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## ARTICLE

### Removal adsorption of LED industrial wastewater by after resource utilization of agricultural waste

Ching-Hua Liao<sup>1,2,3</sup>, Chun-Min Qiu<sup>1</sup>, Chi-En Hung<sup>4</sup>, Sheng-Chung Chen<sup>1,2,3</sup>, Chih-Hung Wu<sup>\*1,2,3</sup>, Shu-Jiao Shen<sup>1</sup>, Qiang Li<sup>1,2,3</sup>, Hai-Qi Lin<sup>1</sup>

<sup>1</sup>School of Resource & Chemical Engineering, Sanming University, Fujian, 365004, China

<sup>2</sup>Fujian Provincial Engineering Research Center of Mine Ecological Construction, Sanming, 365004, China

<sup>3</sup>Cleaner Production Technology Engineering Research Center of Fujian Universities, Sanming, 365004, China

<sup>4</sup>Huaian Huabo Technology Co., Ltd., Jiangsu, 223005 China

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#### ABSTRACT

Nowadays the market value and scope of the Light-Emitting Diode (LED) industry are increasing and the amount of waste in the process has also increased. The wastewater containing gallium (Ga) ion is also produced in the LED process, such as etching, washing, and grinding. This gallium element was very rare and valuable on the earth. In this study, the agricultural waste of pomelo peel was used to be the bioadsorbent to recycle the gallium from the gallium ion wastewater to achieve the purpose of the use of waste to recycle. According to the bioadsorption tests, the use of hydrochloric acid modified bioadsorbent of pomelo peel could achieve 96.80 % bioadsorption efficiency under the optimized condition found in this study.

## 1. Introduction

The development of the modern industrial economy of China is increasing very fast and strong. These industries produce a lot of wastewater containing heavy metals and organic compounds. If this industrial wastewater is not treated, it would be released into the rivers, lakes, and the ocean, which will affect the natural environments and all lives (Ali et al., 2018, Liao et al., 2020, Li et al., 2017, Ma et al., 2018). Heavy metal ions have their toxicity at low concentration and are carcinogenic in natures if released into the water and soil (Chakraborty et al., 2022).

Heavy metals are from a variety of sources, such as photovoltaic, chemical industries, textiles, tanneries, mining, battery manufacturing, paint, paper industries, etc (Babel and Kurniawan, 2004; Geng et al., 2009; Bhuyar et al., 2019, 2020, 2021).

As mentioned above, the heavy metal industries also include a large number of valuable metal industries such as the Light-Emitting Diode (LED) industries and the rare earth fluorescent lamp industries. In particular, environmental protection, energy conservation, and emission reduction are prevalent in recent years. Therefore, LED and rare earth fluorescent lamps have become favorite energy-saving, emission reduction, and environmental protection lamps for ordinary families.

\* Corresponding author.

The methods of heavy or valuable metal wastewater treatments mainly in normal industries use physical and chemical technologies that includes coagulation precipitation, ion exchange, electrodialysis, activated carbon adsorption, etc. But these methods have various disadvantages of widespread secondary environment pollution, high-cost, and low concentration wastewater treatment of poor quality (Zhang and Zhan, 2012).

However, some researchers have found that agricultural waste could be used to solve the high-cost problems in recent years. The methods for treatment of heavy or valuable metal wastewater mainly in normal industries use physical and chemical technologies including coagulation precipitation, ion exchange, electrodialysis, activated carbon adsorption, etc. But these methods have widespread secondary environment pollution, high-cost, and low concentration wastewater treatment (Zhang and Zhan, 2012). In recent years, some researchers have found that using agricultural waste could solve the high-cost problems.

