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***"Gheorghe Asachi" Technical University of Iasi, Romania***

# PRECONCENTRATION OF METHYLENE BLUE WASTEWATER USING THE LAYER CRYSTALLIZATION TECHNOLOGY

**Yingjie Dai[1*], Yujie Feng[2]**

*[1]Northeast Agricultural University, School of Resources Environment, 59 Mucai Str., Xiangfang District, 150030 Harbin, China*
*[2]Harbin Institute of Technology, State Key Laboratory of Urban Water Resource and Environment, 73 Huanghe Road, Nangang District, 150090 Harbin, China*

**Abstract**

This study was carried out to determine the feasibility of applying a freeze-concentration technique to purify wastewater polluted with dye, such as methylene blue (MB) using a stationary wastewater vessel. In this study, we investigated the impact of freezing temperature, initial MB wastewater concentration and vessel depth upon the removal ratio of MB. Results showed that when the freezing temperature was decreased (from –5 °C to –15 °C), the freezing rate increased. The freezing rate was not significantly affected for the different concentrations of the MB solution. The removal ratios of MB at 0-20 mm of ice layer for the concentrations of MB of 1000 mg/L, 2000 mg/L and 4000 mg/L were 84. 29 %, 82.17 % and 80. 02 % respectively at the freezing temperature of –5 °C.

*Keywords:* freeze-concentration, MB, ice crystal, removal ratio, wastewater

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## 1. Introduction

There are more than 100,000 kinds of commercially available dyes with over $7\times10^5$ tons of dyestuff produced annually (Lee et al., 2006; Pearce et al., 2003). It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations, while 10% was discharged from textile and associated industries (Easton and Cooper, 1995).

The discharge of dyes in the environment is a matter of concern for both toxicological and harmful to aquatic living creatures, even highly carcinogenic to human health (Metivier-Pignon et al., 2003). Moreover, some dyes are highly visible to the human eye, this can cause aesthetic contamination even at very low concentrations (Ravikumar et al., 2005). Wastewaters from colorant industrials (such as textile, paper, carpet, leather, cosmetics, food coloring, plastics and printing industries) contain dyes which should be eliminated to avoid environmental contaminations. A number of promising techniques have been established for elimination of dyes from contaminated waters. Effective methods for removal of dyes from the environment include photodegradation and biodegradation (Tsai et al., 2001; Wang et al., 2005; Yener et al., 2006), flocculation (Panswed and Wongchaisuwan et al., 1986), membrane separation (Ciardelli et al., 2000), chemical oxidation (Muthukumar and Selvakumar, 2004; Swaminathan et al., 2003), electro-coagulation (Alinsafi et al., 2005), and physical adsorption (Mahmoodi et al., 2017; Mall et al., 2005). Methylene blue (MB), can cause injuries to humans and animals with symptoms including eye burns (direct contact), rapid or difficult breathing (inhalation), and also nausea, vomiting, mental confusion and others if ingested (Benadjemia et al., 2011).

*Author to whom all correspondence should be addressed: e-mail: dai5188@hotmail.com; yujief@hit.edu.cn; Phone/Fax: +86 451 5519 0825; +86 451 8628 3068.

On the other hand, freeze concentration is a physical process and it involves the fractional crystallization of water and subsequent removal of ice. The process was effective to remove various contaminants from industrial wastewater/liquid waste (Gao et al., 2008). When freeze concentration is used to purify water or liquid waste, impurities are separated from water during the formation of ice crystals. The theories of impurity separation by freeze concentration have been discussed by various researchers (Halde, 1980). For freeze–concentration wastewater treatment, layer crystallization method (Flesland, 1995; Muller and Sekoulov, 1992) and suspension crystallization method (Rousseau and Sharpe, 1980) of ice crystals can be applied. The freezing of layer crystallization method has high effective separation because it yields a larger size of ice unit. However, the freezing of traditional suspension crystallization method produces small ice crystals in the mother solution, and the amount of produced ice, is scarce so it is difficult to separate ice from wastewater solution (Gao et al., 2006). We choose the layer crystallization method because of its simplicity in the separation of solid ice layer from the liquid phase. Some researchers had studied the methods of wastewater treatment using freeze–concentration. Lorain et al. (2001) had purified synthetic wastewater and industrial wastewater using the freezing-concentration process and obtained satisfying results. Study had attained good purification ratios applying outdoor coldness radial freezing and stirring to purify the wastewater (Gay et al., 2003). Jiang et al. (2011) had studied the effects of the removal of inorganic ions and organic pollutants under the artificial frozen condition. The results indicated that the removal ratio of the practical wastewater mixed with inorganic-ion and organic pollutants was about 70-80 %, so, it is better to couple with other technologies for improving the treatment efficiency (Jiang et al., 2011). If freeze-concentration method were made possible using a simple facility, the process will become a powerful treatment method for wastewater while suppressing the operation cost. These findings may be effective and useful in developing wastewater treatment system on an industrial scale.

