that of freezing concentration [10]. Freezing concentration uses atmospheric pressure heat pump technology, and the average energy consumption of heat pump is 1/3 that of its refrigeration capacity. When the refrigeration end (evaporator) of the heat pump cools down and produces ice, it transfers a similar amount of heat to the heat dissipation end (condenser) to melt the ice; therefore, melting ice does not require additional heat energy. However, evaporation concentration requires an additional cold source to cool the steam.

Crystallization of water begins with the formation of small ice nuclei; these nuclei form dendritic ice crystals, which in turn gradually form integral ice nuclei, ultimately resulting in a large ice crystal. These ice nuclei and dendritic ice crystals are pure water crystal solids, and the growth process automatically removes impurities from the liquid [15,16]. When the dendritic ice crystals grow considerably, they form a network of ice crystals, and the impurities are wrapped inside [17], forming a small salt packet containing impurities; thereby, the purity of the large ice crystals is reduced. To state differently, the smaller the size of the ice crystal, the less the dendritic ice crystals produced; in turn, the less salt packets are wrapped, and hence, the ice crystals formed are purer.

The main ice-making methods in the existing freezing water treatment include suspension crystallization freezing method and interface progressive freezing method [18,19]. The ice crystal formed by the former method has a small size and the ice crystals are pure. However, the main disadvantage of this method is that the separation of ice and water is difficult because the ice crystals are immersed in water, making the process more expensive than the interface progressive freezing method [20,21]. The latter method forms layered ice with large ice crystal size wherein large quantities of solute get entrapped [22,23]; the desalination rate of the first freezing is only approximately 50% [24].

There are currently no in-depth studies on the application of the freezing method to treat electroplating wastewater. Therefore, in this study, we utilized the freezing method, and the latest ice-making technology of supercooled water dynamic ice making (SWDIM). This technology was used to freeze-treat three kinds of electroplating wastewater, i.e. that characterised by strong acidity, slight acidity, and strong alkalinity, to freeze and concentrate electroplating wastewater, to investigate the solute removal rate of ice melt water, and to investigate the concentration multiple of concentrated electroplating wastewater.

2. Materials and methods

2.1. Experimental water samples

The plating solution and electroplating washing wastewater sample were collected from the electroplating tank and the primary washing tank of the electroplating factory of LongPu Electroplating Industrial Park, Sihui City, Guangdong Province, China.

The simulated electroplating wastewater from primary washing tank, was configured according to the measured solute concentration in the primary washing tank of the electroplating plant and the theoretical formula of the electroplating bath. The simulated acid copper process washing wastewater was configured using $CuSO_4 \cdot 5H_2O$, H_2SO_4, and NaCl; the simulated nickel plating process washing wastewater was configured using $NiSO_4 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$; and the simulated zincate zinc plating process washing wastewater was configured using ZnO and NaOH.

2.2. Experimental equipment

After studying various frozen ice making methods, we finally chose to use the SWDIM technology. The SWDIM technology is the latest development in ice making used in ice storage air conditioning [25–28]. The SWDIM is a dynamic process wherein ice crystals and water are in continuous motion, and it is easier to realize the automatic separation of ice crystals and wastewater. Herein, the water does not freeze immediately upon reaching 0 °C but is instead supercooled. The safe supercooling temperature for tap water is −3.8 °C. The supercooled water is in a metastable state, and ice crystals only appear when the water temperature drops below the supercooling temperature. When such a metastable state is broken artificially, ice crystals will form when the temperature is higher than the supercooling temperature. Because there is no need to achieve supercooling to form ice, and its heat transfer efficiency between solid and liquid is high (because the size of ice crystal is small), the SWDIM freezing method has higher ice-making rate and energy efficiency than suspension crystallization freezing method and interfacial progressive freezing method [29,30]. The

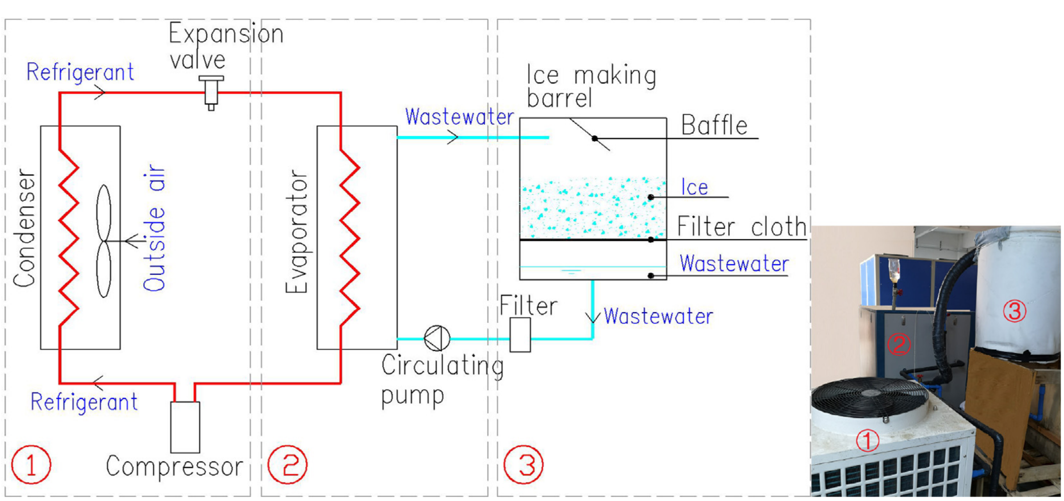

Fig. 1. Supercooled water dynamic ice making equipment used in this study.