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Integrated process for scalable bioproduction of glycolic acid from cell catalysis of ethylene glycol

Xia Hua[a,b,c], Rou Cao[a,b,c], Xin Zhou[a,b,c], Yong Xu[a,b,c,*]

[a] Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, People's Republic of China
[b] College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, People's Republic of China
[c] Jiangsu Province Key Laboratory of Green Biomass-based Fuels and Chemicals, Nanjing 210037, People's Republic of China

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ABSTRACT

Glycolic acid (GA) is presently booming as a versatile raw material in the fields of high-grade cosmetics, polymer degradable materials, and drug production. The biocatalysis of ethylene glycol (EG) to GA is promising, with environmentally friendly benefits, while the effective and straight bioproduction of GA qualified for polymer synthesis purity is a challenge. In this study, we combine whole cell catalysis step and acidification-purification step. A compressed oxygen supply in the sealed aerated stirred tank reaction (COS-SSTR) and a weak basic anion-exchange resins were integrated to develop an efficient process of GA bioproduction from EG. Finally, 110.5 g/L of GA was obtained at the yield of 94.4% and the volume productivity of 2.3 g/L/h in 48 h that presently is the greatest level for GA bioproduction. After 335 resins treatment of 5.0 L catalyzed broth containing 497.2 g EG, we obtained 575.4 g GA at the recovery rate of 98.9%.

1. Introduction

Glycolic acid (GA), containing both hydroxyl and carboxyl groups (Alkim et al., 2016), is the simplest α-hydroxyl acid with the following chemical formula: $HOCH_2$-COOH. It is precisely because of this nature that GA has become an important intermediate chemical product and organic synthetic material. GA is a valuable raw material in the production of chemicals used in adhesives, metal cleaning, and dyestuff additives (He et al., 2010; Krochta et al., 1988). In addition, the most prominent advantage of GA is that it acts as a precursor for many polymer degradation and drug synthesis materials (Wang et al., 2005). GA is widely used in the synthesis of biodegradable polyglycolic acid (PGA) (Shigeno and Nakahara, 1991), an ideal packaging material, and poly (Lactic-co-Glycolic Acid) (PLGA) (Nakajima et al., 2008), for medical applications. The global market demand for GA was USD 93.3 million, equivalent to 40 kilo tons, and it is expected to reach USD 203 million equal 78.1 kilo tons in 2018 (Koivistoinen et al., 2013).

However, the production capacity of GA pales in comparison. Almost all of the existing methods for producing GA rely on chemical methods in a factory, such as chloroacetic acid or hydroxy acetonitrile hydrolysis (Ohshima et al., 2009). Both approaches have some non-negligible defects in industrial production, for example, lagging technology, poor product quality, serious environment pollution, and other issues. These challenges are inconsistent with the concept of green development in the world today. In contrast, microorganism catalysis has superior characteristics, such as mild reaction conditions, good selectivity, and high product purity.

Bacterial strain *Gluconobacter oxydans* is a promising microbe for bio-converting hydroxyl-aldehydes, hydroxyl-ketones, and different kinds of sugar; therefore, it is employed for industrial production of 1,3-dihydroxyacetone (Schweiger et al., 2013), galactonic acid (Zhou et al., 2018a,b,c), gluconic acid (Zhou et al., 2018a,b,c), xylonic acid (Zhou et al., 2015a,b), and other acid compounds. *G. oxydans* is also an excellent strain for producing GA from EG, even though no factory uses the strain to produce GA. There are two main obstacles hindering the development of a process. First, the catalysis yield does not possess competitiveness with chemical methods. Many studies have reported on GA produced by natural *G. oxydans* (Wei et al., 2009a,b), and the highest yield of GA was 93.0 g/L in 48 h (Hua et al., 2018). Second, there have no reports about the separation and purification of GA from microbial products. Therefore, the core task of this paper is to determine an integrated technology suitable for industrial production.