It indicates that the cost-effective bioadsorbents for removing metal ions have been recognized as a sustainable wastewater treatment solution (Afroze and Sen, 2018; Tsade et al., 2020; Tapfuma et al., 2019). China is an agriculturally prosperous country that produces a lot of agricultural wastes every year. These agricultural wastes come from farmland waste, forestry waste, water (hard fruit) waste, etc. These are almost composed of cellulose, hemicellulose and lignin (Wang et al., 2019). The surfaces of bioadsorbents from agricultural wastes contain active substances or functional groups such as -COOH, -OH, and -NH<sub>2</sub>, which can adsorb valuable or toxic metal ions through the physicochemical concept of the ion-exchange method (Zhang and Zhan, 2012; Pavan et al. 2008). These active substances or functional groups play a key role in metal ion adsorption.

Mao et al. (2016) demonstrated that the agricultural waste of pomelo peel modified with oxalic acid could achieve 95.63 % of cadmium ion bioadsorption efficiency in wastewater (Mao et al., 2016). Moreover, using the agricultural waste of orange peel modified with citric acid to treat the chromium (Cr) ion wastewater achieve 98.30 % bioadsorption efficiency (Ma et al., 2018). Wang et al. (2020) showed that using the biochar of pine needle waste modified with hydrochloric acid (HCl) to treat the wastewater containing chromium (Cr) could achieve high bioadsorption efficiency of 97.10% (Wang et al., 2020). It can be known that using chemicals modified agricultural wastes (bioadsorbents) to treat heavy metals ion wastewaters has good bioadsorption efficiency. Because the chemical modification on agricultural wastes could increase the surface area to exhibit higher bioadsorption efficiency (Chakraborty et al., 2022).

This study focuses on the properties of gallium bioadsorption from the LED industry's wastewater during the processes of etching, washing, and grinding. If these wastewaters of gallium are released into the water environment, this is a serious and dangerous concern and may affect water quality, and human health (Larous et al., 2005). Therefore, nowadays bioadsorbents are widely used to treat wastewaters with toxic or dangerous metal ions because bioadsorbent has the concept of L-3 class (i.e. low cost, locally available, low technologically prepared and used) (Banerjee, 2020). In this study, the agricultural waste of pomelo peel has been

tested to absorb the valuable metal ion, gallium, in the LED industrial wastewater.

## 2. Method

### 2.1. Bioadsorbent and gallium ion solution preparation

The pomelo peel (as bioadsorbent) in this study was purchased from the market and dried at 60 °C in the oven for a day (Shanghai Yuejin Medical Instrument Co., LTD). And then the dried pomelo peel was crushed and sieved to less than 50 mesh (< 0.297 mm). Then 0.1 M and 1.0 M hydrochloric acid (HCl)(Analytical Reagent, AR) and citric acid (Analytical Reagent, AR) were used to soak pomelo peel at room temperature for one day to perform chemical modification. The modified bioadsorbents were cleaned with water until pH of cleaning water was neutral. Finally, these modified bioadsorbents were dried at 60 °C in which to broke and screen to less than 50 mesh.

An adsorbate standard solution (1,000 mg/L) of gallium was purchased from Beijing Non-Ferrous Metal & Rare Earth Metal Application Research Institute. This standard solution was used to make further diluted concentrations of interest with deionized water.

### 2.2. Adsorption experiments

In the batch adsorption experiments, one gram of bioadsorbent was added into the 20 mL of gallium solution of known concentration in one 200 mL plastic bottle. The adsorption incubation was performed at room temperature in a rotatory mechanical shaker at 150 rpm. The impact factors, including pH values, oscillation time, target metal ion concentration, bioadsorbent dose, and different chemical modified bioadsorbents, were tested the adsorption efficiency of gallium in this study. The incubated adsorption solution was filtered with the 0.45 µm filter and then the concentration of gallium of filtrate was analyzed by using atomic adsorption spectrophotometer (Beijing PERSEE General Instrument Co., Ltd).

