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*Article*

# Purification of Polymer-Grade Fumaric Acid from Fermented Spent Sulfite Liquor

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**Abstract:** Fumaric acid is a chemical building block with many applications, namely in the polymer industry. The fermentative production of fumaric acid from renewable feedstock is a promising and sustainable alternative to petroleum-based chemical synthesis. The use of existing industrial side-streams as raw-material within biorefineries potentially enable production costs competitive against current chemical processes, while preventing the use of refined sugars competing with food and feed uses and avoiding purposely grow crops requiring large areas of arable land. However, most industrial side streams contain a diversity of molecules that will add complexity to the purification of fumaric acid from the fermentation broth. A process for the recovery and purification of fumaric acid from complex fermentation medium containing spent sulfite liquor (SSL) as carbon source was developed and is herein described. A simple two-stage precipitation procedure involving separation unit operations, pH and temperature manipulation and polishing through the removal of contaminants with activated carbon allowed the recovery of fumaric acid with 68.3% recovery yield with specifications meeting the requirements of the polymer industry. Further, process integration opportunities were implemented that allowed minimizing the generation of waste streams containing fumaric acid which enabled increasing the yield to 81.4% while keeping the product specifications.

**Keywords:** fumaric acid; purification; spent sulfite liquor; biorefineries

## 1. Introduction

To ensure sustainable economic growth in a globalized world, resources have to be used in a smarter, more sustainable way. As many natural resources are finite, finding a more environmentally and economically sustainable way of using them has become a priority. In a circular economy the value of products and materials is maintained for as long as possible. For example, the use of resources is minimized by keeping them within the economy when a product has reached the end of its life, to be used again and again to create further value and reducing the production of waste. Industrial biotechnology provides new processing solutions meeting the requirements to the realization of a circular economy, as it enables the industrial production of added value chemicals from renewable resources and waste streams, including industrial, for example, from the pulp and paper, agricultural and food industries. Indeed, the long-term sustainability of most current industrial processes, that rely on petrochemical sources for raw materials, is compromised. Further, the use of 1st generation feedstocks, which compete for raw material and arable land with food and feed uses is also an issue. Therefore, taking advantage of different, non-conventional carbon sources promotes balance, stability and competitiveness in future processes for the production of chemicals. Concepts of 2nd generation biorefineries, aiming at utilizing the cellulose in non-food biomass have been put forward for the production of ethanol and other platform chemicals, often using existing industrial side-streams, for example, from the pulp and paper industry. Blends of C5 and C6 sugars are used today in production of sulfite ethanol where the cooking liquor from sulfite pulping is used for ethanol production. This cooking liquor, also named spent sulfite liquor (SSL) contains soluble lignosulfonates, with various market

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applications, and hydrolyzed sugars from the wood hemicelluloses. Yeasts are used for fermentation, and only the C6 sugars (mainly mannose from softwood and glucose from hardwood) are fermented to ethanol while the pentoses are left untouched. Global fumaric acid market size was estimated at 233.3 kilo tons in 2013 and is expected to grow to 346.2 kilo tons by 2020 [1]. It is particularly used in food and animal feed for pH adjustment, preservation and flavor enhancement, but increasing unsaturated polyester resins and paints demand from increasing infrastructure spending coupled with growing automobile production particularly in countries such as China, India and Brazil is likely to surge the demand. Although fumaric acid is already available from fermentation on glucose using *Rhizopus* strains, such production route is only competitive at high oil and gas prices. *Rhizopus* strains are however able to utilize C5 sugars such as xylose and arabinose [2], and recombinant systems based on *E. coli* and *S. cerevisiae* may enable the production of fumaric acid from streams rich in C5 sugars with *S. cerevisiae* providing the extra benefit of allowing the production to be carried out at lower pH, hence obtaining most of, if not all, the product in its fully protonated form instead of a salt. The production of polyesters from bio-based diacid monomers, such as fumaric acid, requires the polymerization in solution by direct reaction of diacids and diols at high temperature, using organometallic catalysts and is hindered by the presence of impurities contained in the side and waste streams.

This study aims at providing processing options that allow the purification of fumaric acid extracted from fermentation broths that used complex raw materials, such as SSL, as main carbon source, in order to obtain specifications of the purified product that meet the requirements to enable its use in the manufacture of polymers.