In 2015, the market price of 70% GA-water solution was approximately USD 4000/ton; for 99% high purity GA crystals, the price was as

Abbreviations: GA, glycolic acid; EG, ethylene glycol; ASTR, aired stirred tank reactor; COS-SSTR, compressed oxygen supply in the sealed aerated stirred tank; *Gluconobacter oxydans*, *G. oxydans*; HPLC, high performance liquid chromatography

* Corresponding author at: College of Chemical Engineering, Nanjing Forestry University, No. 159 Longpan Road, Nanjing 210037, People's Republic of China.
E-mail address: xuyong@njfu.edu.cn (Y. Xu).

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high as USD 15,000/ton. As demand for GA grows, there is ample space for profit. Therefore, it is urgent to development an economic integrated technology for GA, especially using products from microbial catalysis. In this study, we adopted an economic method of compressed oxygen supply in the sealed stirred tank reaction (COS-SSTR) to improve the performance of *G. oxydans* biocatalysis (Zhou et al., 2017). For the COS-SSSTR, a pure-oxygen gas cylinder is connected to a stirred fermentor. Because of no waste gas generated during microbial fermentation, the exhausted gas valve is shut off and oxygen gas was automatically supplied into stirred medium at the inlet pressure of 0.02–0.03 MPa. For purification process, the ion-exchange resins have been used in many fields, such as in drug separation, the refining of chemical products, sewage treatment and agricultural (Qian and Schoenau, 2002). At the same time, ion-exchange resins have extremely competitive properties, such as low cost, high utilization rate, and suitability for renewable recycling. In this paper, after filtering, the weak basic anion-exchange resin 335 was selected as the best material for synchronously purifying and acidizing GA. It is a promising method to produce high quality GA by microorganisms, and this method provides a valuable reference to promote GA production by biocatalysis in factories.

2. Materials and methods

2.1. Materials

Gluconabcter oxydans NL71, derived from the strain of ATCC 621, was preserved at 4 °C on sorbitol-agar medium containing 50 g/L sorbitol, 5 g/L yeast extract, and 15 g/L agar. *G. oxydans* NL71 inocula were cultivated in a continuously shaken 250-mL Erlenmeyer flask containing 50 mL medium including sorbitol (100 g/L) and yeast extract (10 g/L) for 24–36 h at 220 rpm and 30 °C. The cell pellet was harvested by centrifugation (Avanti J-26 XP, BECKMAN COULTER Co., Inc.) at 6000 rpm for 5–10 min (Zhou et al., 2015a,b).

The resins, including three macroporous resins (XAD-16N, HZ-801, and AB-8) and three weak basic anion-exchange resins (D900, 335, and D311), were purchased from Shanghai Huazhen Technology Co., Ltd. (Shanghai, China). The detailed physical and chemical properties of the selected resins are as follows. The particle diameters were all between 0.315 and 1.25 mm. The polarity of XAD-16N, AB-8, HZ-801 were strong, weak and nonpolarity. The functional groups of three weak basic anion-exchange resins were –NH2. The moisture of each resin was detected by infrared moisture meter. Chemicals and reagents used for purification technologies, such as NaOH, HCl, NaCl, KCl, acetone, EG, and GA, were obtained from Sigma Co., Shanghai, China. Deionized water produced by an ultra-pure water system was used for cleaning the resins and HPLC analyses.

2.2. Whole-cell catalysis

Bio-production of GA was conducted in a 3.0-L COS-SSTR (New Brunswick Gelligen 115) with 1.0 L catalysis broth containing $MgSO_4$ (0.5 g/L), KH_2PO_4 (1 g/L), K_2HPO_4 (2 g/L), $(NH4)_2SO_4$ (5 g/L), yeast extract (15 g/L) and1 g/L sorbitol for every 20 g of EG at 30 °C and 500 rpm and 3 vvm airflow (Zhou et al., 2018a,b,c). Sorbitol acted as a cofactor for cell growth and metabolism. In COS-SSTR, the technique of successive whloe-cell catalysis which adding EG continuously by peristaltic pump was employed. The pH was adjusted to 5.5–6.5 by 10% NaOH. After one batch cycle, the catalysis broth and *G. oxydans* cells were separated by centrifugation at 6000 rpm for 5–10 min by tubular bowl centrifuge. In addition, pure-oxygen offered by an oxygen cylinder (Purity ≥ 99.9%) was pushed at the gas inlet pressure of 0.02–0.03 MPa. Due to the difference of experiment data, five parallel assays were performed for fermentation experiment.