Each adsorption experiment was performed in triplicate. Deionized water was used in preparing stock solutions and also throughout the experimental analysis. The gallium ion concentrations of 80-250 mg/L and the bioadsorbent doses with 0.5, 1, 3 and 5 g were evaluated to find the optimum condition for the highest gallium bioadsorption efficiency.

After each batch of experiment attained the equilibrium, the target metal uptake capacity for these bioadsorbents was calculated according to mass balance on the metal ion using:

$$q_e = \frac{(C_0 - C_t)}{m} \times V \quad (1)$$

$$\text{Bioadsorption efficiency (\%)} = \left( \frac{C_0 \times V_0 - C_t \times V_t}{C_0 \times V_0} \right) \times 100\% \quad (2)$$

$$\text{Bioadsorption dose (mg)} =$$

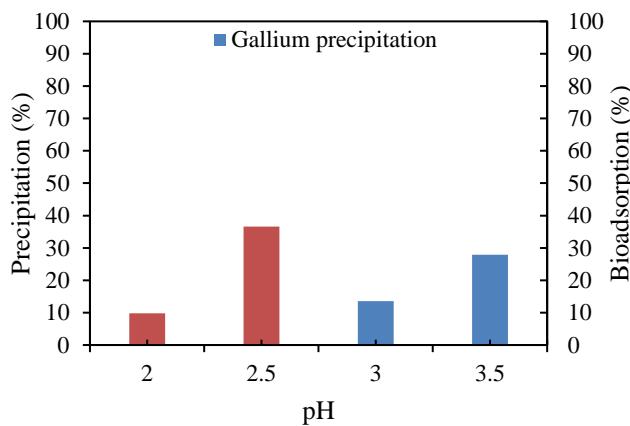
$$\text{Start Gallium weight (mg)} \times \text{Bioadsorption efficiency (\%)} \quad (3)$$

Where,  $q_e$  is the bioadsorption capacity in mg/L,  $C_0$  is the initial concentration,  $C_t$  is a period of concentration at time,  $V$  is the volume of the solution in liter (L), and  $m$  is the bioadsorbent mass (g).

### 3. Result and discussion

#### 3.1 Effect of pH on gallium bioadsorption

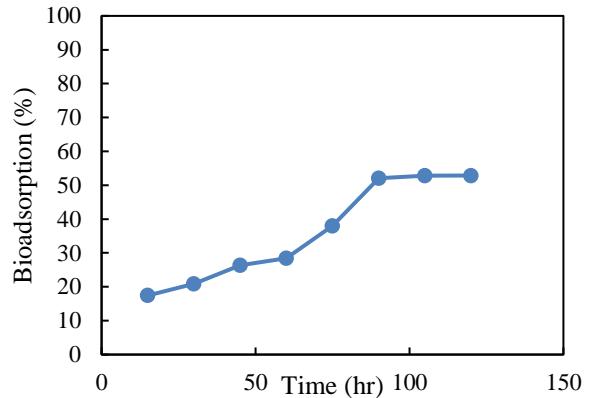
The pH range of 2 to 3.5 pH were selected to evaluate its effect on metal ions bioadsorption and precipitation (Fig. 1). In order to find the highest bioadsorption of gallium without gallium precipitation, this study tried to find which pH has the 0 % precipitation of gallium in the pH range into 2-3.5. Gallium ion ( $Ga^{2+}$ ) was found to have the 0 % precipitation at both pH values of 2 and 2.5. In addition, the result showed the higher adsorption efficiency of 36.61% was found at pH value of 2.5. Therefore, all later tests were performed at pH value of 2.5. These experiments conditions were performed using 1 g unmodified bioadsorbent incubated in 20 ml wastewater (gallium solution, 80 mg gallium/L) for 15 min.