The downstream processing of extracellular fermentation products such as fumaric acid, typically starts by removing biomass from the fermentation broth, producing a clarified broth where the product, sugars, organic acids and other contaminant substances are still present. However, since fumaric acid is a dicarboxylic acid with $pK_{a1} = 3.02$ and $pK_{a2} = 4.38$ [3] is actually present in solution as three differently protonated species, the relative amounts of which will depend on the pH of the solution. At low pH, $H_2FA$ is the prevailing form and if the aqueous solution is saturated, fumaric acid can crystallize. At high pH, bivalent fumarate ion $FA^{2-}$ is prevailing and at intermediate pH monovalent hydrogenfumarate $HFA^-$. Varying the pH of the medium will impact on the existing species and on the dissolved/precipitated fractions of fumaric acid [4] and on its capability to be adsorbed to sorbent materials. This paper describes the development of an efficient, simple, and cost-effective process of obtaining polymer-grade fumaric acid from a fermentation broth based on spent sulfite liquor.

## 2. Materials and Methods

### *2.1. Preparation of SSL-based fermentation broth*

### 2.1.1. SSL pretreatment

Crude acidic *Eucalyptus* SSL (Borregaard, Sarpsborg, Norway) was filtered using a Schott Duran® filter funnel G-2 with a 40-100 µm pore size for the removal of solids in suspension and processed by tangential flow filtration (TFF) using a Cogent M1 TFF equipment (Merck Millipore), equipped with a Pellicon® 2 filter cassette membrane (Merck Millipore) with a 5 kDa cut-off to remove the larger molecular weight lignosulphonates. The pH of the 5 kDa permeate was adjusted to 5 using 5N NaOH and the permeate was pasteurized at 70ºC for 1 hour and stored at 4ºC before further usage.

### 2.1.2. Microorganism and culture

*Saccharomyces cerevisiae* GSE16 (kindly provided by Dr. J. Thevelein, VIB - KU Leuven, Belgium), capable of metabolizing xylose and tolerant to inhibitors [5] was used. The fermentation medium was composed by 30% (v/v) of pasteurized 5 kDa SSL permeate, 10g/L of yeast extract (BioSpringer), 20 g/L of bacterial peptone (Oxoid) with 40 g/L of total sugars (adjusted with addition of xylose (Danisco)). Cultures were prepared in 500 mL shake flask with a total cultivation medium volume of 125 mL incubated at 150rpm and 30ºC for 140h. At the end of the cultivation, cells were removed from the fermented SSL-containing medium by centrifugation (Beckman Coulter, USA) at 6000rpm, 9000 g for 20 minutes at 20ºC.

## *2.2. Precipitation of fumaric acid*

### 2.2.1. Fumaric acid solubility studies

FA-containing suspensions were prepared by adding FA (Merck, ≥ 99.0%) to 100 mL shake flasks containing 25 mL of reverse osmosis water. The suspensions were incubated at the different temperatures for 1 h in an orbital shaker (New Brunswick Orbital incubator Innova 43). The non-solubilized FA crystals were allowed to settle for 1 h. The crystals were collected by vacuum filtration (VWR 110mm qualitative filter paper, 5-13µm particle retention) and oven dried at 60ºC for 24 h. FA solubility was determined by the difference between the known amount of FA used for preparing the solutions and the amount of FA recovered in the filtration and confirmed by HPLC analysis of the filtrate.

### 2.2.2. Fumaric acid recovery

All downstream processing studies were performed using the SSL-based fermentation broth supplemented with different amounts of FA. In all cases, the pH was adjusted to 4.5 using 10 N NaOH (Applichem Panreac, 98%) to promote complete FA dissolution. A two-stage precipitation protocol was used. In the first stage, 500 g of a 5%(w/w) solution was acidified to pH 0.75 by addition of 5 N $H_2SO_4$ (Fisher Scientific, >95%) and left without agitation at 4ºC overnight, after which the solids were recovered by vacuum filtration as described above. The recovered solids were rinsed with a known amount of ice-cold 0.4 M $H_2SO_4$ solution. The solids were then placed in 250g of water to resuspend the material in a shake flask heated at 80ºC. The solution was allowed to cool to room temperature and was then slowly acidified to pH 0.75 by addition of 5 N $H_2SO_4$. The same experimental conditions were employed in the second stage to obtained the washed FA. At the various steps, the recovered precipitate containing FA was dried and weighed. The percentage of FA in the retained solids was assessed by HPLC after re-suspending the solid material in a known amount of water and, upon heating at 80ºC, achieving the complete dissolution of FA from the recovered precipitate. The FA concentration in the liquid streams was determined by HPLC.