2.3. Pretreatment of resins

The pretreatment process of the selected macroporous resins included soaking with 75% ethanol wile shaking for 1 h, then washing with deionized water until the resins were alcohol-free and the lotion was clear. The above steps were repeated three times to ensure resins were fully treated. Finally, the pretreated resins were stored in 5% ethanol at 4 °C. For weak basic anion-exchange resins, they were sequentially soaked with 10% NaOH, 10% HCl, and 10% NaOH by shocking for 1 h, and then they were washed with deionized water until the lotion was neutral. Similarly, the pretreated ion-exchange resins were stored in 5% NaOH at 4 °C. For subsequent uses, the stored ion-exchange resins were cleaned by ethanol or NaOH, and the moisture content was measured by an infrared moisture meter to calculate the wet weight that corresponded to the dry weight ion-exchange resin (Praharaj et al., 2004; Yue et al., 2018).

2.4. Static/dynamic adsorption and desorption studies

Static adsorption and desorption studies were conducted in 250-ml Erlenmeyer flasks with flaps containing 2 g dry resins and 20 mL broth (110.5 g/L GANa, 3.9 g/L EG). Then, they were shaken at 25 °C with 150 rpm for 12 h. After the adsorption process, the filtrate was analyzed by HPLC. The unadsorbed GANa on the surface of the resins was washed away by 200 mL deionized water, and then desorption experiments with the macroporous resins and weak basic anion-exchange resins were carried out with 200 mL 75% ethanol and 5% NaOH, respectively, at 25 °C with 150 rpm for 12 h. Finally, the eluent was analyzed by HPLC, and the absorbance value was measured by an ultraviolet spectrophotometer. To select a desorption agent, the process was basically the same as above, except for the addition of three desorption agents (5% HCl, 5% NaOH, and 5% KCl) with 200 mL (Cao et al., 2002).

The dynamic adsorption and desorption experiments were carried out in a lab-scale glass chromatographic column loaded with 10 g of the pretreated 335 resins. Then, 200 mL broth was added to the ion-exchange resin column at a speed of 1.2 mL/min using a peristaltic pump, and a sampling analysis was conducted for every 5 mL of permeate collected. Then, the ion-exchange resin column was cleaned by deionized water (Shu and Yang, 2010). The 5% HCl elution process was consistent with the above steps, except that the sampling interval was expanded to 10 mL (Li and Li, 2012).

2.5. Ion-exchange resin recovery and mass balance studies

Based on the dynamic adsorption and desorption experiments and recovery experiments, the volume of broth and quantity of ion-exchange resins used in mass balance experiments was expanded to 1 L and 50 g, respectively. The ion-exchange resin cleaning process between each batch of experiments was as follows: the column was first washed with 200 mL deionized water, and then the remaining pigment attached to the ion-exchange resin was removed by 10% acetone with 200 mL. Finally, acetone and other impurities were removed with 200 mL deionized water (Wang et al., 2008). The design of whole technology including catalytic reaction and purification process is shown in Fig. 1.

2.6. Analytical methods

The properties of the selected resin were compared by the following formulas:

$$\text{Adsorption capacity(mg/g)} = \frac{(C_0 - C_e)\times V}{W},$$

$$\text{Desorption capacity(mg/g)} = \frac{C_d \times V_d}{W},$$

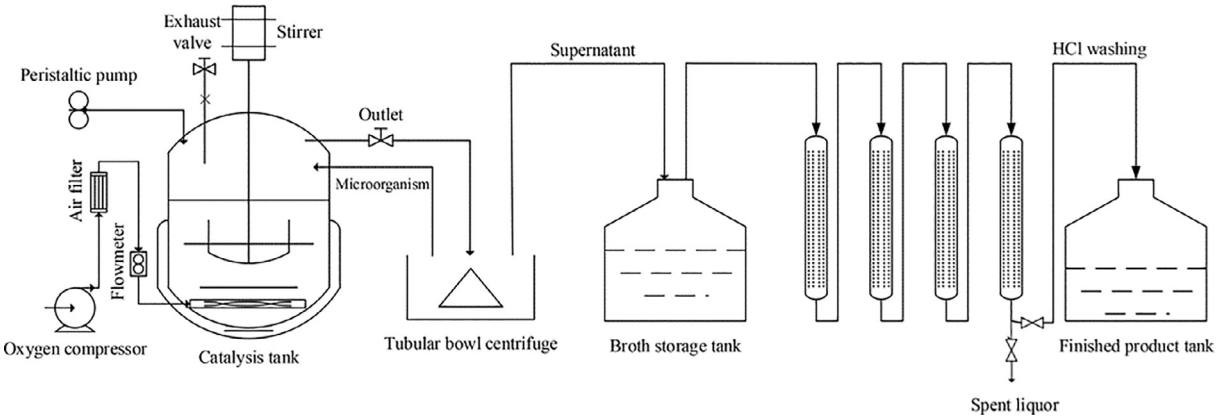

Fig. 1. Diagram of the COS-SSTR and purification for GA successive production carried out in a lab-scale glass chromatographic column loaded with the pretreated anion-exchange resins 335.

$$\text{Desorption ratio}(\%) = \frac{C_d \times V_d}{(C_0 - C_e) \times V_e} \times 100,$$

$$\text{Re moval rate of EG}(\backslash\%) = \frac{C'_0 \times V'_e - C'_d \times V}{C'_0 \times V'_0} \times 100,$$

$$\text{Decolorization rate}(\%) = \frac{A_0 - A_d}{A_0} \times 100,$$

$$\text{Recovery rate of GA}(\%) = \frac{C_d \times V_e}{C_0 \times V_0} \times 100,$$

where C_0, C_e, C_d, C'_0, C'_e, and C'_d represents the concentration of GA and EG in the initial, adsorbed, desorbed broth, respectively; V_0, V_e, and V_d represents the volume of initial, adsorbed, and desorbed broth, respectively. W represents the dry weight of the resins; A_0, and A_d represent the absorbance of the initial and desorbed broth.

Three parallel assays were performed for each experiment.

3. Results and discussion

3.1. Continuous feeding-cell fermentation by using COS-SSTR

After previous experiment exploration, we successfully achieved 93.0 g/L GANa and the bioreactor productivity reached 1.94 g·L·h^{-1} in a 3-L aired stirred tank reactor (ASTR) containing 1 L broth within 48 h. During catalysis process, the integration of the continuous EG feeding and increasing the concentration of yeast extract has markedly improved bio-production of GA. This achievement basically reached the highest level of GA production in the same batch. However, during fermentation, the dissolved oxygen level of EG bio-converted to GA was always below 20%, but oxygen as electron acceptor in the fermentation process. When the content of oxygen is insufficient, it will affect the catalytic performance of *G. oxydans*. To solve this problem, COS-SSTR designed by Zhou et al., was conducted in the GA production by *G. oxydans*. In the catalytic process, foaming issue is a defect that can't be ignored. The foaming was very severe at the initial stage of the reaction and out of control in the final stage if we didn't add any defoamer of polyether-ether-ketone. In the case of *G. oxydans*, foaming can seriously inhibit the efficiency of oxygen transfer in catalytic reaction. Moreover, the addition of defoamer had negative effects of GA quality and ion-exchange resins' performance. The COS-SSTR technology can provide a certain pressure to effectively inhibit foam generation. Therefore, there is still more space for improvement in GA quality.

As is shown in the Fig. 2, the performance of *G. oxydans* has been further improved in COS-SSTR which could be judged by the level of dissolved oxygen in the reactor. Through the operation of compressed oxygen supply, the dissolved oxygen level was greatly increased that overcome the issue of *G. oxydans* demand for oxygen. The dissolved oxygen in two catalysis systems increased slightly due to the *G. oxydans* demanded for oxygen decreased gradually as the cumulative reaction rate decreased. From Table 1, compare with ASTR, COS-SSTR effectively solved the problem of foam formation in catalytic reaction, and no defoamer was added into broth that commendably improved GA quality. Moreover, compressed oxygen supply also enhanced the transfer efficiency and utilization of oxygen. As a result, in COS-SSTR system, about 110.5 g/L of GA was obtained within 48 h at the yield of 96.5% and the productivity reached 2.3 g/L/h. Both production/productivity and the yield increased by 18.8% and 3.6% respectively. In addition, previous studies have confirmed the feasibility of cell-recycling technology that ensured the techno-economics to meet requirements. Therefore, COS-SSTR lays a good foundation for the follow-up GA purification process and also has economic and practical reference value for the production of high quality GA in a factory.