The objective of this research was to investigate the removal of MB from aqueous solution using layer crystallization method. The influence of several parameters, such as freezing temperature, initial concentration of MB, the freezing rates and the vessel depth upon removal ratio of MB were investigated.

## 2. Material and methods

### *2.1. Material*

The methylene blue (MB) was purchased from Wako Pure Chemicals Co., Osaka, Japan. The MB concentrations of about 1000 mg/L, 2000 mg/L and 4000 mg/L, respectively, were prepared using deionized and distilled water. The freeze-concentrating technique using stationary vessels was used to preconcentrate the MB wastewater. The MB solution was stored at 0 ± 0.5 °C.

### *2.2. Experimental apparatus and procedure*

The MB solution was frozen in stationary vessels (acrylic resin, diameter 40 mm, depth 80 mm) that was located in a refrigerator. The sides and bottom of the vessels were insulated by a polyurethane sheet (thickness, 20 mm), so the MB solution would freeze from the upper side only. The temperature of the refrigerator was set at –5 °C, –10 °C and –15 °C, respectively. When all or most of the MB solution from the top was frozen, the ice was cut and picked up by a saw at every about 20 mm from the top. The concentration of MB in the sample solutions and the melted ice layer formed in the sample solutions were measured using an ultraviolet visible spectrophotometer V-550 (Jasco Co., Tokyo, Japan) at wavelength 665 nm for MB. Three replicate runs were carried out for each experimental treatment.

## 3. Results and discussion

### *3.1. Effect of freezing rate with different temperatures and concentrations*

Comparison of ice thickness at different freezing temperatures (from –5 °C to –15 °C) at the MB concentration (1000 mg/L) in the ice layer using a 80 mm-deep vessel is shown in Fig. 1. The temperatures being one of the most important parameters affecting the freezing rate can be observed from Fig. 1. All of the MB solution was frozen in stationary vessels (100 mL volume with diameter 40 mm, depth 80 mm) at –5 °C, –10 °C, and –15 °C, the freezing times were about 64h, 53h, 30h, respectively.

The relationship between ice thickness and freezing time under different concentrations (from 1000 mg/L to 4000 mg/L) of the MB solution and temperatures (from –5 °C to –15 °C) in the ice layer using a 80 mm-deep vessel is shown in Fig. 2.