## *2.3. Use of activated carbon*

### 2.3.1. Determination of fumaric acid adsorption capacity

All downstream processing studies were performed using the SSL-based fermentation broth Different amounts of activated carbon (Sigma-Aldrich, >90%) were added to 25 g/L FA solutions at different pH in a shake flask at 150 rpm. The concentration of FA in solution was monitored by HPLC in samples collected after 10, 20, 40, 60 and 80 minutes of incubation. After vacuum filtration, as described above, FA concentration of the filtrate was assessed by HPLC.

### 2.3.2. Removal of contaminants of fumaric acid

The precipitate originated from the 2-stage precipitation FA recovery process was dissolved by adding 10 N NaOH until the pH reached 10. The volume of solution was then adjusted to obtain a 30 g/L FA solution to which 0.02:1 (w/w) activated carbon was added. The mixture was incubated at 35ºC, 150rpm for 60 minutes. After incubation, the solution was vacuum filtered to remove the activated carbon and any other particulate impurities. The amount of filtrate was determined and

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FA was analyzed by HPLC. To recover the fumaric acid in solution, the filtrate was acidified to pH 0.75 by addition of 5 N $H_2SO_4$ and then incubated overnight at 4ºC without agitation for the precipitation of FA.

### 2.3.3. Recovery of fumaric acid from dilute solutions

1L of diluted FA solution was placed in a shake flask and 0.1:1 (w/w) activated carbon was added. The suspension was incubated for 60 minutes at 35ºC, 150rpm. The suspension was then vacuum filtered, the retained activated carbon was collected and the recovered filtrate was analyzed by HPLC. The thus collected activated carbon was treated with a solution of 1N NaOH used as desorbent. A 1:1 mixture of wet activated carbon and NaOH solution was incubated for 60 minutes at 35ºC, 150rpm. After incubation, the suspension was vacuum filtered and the filtrate was analyzed by HPLC. In order to recover fumaric acid from the filtrate, the solution was acidified to pH 0.75 by adding 5 N $H_2SO_4$ and placed at 4ºC overnight. The solution was then vacuum filtered and the filtrate sampled and analyzed by HPLC. The obtained solids were dried, weighed and the fumaric acid content was determined as above.

### *2.4. Analytical methods*

Optical density of cultures was monitored in a Shimazu UV-1700 spectrophotometer at 600nm. Organic acid and sugar analysis were performed in Shimadzu LC-20AD Prominence HPLC equipped with a Rezex RHM-Monosaccharide $H^+$ (8%) LC Column 300 x 7.8 mm, from Phenomenex, oven temperature set to 35ºC, using as eluent $H_2SO_4$ 5mM at a flow rate of 0.6mL/min, 20µL injection volume. Organic acids were quantified through a Shimadzu SPD-M20A diode array detector at 205 nm and sugars were quantified through a Shimadzu RID-10A detector. Samples were prepared in 50mM $H_2SO_4$.

## 3. Results and Discussion

### *3.1. Influence of pH and temperature on the precipitation of fumaric acid*

Solutions of different total concentration of fumaric acid (FA) species (5, 15, 35 and 50 g/L) were prepared and incubated at different temperatures. Upon reaching equilibrium, the amounts of FA that precipitated and that remained in solution were assessed. Total dissolution of the FA in the 0.5% solution and in the 1.5% solution are achieved above 25ºC and at above 45ºC, respectively (Figure 1). In the case of the 35 and 50 g/L solutions, part of the FA did not dissolve within the temperature ranges tested (5ºC and 65ºC). The pH of the solutions in equilibrium was measured (Figure 1). At low temperatures, most FA is precipitated and only a small fraction remains in solution, hence the higher pH. When the temperature increases, a higher fraction of FA is solubilized, hence more $H^+$ is freely in solution and the pH thus decreases. The plateaus on the pH values at temperatures above 25ºC for the experiment with a total 5g/L FA concentration and above 45ºC for the experiment with a total 15g/L FA concentration are explained by the total solubilization of FA and no further variation of the concentration of $H^+$. These results suggest that effective precipitation of FA will occur at temperatures below 15ºC. Further, in order to obtain a high purity of $H_2Fa$ with respect to total FA species, the pH should be well below $pK_{a1}$ of fumaric acid, for example at or below 2.5.