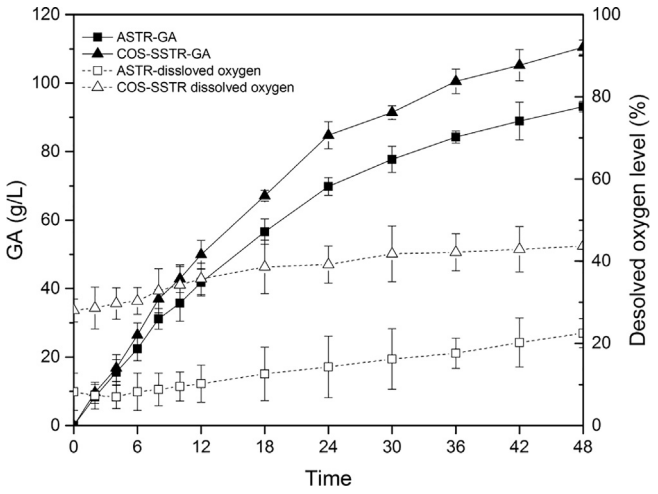

Fig. 2. Catalysis profiles of ASTR (500 rpm, 3 vvm-air) and COS-SSTR (500 rpm, 0.02 Mpa-compressed oxygen).

Table 1
Comparison of catalytic properties between ASTR and COS-SSTR.

Performance	ASTR	COS-SSTR
Glycolic acid (g/L)	93.0	110.5
Ethylene glycol (g/L)	5.6	3.8
Productivity (g/L/h)	1.9	2.3
Yield (%)	93.2	96.5
Foaming	√	×
Defoamer	√	×

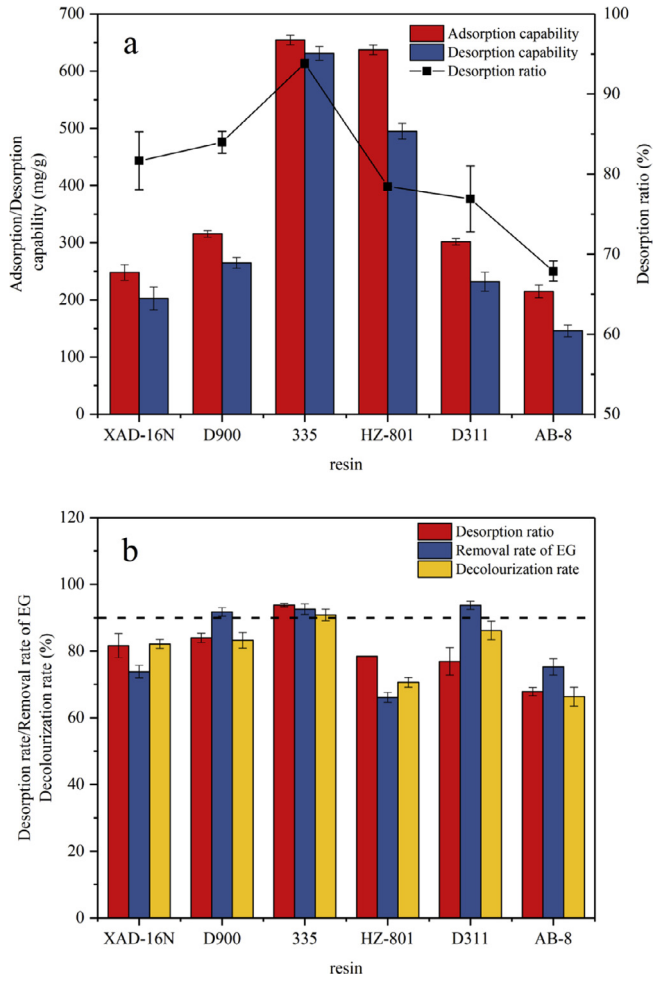

Fig. 3. (a) Adsorption/desorption capacities and desorption ratio of GA on different resins (b) Desorption ratio, removal rate of EG and decolorization rate of GA on different resins.