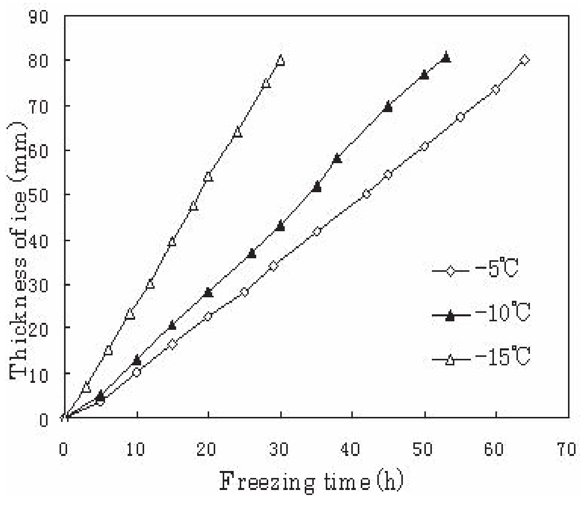
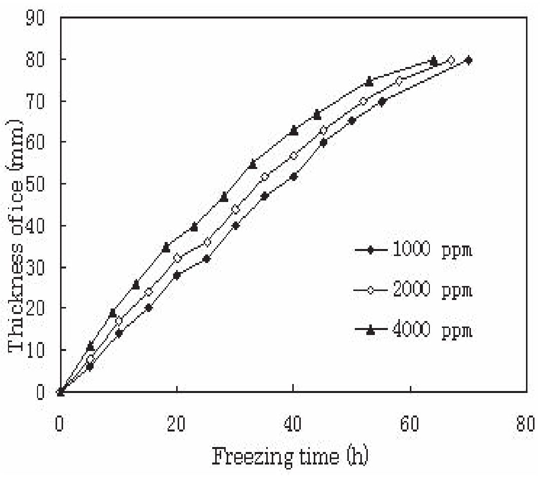
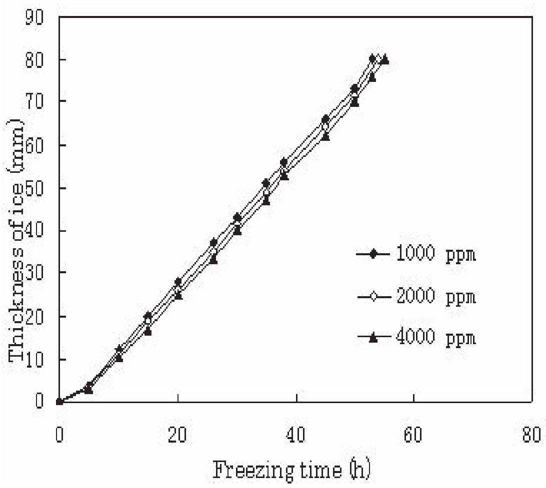


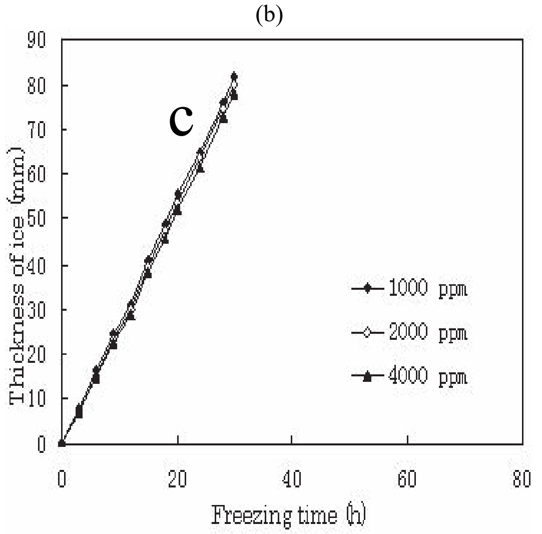

**Fig. 1.** Comparison of ice thickness at different freezing temperatures




(a)




(b)




(c)

**Fig. 2.** Relationship between ice thickness and freezing time under different concentrations ((a) at –5 °C; (b) at –10 °C; (c) at –15 °C)

The freezing ratio (1.56 mL/h) of the MB solution for 1000 mg/L was slightly larger than that (1.43 mL/h) of 4000 mg/L at the freezing temperature of –5 °C (Fig. 2 (a)). However, results had shown that the readings of thickness procuded ice mass were almost the same as those MB solution with different concentrations (from 1000 mg/L to 4000 mg/L) under the freezing temperatures of –10 °C and –15 °C Fig. 2 (b and c). Therefore, the freezing rates were not significantly affected for the different concentrations of the MB solution (Beier et al., 2007).

*3.2. Effect of freezing temperature and depth of ice layer*

The initial concentration of MB solution was 1000 mg/L in this run. After freezing most of the MB solution at –5°C, –10 °C, and –15 °C, the ice was divided at every 20 mm from the top. The parameters in Eq. (1), which were determined from freezing experiment, are summarized in Fig. 3.

$$R = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where: $R$ is the MB removal ratio (%); $C_0$, the initial concentration of the MB solution (mg/ L); $C$, the MB concentration in the ice (mg/ L).