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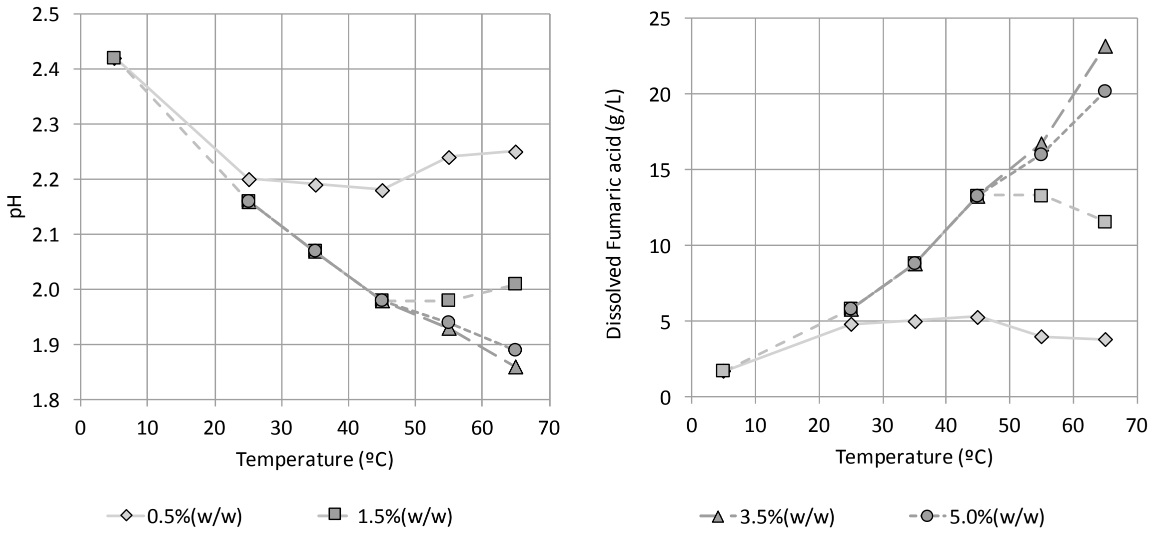

**Figure 1.** Variation of pH of different fumaric acid solutions with varying temperature (left) and equivalent calculated dissolved fumaric acid concentration (right).

### *3.2. Direct recovery of fumaric acid from SSL-based fermentation media*

The present work addresses the recovery of FA from two alternative but comparable streams: (i) a ultrafiltered stream of SSL that has been fermented and then centrifuged for cell removal; (ii) a stream of SSL that has been fermented and then centrifuged for cell removal and ultrafiltered. A significant part of the lignosulphonates are removed in a 5 kDa ultrafiltration, but lower molecular weight lignosulphonates and other molecules such as phenolics and aldehydes in addition to metabolites produced by the yeast cells in addition to FA will be present in the stream from which FA is to be recovered. The concentration of the FA produced during the fermentation is not only important to meet the productivity requirements of the process, but may also influence the downstream process. To assess this, two broths with different FA concentrations, 15 g/L and 50 g/L were prepared and a simple one-stage precipitation process was carried out by acidifying the fermentation broth with $H_2SO_4$ to a pH of 0.75, cooling to 4ºC and filtering out the precipitated material. The thus recovered precipitate was then washed with chilled 0.4 M $H_2SO_4$ solution to remove impurities while minimizing the loss of fumaric acid. Only 22.6% of the FA was recovered in the precipitated material obtained from the broth containing 15 g/L FA, while 92.4% FA was recovered in the precipitated material obtained from the broth containing 50 g/L FA, highlighting the impact of the composition of the starting material. In all remaining tests, a broth with a concentration of 50 g/L FA was used, below which a production process is deemed not feasible.

Another important requirement of the process is the ability to provide a product with a purity meeting the specifications for enabling its use in the production of polymers. After this one-stage purification protocol, a purity of 47.5% was obtained with the broth containing 50 g/L FA, clearly showing that the product still contained too many impurities entrained from the fermentation broth. The precipitated material was then used in a second purification stage. The filtered material was washed with water at 80ºC to dissolve the fumaric acid while retaining insoluble impurities in the filter. The thus obtained FA-rich stream was then acidified to a pH of 0.75, cooled to 4ºC and the precipitated material is filtered out, washed with a chilled 0.4 M $H_2SO_4$ solution, dried and recovered. After this two-stage procedure, a recovery yield of 77.8% and a purity of 89.6% were obtained. Despite the fair purity value, the recovered solid was very dark, indicating that a significant amount of impurities from the SSL-based fermentation broth were still present in the product.