**Figure 1** Tests of gallium precipitation and adsorption efficiency at different pH values.

#### 3.2 Effects of incubation time on gallium bioadsorption

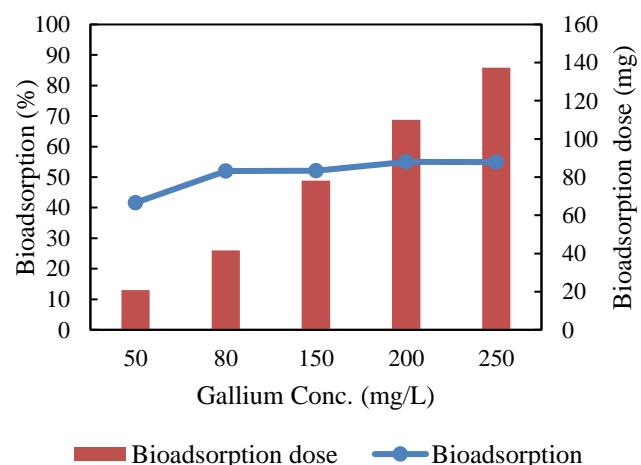
In Figure 2, the results showed that the gallium bioadsorption efficiency was increased with an increase in incubation time. After the 90 min incubation, the gallium bioadsorption efficiency was stable, which indicates it achieved the maximum bioadsorbed capacity after this time point (at 90 min). Moreover, the gallium bioadsorption efficiencies were 52.03 %, 52.86 %, and 52.86% at time points of 90, 105 and 120 min, respectively. Therefore, the optimum condition of the incubation time would be 105 min in this research.



**Figure 2** Effect of incubation times on the gallium bioadsorption with the bioadsorbent.

#### 3.3 Effect of the gallium concentrations in wastewater on gallium bioadsorption

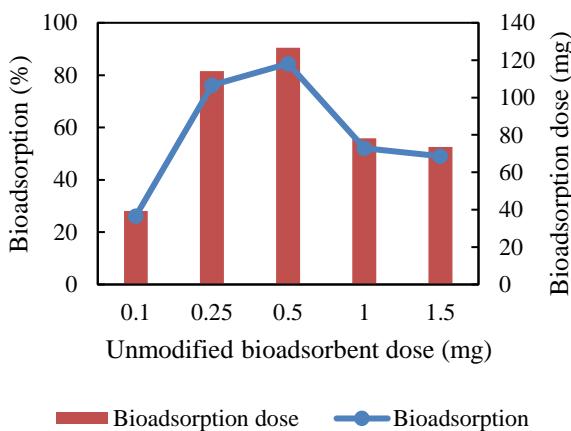
The tests of different concentrations of gallium (80 to 250 mg/L) for the gallium bioadsorption efficiency were performed under the conditions of 1 g of bioadsorbent, pH value of 2.5 and incubation time of 105 min (Fig. 3). The results showed that the gallium bioadsorption efficiency was increasing slowly with the increasing gallium concentration in wastewater (Fig. 3). This indicated that the maximum gallium bioadsorption efficiency is about 52.03 % to 54.98 % with 1 g of bioadsorbent in the gallium solution of 150 to 250 mg/L. In addition, the average gallium bioadsorption dose is 108.53 mg with 1 g bioadsorbent of pomelo peel powder.