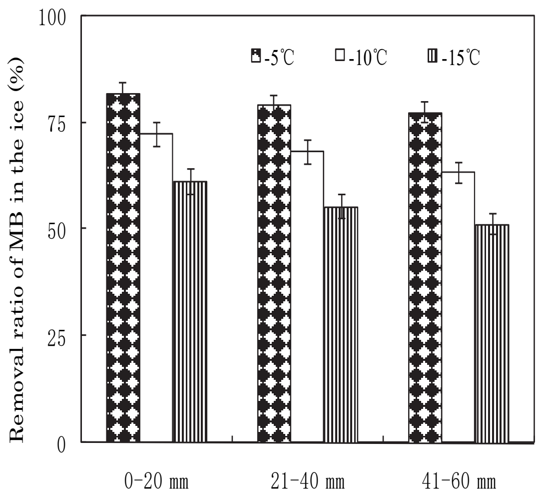



**Fig. 3.** Removal ratio of MB in the ice layer from different freezing temperatures at MB concentration (1000 mg/L) of the wastewater

Fig. 3 shows that the removal ratios of MB in the ice layer with different freezing temperatures (from –5 °C to –15 °C) at MB concentration of 1000 mg/L. It shows that the removal ratios of MB in the 0-20 mm ice layer were 78.26-84.29 %, but the removal ratios of MB in the 41-60 mm layer were 55.31-64.06 %. Under the conditions of rapid freezing (such as –15 °C), there appears ice crystals with tree branches and needle-like crystals at the solid-liquid interface. Much more ice crystals were obtained by caging pollutants (the MB), from decreasing the removal ratio of MB solution, because the speed of freezing for water molecule was faster than that of exceed for pollutant (the MB) from MB solution.

*3.3. Effect of concentration of MB solution*

The MB solution (1000 mg/L, 2000 mg/L and 4000 mg/L) was frozen using a 80 mm–deep vessel at the freezing temperature of –5 °C. The removal ratios of MB in the 0-20 mm ice layer is shown in Fig. 4. The removal ratios of MB at this ice depth (in the 0-20 mm) for the MB concentrations of 1000 mg/L, 2000 mg/L and 4000 mg/L were 84.29 %, 82.17 % and 80. 02 %, respectively. Results (see Fig. 4) show that the removal ratios of MB in the 0-20 mm ice layer were not significantly affected for the different concentrations (1000 mg/L, 2000 mg/L and 4000 mg/L) of the MB solution.

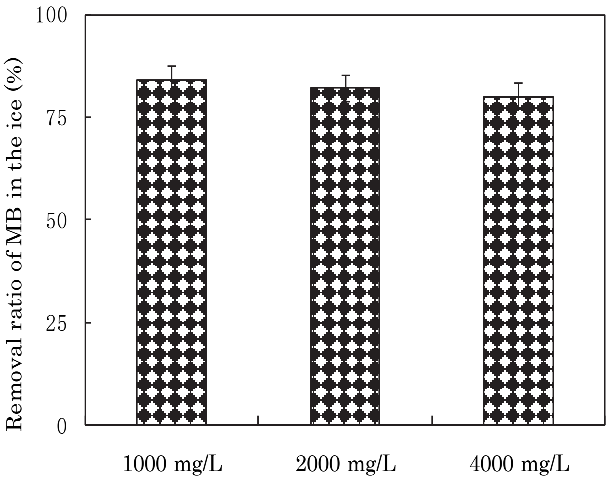



**Fig. 4.** Removal ratio of MB in the 0–20 mm ice layer from different initial concentrations of the wastewater in 80 mm vessel at the freezing temperature of –5 °C

## 4. Conclusions

When the freezing temperatures (from –5 °C to –15 °C) were decreased, the freezing rate increased. The freezing ratios were not significantly affected for the different concentrations of the MB solution. As the freezing temperature decreased, the concentration of MB varied with the location within the ice layer, such that the concentration of MB was lowest at the ice surface and increased with ice depth.

The removal ratios of MB at this ice depth (in the 0-20 mm) for the concentrations of MB for 1000 mg/L, 2000 mg/L and 4000 mg/L were 84.29 %, 82.17 % and 80.02 %, respectively at the freezing temperature of –5 °C.

## Nomenclature

$R$ = removal ratio of MB [%]
$C_0$ = initial concentration of MB [mg/ L]
$C$ = the MB concentration in the ice [mg/ L]

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