### *3.3. Improving the purity of fumaric acid with activated carbon*

Since a 89.6% purity is still below specification and the visual inspection clearly showed contamination of the product by compounds from the initial raw material, treatment of the obtained product with activated carbon (AC) was envisaged. AC is a known adsorbent commonly applied in industry, and has been already tested in the purification of FA from fermentation broth using a defined culture medium [6]. The effects of temperature, contact time and pH on the adsorption capacity of FA were tested. It was found that contact time and temperature do not influence the adsorption capacity of AC (data not shown). However, by varying pH the capacity of AC to adsorb FA varied markedly (Figure 2).

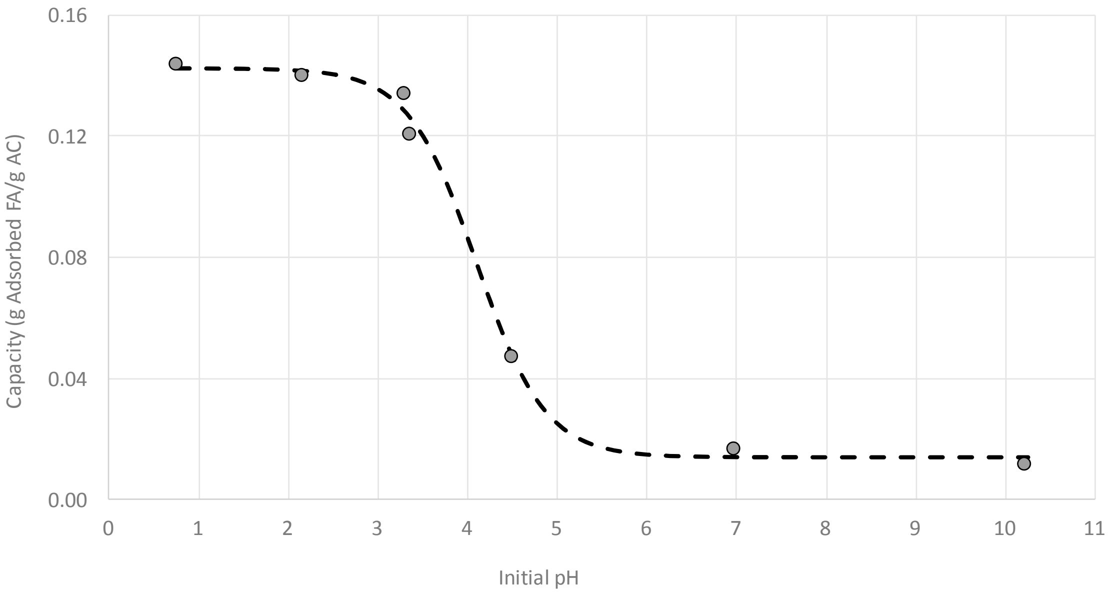

**Figure 2.** Capacity for fumaric acid adsorption of activated carbon as function of pH. The dashed line is a fit of the experimental data to a sigmoid function.

At the tested conditions, the AC adsorption capacity decreases with increasing pH. Interestingly, a shift occurs at about pH 4, below which the fraction of FA which is fully protonated increases. In order to remove the impurities from the obtained material while minimizing the losses of fumaric acid, the dried materials were dissolved in a NaOH solution, to obtain a concentration of around 30 g/L FA and a final pH of 10 at which very low adsorption of fumaric acid on the activated carbon occurs. This solution was finally contacted with 0.02:1 (w/w) AC. After 1 hour with agitation, the AC was removed by filtration, the obtained solution was acidified to pH 0.75 and cooled at 4ºC to allow for the precipitation of FA. As before, the precipitate was recovered by filtration and washed with a chilled 0.4M $H_2SO_4$ solution, dried and recovered. After this AC polishing step, no measurable amounts of impurities were detected in the obtained FA and a white powder was obtained (Figure 3) that could successfully be polymerized with diols (results not shown), thus validating that the FA purity grade obtained meets the requirements. The yield of the AC treatment was 87.8%.

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**Figure 3.** Side-by-side comparison of dry solids obtained without activated carbon treatment (left) and with activated carbon treatment (right).