3.2. Comparison of resins properties and technical index

When purifying GA by resins, the adsorption and desorption capacity of resins are not the only indexes; the expected technical index is another important indicator. Therefore, to compare different resins in the purification process of GA more directly, the four criteria of adsorption and desorption capacity, removal rate of EG, and decolorization rate were comprehensively considered. GA is a weak acid, and the content of pigment in broth is high, therefore, different microporous adsorbent resins and weak basic anion-exchange resins were employed. Based on these factors, the optimal resin was selected by comparisons. As described in Fig. 3a, notably, the adsorption capacities of resin 335 and HZ-801 were far greater than the other resins in this study, respectively, up to 654.58 and 637.38 mg/g. However, the desorption ratio of HZ-801 was not satisfactory at only 78.44%. In contrast, the desorption capacity of resin 335 was also great, with the desorption ratio reaching 93.81%. Furthermore, comparisons of the technic index are clearly portrayed in Fig. 3b. Since GA is a precursor for many polymerized materials, the purity of GA is very important. Therefore, the purification process was only evaluated when the removal rate of EG and the decolorization rate were over 90%. According to these limits, only the resin 335 met all of the requirements. Although the performance of D311 was close to the requirements, its adsorption capacity was much weaker than 335, as displayed in Fig. 3a. Therefore, taking all of the factors into consideration, resin 311 was the most effective medium for the process.

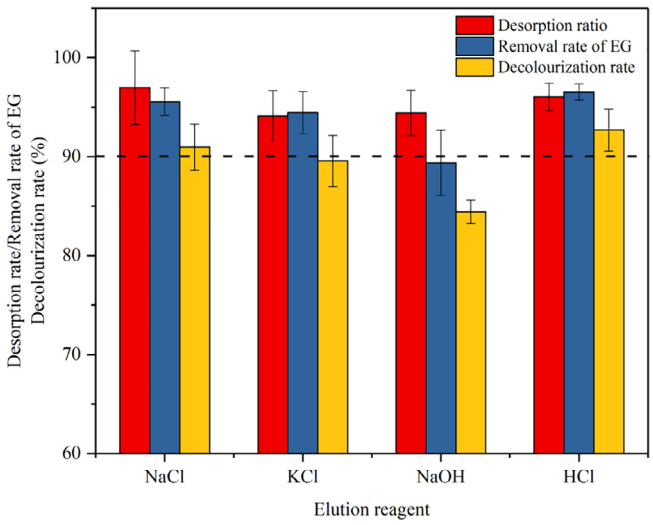

Fig. 4. The influence of different elution reagents on the performance of purification technology.

3.3. Influence of different elution reagents on purification process

For weak basic anion-exchange resins, using NaCl or NaOH as elution reagent is the best choice. However, they have serious flaws: the eluted products are mainly in a form of sodium salt, which requires an additional electrodialysis step during the purification process. This is not compatible with the primary purpose of this study, that is, synchronous purification and acidification of GA. Therefore, the use of 5% HCl as an elution reagent was compared with 5% NaOH, 5% NaCl, and 5% KCl. From Fig. 4, the desorption capacity of four elution reagents was excellent, and the desorption ratios were all greater than 90%. However, the technical index reached the desired level only when NaCl and HCl were employed as an elution reagent. Both the removal rate of EG and the decolorization rate exceeded the set limit. In addition, by adding HCl to the eluent, the purification and acidification of GA could be simultaneously accomplished. A brief description of the experimental model included acid ions exchanging with the cross-linking groups of ion-exchange resin when sodium glycolate was adsorbed by the ion-exchange resins. Then, the free sodium glycolate was washed away with deionized water. HCl facilitated the release of GA, because the attached acid ion could be replaced with Cl^-. Finally, the eluent contained a large amount of pure acid without sodium salt. Although using HCl as an eluent adds Cl^-, testing showed that the concentration of Cl^- was less than 3%. This concentration did not affect the final crystallization process or the quality of the crystalline product. Thus, while NaCl was an excellent elution reagent, but in contrast, HCl was undoubtedly the best choice.