**Figure 3** Effect of different gallium concentrations on the gallium bioadsorption.

### 3.4 Effects of different doses of unmodified bioadsorbents on gallium bioadsorption

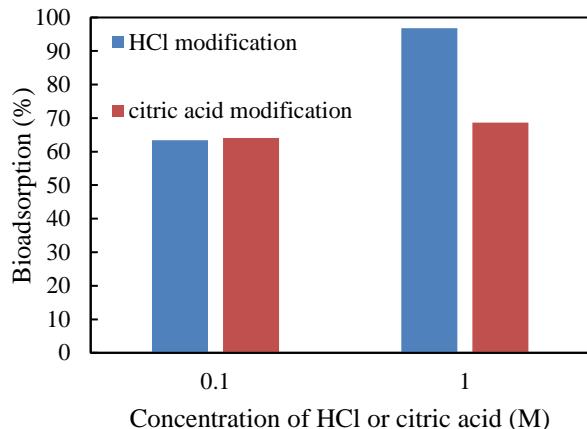
Five different doses of unmodified bioadsorbent of 0.1 g, 0.25 g, 0.5 g, 1.0 g, and 1.5 g were selected to test the gallium bioadsorption efficiency and doses (amounts) under the condition of pH 2.5, incubation time of 105 min and in the gallium solution of 150 mg/L (Fig. 4). The maximum bioadsorption efficiency was found at the dose of 0.5 g bioadsorbent of pomelo peel powder with the ratio of 84.40 % (Fig. 4). The results also showed that the 5 different doses of unmodified bioadsorbents harbored the gallium bioadsorption doses of 39.27 mg, 114.15 mg, 126.60 mg, 78.18 mg, and 73.50 mg, respectively. The highest gallium bioadsorption dose of 126.60 mg was occurred under the condition of the dose of 0.5 g unmodified bioadsorbent.



**Figure 4** Effects of different doses of unmodified bioadsorbent on the gallium bioadsorption efficiency and doses (amounts).

### 3.5 Comparison between before/after chemically-modified bioadsorbents on the gallium bioadsorption

The bioadsorbent in this study was modified with the different concentrations of hydrochloric acid or citric acid. This section showed the effects of four types of chemically-modified bioadsorbents on gallium adsorption efficiency in Fig. 5. It showed that the hydrochloric acid modified bioadsorbent of pomelo peel powder was better than the citric acid modified one. And the bioadsorbent modified with higher concentration of hydrochloric acid could achieve higher bioadsorption efficiency (Fig. 5). It is concluded that using the bioadsorbent modified with 1 M hydrochloric acid could achieve the highest gallium bioadsorption efficiency of 96.80%.



**Figure 5** Effects of four different types of chemically-modified adsorbents on gallium bioadsorption efficiency.

## 4. Conclusion

This study selected the agricultural waste of pomelo peel to be the bioadsorbent because it has the amount of agricultural waste in China and can guarantee the provision of stable. Bioadsorption technique is widely used to remove different types of pollutants from water and wastewater. But it is seldom to use in rare metals recovery or adsorption in wastewater. Therefore, this study has tried to test the factors as using the agricultural waste of pomelo peel to bioadsorb the gallium in LED industrial wastewater.