### *3.4. Improving the yield of the fumaric acid purification process*

The overall yield of the two-stage fumaric acid precipitation process and of the activated carbon treatment is 68.3%. The major contributors for losses of product are the liquid streams generated in the chilled washes of FA-rich precipitates, which combined account for the loss of 28.5% of the FA initially present in the broth. However, their FA concentration is fairly low, between 2 and 7 g/L, which makes the FA recovery more challenging. We thus envisaged the recovery of FA using again AC, but this time under acidic conditions to retain and concentrate the FA in the AC and desorbing the thus retained FA using a NaOH 1 M solution. This desorption method is more compatible than that described by Zhang et al. [6], which uses acetone, a petrochemically-derived organic solvent, posing safety and environmental concerns and aggressive to most sealing materials used in processing equipment. This procedure allowed recovering 42% of the FA that would have been lost in the water wash streams from the former processing steps, and allowing the overall yield to increase from 68.3% to 80.4%.

### *3.5. Integration of the steps*

The FA purification process from the fermented SSL-based medium is then effectively achieved by performing a two-stage precipitation process, polishing the thus obtained FA by removing most of the contaminants through AC adsorption under basic conditions and increasing the overall yield by capturing residual FA from liquid waste streams also by AC under acidic conditions. Figure 4 shows a process flow diagram of these operations together with the FA mass balance and concentration in each stream (w/w). By analyzing the processes, a number of optimization opportunities become evident: (i) The FA-rich stream 13 can be sent directly to the polishing step with AC under basic conditions without requiring the energy-consuming drying step. (ii) Stream 37, a slurry with the FA recovered from the chilled washes of FA-rich precipitates (see §3.4), contains only about 7.5% of FA, which will not meet purity targets and is too diluted to be dried, but it has a very similar composition to the acidic solution of stream 10. It was thus decided to redirect stream 37 back to the 2-stage precipitation process by mixing with stream 10, thus subjecting the contents of stream 37 to a second wash step. Another possibility would be to mix stream 34 with stream 10, since both are acidic solutions generated upon the addition of $H_2SO_4$, but this would yield a significant dilution of stream 10, thus affecting the efficiency of the subsequent filtration and wash step and

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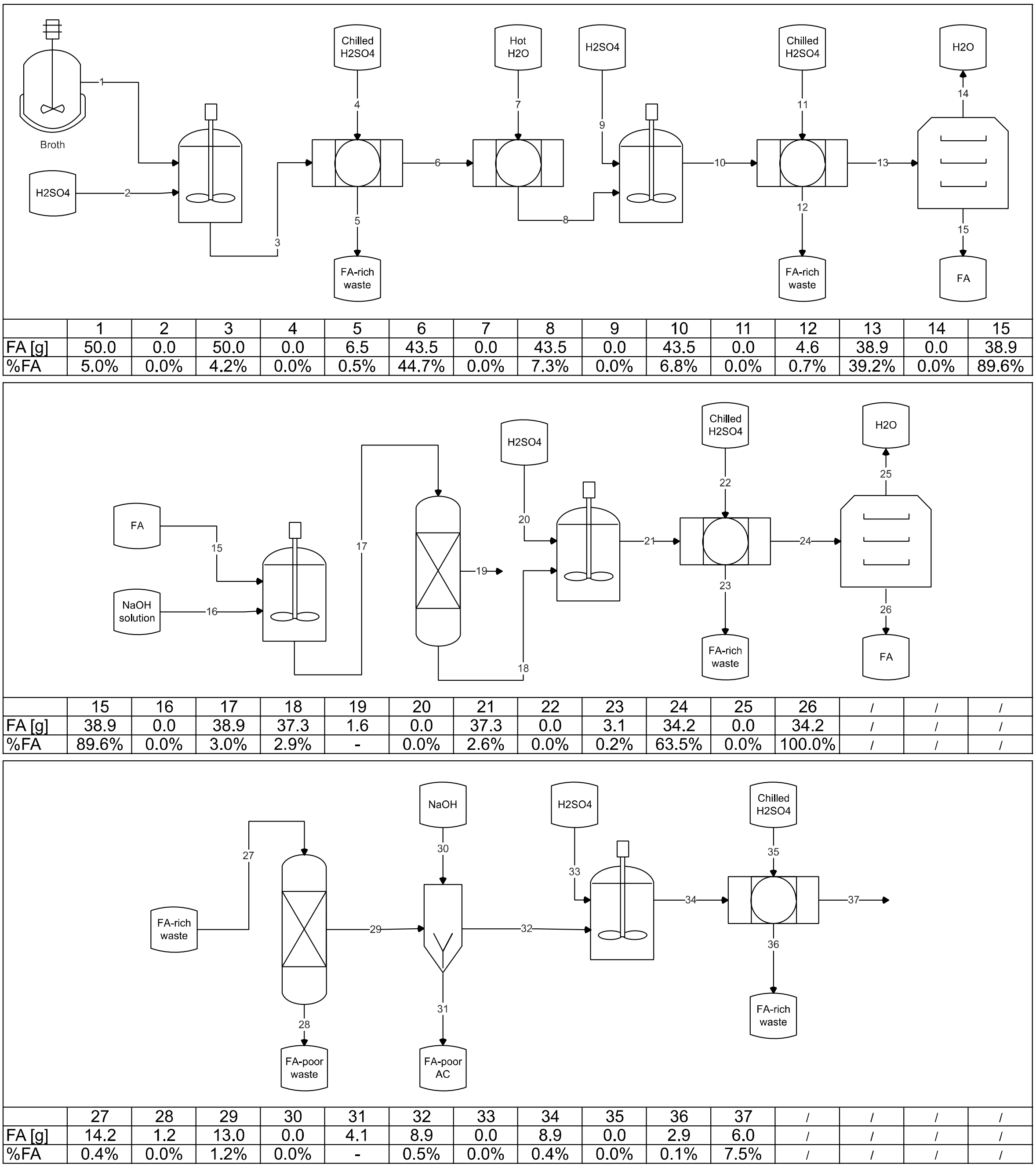
hence such possibility was ruled out. (iii) Stream 36 also generates a waste stream containing FA, which actually corresponds to 20.3% of the FA that is to be recovered from the chilled wash of FA-rich precipitates in the process described in §3.4. This stream can also be recovered and recycled back to the activated carbon treatment under acidic conditions.



