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# A novel and cleaner technological process of extracting L-glutamic acid from fermentation broth by two-stage crystallization

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ABSTRACT

The fermentative L-glutamic acid is one of the important bio-products in the world. In 2009, China produced 1.6 Mt of GA occupying more than 70% of the entire production globally. However, the problems of high sulfuric acid/liquid ammonia consumption and severe pollution in GA production process strongly limit the sustainable development of the fermentative GA industry. In this study, a novel GA extraction technology, two-stage crystallization technology (TSC), was proposed and testified in pilot scale aiming at reducing sulfuric acid/liquid ammonia consumption and wastewater pollution in GA production process. The proposed TSC process could totally recover 95% GA: extracting about 83% of GA from fermentation broth in the first-stage with isoelectric crystallization technique, and recovering more than 70% of remaining GA in isoelectric mother liquor in the second-stage with evaporative crystallization technique. With the proposed TSC process, consumption of sulfuric acid, liquid ammonia and other supplemental materials could be substantially reduced, while the amount of high concentrated wastewater decreased from 9.8 $m^3$/t-GA to 1.6 $m^3$/t-GA. Through further treatments of evaporation and centrifugation, the ammonium sulfate in the mother liquor originated from the second-stage crystallization could be recovered. The mother liquor after ammonium sulfate recovery could be consecutively concentrated into a substance in semi-molten state again, and then the substance can be manufactured as organic-inorganic compound fertilizers after quick cooling and extrusion granulating. Comparing with the existing process of isoelectric crystallization with ion exchange (IEIE), the TSC process has the advantages of high quality of GA product, less sulfuric acid/liquid ammonia consumption and no wastewater/emission gas disposals. Furthermore, the solid waste could be utilized as the value-added fertilizer at the same time. In this way, the proposed TSC process greatly promotes the economic and environmental effect of the GA production process.



## 1. Introduction

L–glutamic acid (GA) is one of the most important amino acid products with a wide range of applications. In pharmaceutical industry, GA or its salt-derivates can be used as nutrition elements and participate in body metabolism. At the same time, GA can improve the function of nervous centralize and cortical brain for neurasthenia patients (Williams et al., 2005). In food industry, L-glutamate monosodium salt, namely monosodium glutamate (MSG) is an important freshness enhancer widely used in the fields of cooking as well as food processing, playing a key for food flavor regulation (Tiziana et al., 2007; Cairns et al., 2007). A recent study showed that the fermentative GA could also be used to produce biodegradable materials (poly L-glutamate), attributing the potential characteristics of application diversity for GA industry (Richard and Margaritis, 2003; Ashiuchi et al., 2003).

Currently, most of GA is produced fermentatively. For nearly a decade, GA industry develops rapidly, and the GA production amount in China reaches 1.60 Mt (equivalent to 2.02 Mt of MSG) that is about 70% of the global production. More than 200,000 t of MSG is exported every year. However, the huge demands in consumption of sulfuric acid, liquid ammonia and other chemical supplemental compounds deteriorate the economic benefits in GA production. On the other hand, the GA extraction process also produces a large amount of high concentrated wastewater that seriously pollutes the surrounding environment (Xue et al., 2008; Yang et al., 2005). Therefore, Chinese MSG production enterprises and the government urgently need economic and effective new technique to solve these problems. In the past twenty years,

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extreme efforts have been made by GA enterprises and related scientific research groups in order to solve the above mentioned problems (Xue et al., 2008; Yang et al., 2005; Bai, 2001). However, many practices have proved that the huge amount of high concentrated wastewater produced in GA extraction process is difficult to be handled with the traditional end-of-pipe treatment method.

During the past half century, it has been recognized that end-of-pipe treatment is not a good ways for environmental pollution control and the relatively high cost is also not acceptable by many enterprises (Lindsey, 2011). It has been proved that only adopting cleaner production technique and controlling pollution at the very beginning in the production process, the problems and the high operation cost in environment pollution control could be somewhat relieved (Schnitzer and Ulgiati, 2007; Frijns and Vlient, 1999). In 2008, The National Ministry of Environmental Protection (NMEP) of China issued the industrial cleaner production standard of MSG [HJ 444-2008], requesting a comprehensive and overall implementation of cleaner production in MSG industry in China. The current GA production situation indicated that high raw-materials consumption and high pollution in GA extraction process are the dominating factors limiting the economics of GA production process. Modification of GA extraction technology has become one of the major issues in achieving the target of "energy-saving, raw-material consumption and emission reduction". In the past three years, a novel and cleaner GA extraction technique, called two-stage crystallization technology (TSC), was proposed and tested in pilot scale (20,000 t-GA/y), in Shandong Linghua Monosodium Glutamate Co., Ltd., of China. With this technique, a very good performance in the terms of minimizing of raw-materials consumption, wastewater disposal, and fresh water usage has been achieved.

This paper was focused on introducing and reporting the concepts of the novel cleaner technological process and its performance in achieving of minimization in both wastewater and raw materials including usage of sulfuric acid and liquid ammonia.