3.4. Dynamic adsorption/desorption of GA and online recovery of ion-exchange resin

The selection of resins and the elution reagent were all conducted by static experiments. However, static experiments are not suitable for continuous production in industry. Hence, a one-step and simple column packed with 335 resins was designed for the separation and recovery of GA content from *G. oxydans* catalytic broth. After a preliminary dynamic adsorption study, the calculation demonstrated that the maximum broth volume processed by 10 g ion-exchange resins was 200 mL, and the working exchange capacity of the ion-exchange resin was 658.2 mg/g. For the desorption process, a total of 6326 mg GA was obtained by desorption means, with a recovery rate of up to 96.1%. Using an experiment of dynamic adsorption and desorption, the optimum adsorption and desorption volume for 10 g ion-exchange resins

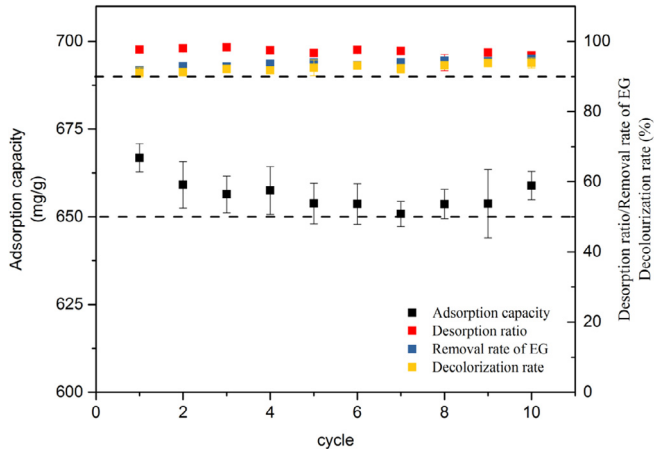

Fig. 5. Effect of resin online recovery on adsorption capacity, desorption ratio, removal rate of EG and decolorization rate.

were determined to provide a reference standard for material usage in subsequent ion-exchange resin recovery and mass balance experiments.

From a techno-economics point of view, whether the ion-exchange resin can be recycled and the efficiency after regeneration are decisive factors for whether this technology can be used in a factory (Laszlo, 2000). Therefore, to ensure the integrity and feasibility of 335 resins' purification and acidification technology, an online recovery experiment must be implemented. Based on this requirement, a total of 10 rounds of online recycling experiments were conducted, and the purification and acidification indictors of the ion-exchange resin were evaluated in detail. Fig. 5 displays four indexes, including adsorption capacity, desorption ratio, removal rate of EG, and decolorization rate. Furthermore, qualified performance was defined as a desorption capacity of greater than 650 mg/g, with the remaining three indictors exceeding 90%. As shown in Fig. 5, it is clear that the adsorption capacity of each cycle was higher than 650 mg/g, the set limit. In addition, the other three indexes were also greater than the determined standard and there was no downward trend. Thus, the recovery and utilization of the 335 resins had no negative effects on the technology and all requirements reached or exceeded the excepted values. Taken together, the 335 resins purified and acidized GA from catalytic broth to meet the principles of techno-economics.

3.5. Mass balance of GA bio-production from EG

The mass balance of the entire process to produce GA via whole-cell catalysis and downstream processing was also systematically analyzed. As shown in Fig. 6, in one round, 95 g EG was added continuously into an aired and stirred tank reactor that contained 1 L of liquid. Then, substrates were successively catalyzed at 30 °C by shaking at 500 rpm for 48 h, and the pH of the entire reaction system was maintained by NaOH. After one round, the quantity of sodium glycolate accumulated within 48 h was 110.5 g, and the remaining 3.8 g substrates were not completely consumed. The obtained broth was absorbed by 50 g of 335 resins and the desorbed by 5% HCl over 4 cycles. According to the sampling analysis of the eluent, only 0.7 g/L of GA was detected when the broth was purified 4 cycles. Therefore, for 1 L of catalysis broth, 4 cycles of ion-exchange resin experiments were sufficient to absorb almost all of the GA. Finally, the collected product, eluted by HCl, contained 108.7 g GA, with only 0.22 g EG remaining. Comparing the purified product with that in the broth, the recovery rate of GA and the removal rate of EG reached 98.4% and 94.2%, respectively. In addition, the decolorization rate of this process was also up to 90%. To better confirm actual production capacity for a factory, we used the same five batches of the ion-exchange resins to purify the broth obtained from the cell-recycling experiment. Unsurprisingly, the results were still excellent. After 5 rounds experiment, about 545.3 g GA was achieved, and a recovery rate up to 98.9% reflected outstanding technical economics. Based on this data, the resin 335 has been verified as an excellent medium for purifying and acidizing GA from catalysis broth which perfect for industrial production.