The conclusion of this study indicated that the bioadsorption efficiency of gallium ions depends heavily on the amount of bioadsorbent dose, concentration of target metal ion, stirring contact time, pH adjustment, and the chemically-modified bioadsorbent. And the optimum bioadsorption conditions were to be: pH 2.5, 0.5 g bioadsorbent dose, stirring contact time of 105 min, 150 mg/L concentration of gallium, and chemical modification with 1 M hydrochloric acid (HCl), which could achieve 96.80 % bioadsorption efficiency. In conclusion, this study indicates that the chemically-modified agricultural waste of pomelo peel powder has the ability to bioadsorb rare metal ions present in water or wastewater.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- Afroze, S., & Sen, T. K. (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water, Air, & Soil Pollution*, 229(7), 1-50.
- Ali, N., Kamal, T., Ul-Islam, M., Khan, A., Shah, S. J., & Zada, A. (2018). Chitosan-coated cotton cloth supported copper nanoparticles for toxic dye reduction. *International journal of biological macromolecules*, 111, 832-838.
- Babel, S., & Kurniawan, T. A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54(7), 951-967.
- Banerjee, K. (2020). Bioadsorbents as Green Solution to Remove Heavy Metals from Waste Water-Review J. Adv. Sci. Eng, 6, 43-45.
- Bhuyar, P., Farez, F., Pragas Maniam, G., & Govindan, N. (2021). Removal of nitrogen and phosphorus from agro-industrial wastewater by using microalgae collected from coastal region of peninsular Malaysia. *African Journal of Biological Sciences*, 3(1), 58-66.
- Bhuyar, P., Hong, D. D., Mandia, E., Rahim, M. H. A., Maniam, G. P., & Govindan, N. (2020). Salinity reduction from poly-chem-industrial wastewater by using microalgae (*Chlorella* sp.) collected from coastal region of peninsular Malaysia. *J Bio Med Open Access*, 1(1), 105.
- Bhuyar, P., Hong, D. D., Mandia, E., Rahim, M. H. A., Maniam, G. P., & Govindan, N. (2019). Desalination of polymer and chemical industrial wastewater by using green photosynthetic microalgae, *Chlorella* sp. *Maejo International Journal of Energy and Environmental Communication*, 1(3), 9-19.
- Chakraborty, R., Asthana, A., Singh, A. K., Jain, B., & Susan, A. B. H. (2022). Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, 102(2), 342-379.
- Geng, B., Jin, Z., Li, T., & Qi, X. (2009). Preparation of chitosan-stabilized Fe0 nanoparticles for removal of hexavalent chromium in water. *Science of the Total Environment*, 407(18), 4994-5000.
- Larous, S., Meniai, A. H., & Lehocine, M. B. (2005). Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination*, 185(1-3), 483-490.
- Li Z., Ai T., Jia H., Tian X., Liu J., Yan L., & Jiang X. 2017. Adsorption of Cr (VI) from aqueous solution by tartaric acid modified pine needle powder. *Journal of University of Science and Technology Liaoning* 40(5): 56-61.
- Liao, C. H., Shiu, J. Y., Hung, C. E., Wu, C. H., & Liu, M. Z. (2020). Treatment of Chromium in Wastewater by using Loquat Leaves as Biosorbent. *Maejo International Journal of Energy and Environmental Communication*, 2(3), 6-10.
- Ma M., Wang X. B., Da H. W., Cao J. J., & Chang W. H. 2018. Study on Removal of Cr(VI) in Surface Water Using Peanut Shell Modified by Citric Acid. *Popular Science & Technology* 20(230): 24-27.
- MA, M., WANG, P., & QIAO, L. M. (2018). Removal of Chromium Cr (VI) from Water by Citric Acid Modified Orange Peel. *Journal of Anhui Agricultural Sciences*, 46(36), 64-66.
- Nan, W., Wei, W., Chenguang, Y., Tianyin, H., Jiabin, C., & Jingjing, Y. (2020). Adsorption performance of hydrochloric acid-modified pine needle biochar on sulfamethoxazole. *Chinese Journal of Environmental Engineering*, 14(6), 1428-1436.
- Pavan, F. A., Lima, E. C., Dias, S. L., & Mazzocato, A. C. (2008). Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. *Journal of hazardous materials*, 150(3), 703-712.
- Tapfuma, A., Chakawa, D. P., Moyo, L. B., Hlabangana, N., Danha, G., & Muzenda, E. (2019). Investigating the feasibility of using agricultural waste as an adsorbent of gold ions in small scale gold processing plants. *Procedia Manufacturing*, 35, 85-90.
- Tsade, H., Murthy, H. A., & Muniswamy, D. (2020). Bio-sorbents from agricultural wastes for eradication of heavy metals: a review. *J Mater Environ Sci*, 11, 1719-1735.
- Wang, Q., Huang, L., Huangling, G. U., & Liu, Z. (2019). Biomass waste pomelo peel as a potential adsorbent for wastewater treatment. *Journal of Hunan University of Technology*. 33(6), 89-94.
- Yan, Z. W. Z. (2012). Research advance on modification technologies of wastes from agriculture and forestry. *Modern Agricultural Science and Technology*.
- Yanli, M., Haiyan, K., & Junfeng, W. (2016). Adsorption performances of Cd ( II ) from water by oxalic acid modified pomelo peel. *Chinese Journal of Environmental Engineering*, 10(1), 65-72.