## 2. The current extracting process of GA: the IEIE process

### 2.1. The working principle of the IEIE process

GA is a zwitterion and it will be crystallized from fermentation broth at its isoelectric point (pI, 3.22) where its solubility is lowest. This is called isoelectric crystallization. When pH is lower than 3.22, GA is mainly positively charged (cationic), and could be absorbed by cationic resin. While pH is higher than 3.22, GA is mainly negatively charged (anionic) and could be eluted from cationic resin. The GA absorption/elution process is called ion exchange.

The details of the isoelectric crystallization and ion exchange (IEIE) process could be described as follows:

$$\text{Isoelectric crystallization(pH 3.2)}: \quad 2GA^- + 2H^+ + SO_4^{2-} \Rightarrow 2GA^{\pm}\downarrow + SO_4^{2-} \tag{1}$$

$$\text{Acidification(pH 1.5)}: 2GA^{\pm} + 2H^+ + SO_4^{2-} \Rightarrow 2GA^+ + SO_4^{2-} \tag{2}$$

$$\text{Resin absorption(pH 1.5)}: R-SO_3NH_4 + GA^+ \Rightarrow R-SO_3GA + NH_4^+ \tag{3}$$

$$2NH_4^+ + SO_4^{2-} \Leftrightarrow (NH_4)_2SO_4 \tag{4}$$

$$\text{Elution(pH 9.0)}: R-SO_3GA + NH_4^+ \Rightarrow R-SO_3NH_4 + GA^+ \tag{5}$$

### 2.2. The flow of the IEIE process

The flowchart of IEIE process is shown in Fig. 1. Using sulfuric acid to adjust pH of fermentation broth from 6.5 to 3.2, about 75% (w/w) of GA is recovered from broth by this isoelectric crystallization process followed solid/liquid separation with centrifugation. However, the GA concentration in isoelectric mother liquid still remains at about 20–25 g $L^{-1}$ (Liu et al., 2008). To increase GA recovery ratio, pH of isoelectric mother liquor is further reduced to 1.5 with sulfuric acid allowing GA to be adsorbed with cationic exchange resins. The GA adsorbed by resin is then eluted using diluted ammonia solution, the eluted liquor is returned to isoelectric crystallization process for re-crystallization. In this ion exchange process, about 80% (w/w) of GA could be recovered from the isoelectric mother liquor and the total recovery reaches around 95%. This process has the advantage of higher GA recovery, however, sulfuric acid and liquid ammonia are largely consumed in this process, and wastewater production is also huge.

### 2.3. Characteristics of IEIE process and wastewater treatment

#### 2.3.1. Characteristics of wastewater

In IEIE process, two kinds of wastewater are disposed. One is the waste mother liquor (wastewater-1, in Fig. 1) with high wastes concentrations that is originated from cationic resin adsorption. The other is the wastewater with middle wastes concentrations (wastewater-2, in Fig. 1) that is produced during resin washing and regeneration. The main components and the characteristics of the two kinds of wastewater are summarized in Table 1. Wastewater-1 contains a large amount of organic and inorganic substances. The organic substances mainly originated from fermentation process, including cells (*corynebacterium*), residual sugar and other metabolites. Ammonium sulfate, the major inorganic substance in the wastewater, is the product of adding liquid ammonia and sulfuric acid during ion exchange process. Therefore, wastewater-1 characterized with high solids concentration, COD and ammonia nitrogen, as well as low pH, etc. The concentrations of waste solid and COD in wastewater-2 are relatively low, but the ions concentration of ammonia and sulfate remained at high level. Generally, more than 12 $m^3$ wastewater-1 and more than 10 $m^3$ wastewater-2 are produced for 1 t GA production.

#### 2.3.2. Treatment of wastewater

The wastewater-2 is generally treated by sequencing batch reactor (SBR) anoxic-aerobic activated sludge process after adjusting pH over 7.0 with $Na_2CO_3$ and mixing with some domestic sewage. With the treatment using SBR anoxic-aerobic, wastewater-2 could reach the 'grade II' disposal standard for MSG industry (GB8978-96) (Huang et al., 2001). However, wastewater-1 is difficult to deal with because of the existence of high concentrated sulfate salt. In anaerobic wastewater treatment process, sulfate-reducing bacteria deoxidize sulfate salt into $H_2S$ that is toxic to the denitrifying microorganisms and other microorganisms when $H_2S$ reaches high level. In addition, the consumption of organic carbon sources for sulfate-reducing bacteria is also harmful to the anti-nitrification process (Cohen, 2006). Therefore, the conventional anaerobic - aerobic treatment technique is difficult to handle this kind of wastewater.

Some researches have proved that wastewater-1 could be used as the raw materials after dilution to cultivate *Candida halophila* or *Rhodotorula glutinis* to produce single cell protein (SCP). During the processes, the COD removal rate exceeds 85% accompanied with the valuable SCP production, however the removal rates of ammonia nitrogen and sulfate ion were nearly zero (Xue et al., 2008; Yang et al., 2005; Zheng et al., 2005). On the other hand,