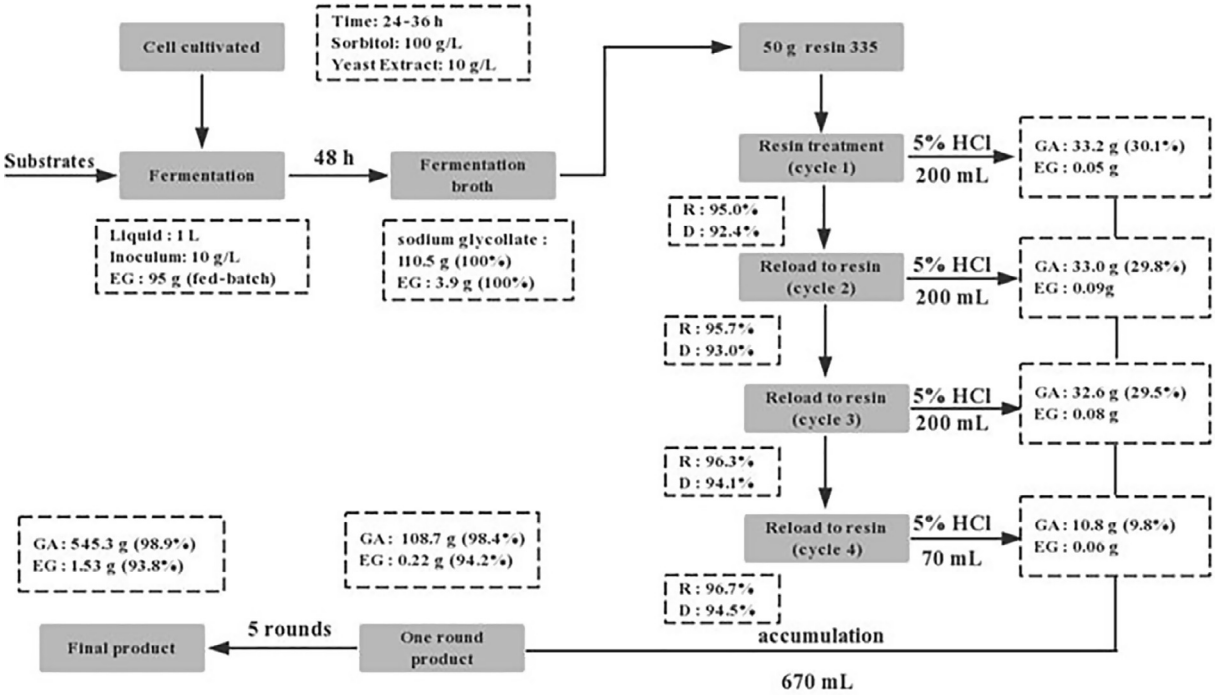

Fig. 6. Mass balance of catalysis and purification of GA and the performance of whole technology (A: adsorption capacity; R: removal rate of EG; D: decolorization rate).

4. Conclusions

Based on the techno-economic analyses, the quality and production of GA catalyzed by *G. oxydans* was improved by employed COS-SSTR and GA from culture broth was markedly purified by fully utilizing the 335 resins. More importantly, the integrated technology of GA production satisfied the basic requirements of industrial production. To further demonstrate the feasibility and efficiency of the technology, we evaluated the mass balance from catalysis to purification, and the results demonstrated that all indicators were excellent. This study provides a practical approach for industrial bio-production of high quality GA, which enable microbial production of GA from EG in factories.

Acknowledgements

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