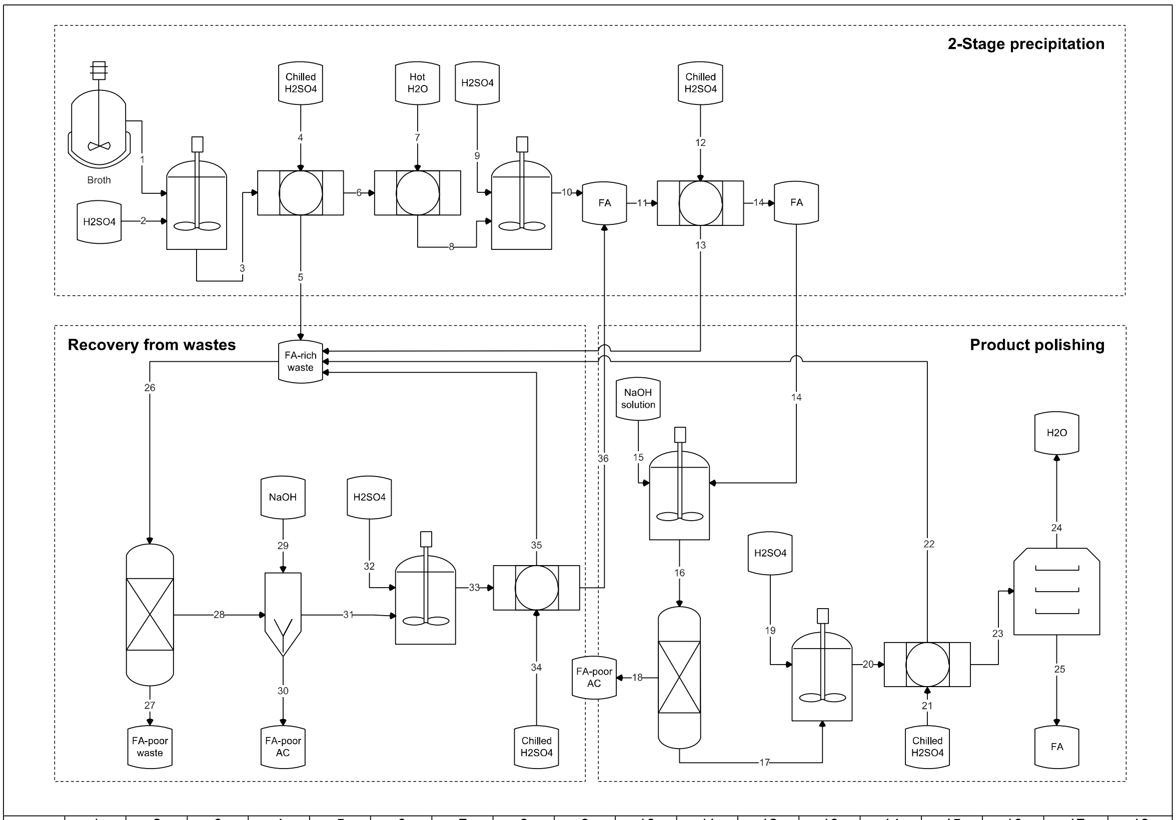
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FA [g] | 50.0 | 0.0 | 50.0 | 0.0 | 6.5 | 43.5 | 0.0 | 43.5 | 0.0 | 43.5 | 0.0 | 4.6 | 38.9 | 0.0 | 38.9 |
| %FA | 5.0% | 0.0% | 4.2% | 0.0% | 0.5% | 44.7% | 0.0% | 7.3% | 0.0% | 6.8% | 0.0% | 0.7% | 39.2% | 0.0% | 89.6% |

| | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | / | / | / |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FA [g] | 38.9 | 0.0 | 38.9 | 37.3 | 1.6 | 0.0 | 37.3 | 0.0 | 3.1 | 34.2 | 0.0 | 34.2 | / | / | / |
| %FA | 89.6% | 0.0% | 3.0% | 2.9% | - | 0.0% | 2.6% | 0.0% | 0.2% | 63.5% | 0.0% | 100.0% | / | / | / |

| | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | / | / | / | / |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FA [g] | 14.2 | 1.2 | 13.0 | 0.0 | 4.1 | 8.9 | 0.0 | 8.9 | 0.0 | 2.9 | 6.0 | / | / | / | / |
| %FA | 0.4% | 0.0% | 1.2% | 0.0% | - | 0.5% | 0.0% | 0.4% | 0.0% | 0.1% | 7.5% | / | / | / | / |

**Figure 4.** Process flow diagram and mass balance for fumaric acid of the two-stage precipitation process (top), polishing the thus obtained fumaric acid by removing most of the contaminants through activated carbon adsorption under basic conditions (middle) and increasing the overall yield by capturing residual fumaric acid from liquid waste streams also by activated carbon under acidic conditions (bottom). FA: fumaric acid; AC: activated carbon.

Figure 5 shows a process flow diagram summarizing the process after the operations have been integrated. In addition to reducing the processing and streams, such integration allows further increase of the yield of recovery of FA to 81.4%. Some FA loss occurs in stream 27, but this is considered too diluted to feasibly enable the product recovery. From the mass balances, it can be seen that most FA losses occur in streams 18 and 30, both corresponding to FA adsorbed to AC. In stream 18 most compounds adsorbed together with FA are the contaminating compounds that render the end-product useless, hence the selective separation of FA from these contaminants in this stream does not seems feasible. However, in stream 30, the main compound adsorbed to the AC is actually FA and the losses to the overall process are of FA that has not been desorbed from the activated carbon, so the re-use of at least part of this AC can be envisaged and will be studied in future work. In case 50% of such activated carbon could be reused, the overall process yield could increase to about 87%.



| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FA [g] | 50.0 | 0.0 | 50.0 | 0.0 | 6.5 | 43.5 | 0.0 | 43.5 | 0.0 | 43.5 | 51.8 | 0.0 | 5.5 | 46.4 | 0.0 | 46.4 | 44.4 | 1.9 |
| %FA | 5.0% | 0.0% | 4.2% | 0.0% | 0.5% | 44.7% | 0.0% | 7.3% | 0.0% | 6.8% | 6.9% | 0.0% | 0.7% | 39.2% | 0.0% | 3.0% | 2.9% | - |

| | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FA [g] | 0.0 | 44.4 | 0.0 | 3.7 | 40.7 | 0.0 | 40.7 | 19.7 | 1.7 | 18.1 | 0.0 | 5.7 | 12.4 | 0.0 | 12.4 | 0.0 | 4.0 | 8.4 |
| %FA | 0.0% | 2.6% | 0.0% | 0.2% | 63.5% | 0.0% | 100.0% | 0.3% | 0.0% | 1.2% | 0.0% | 100.0% | 0.5% | 0.0% | 0.4% | 0.0% | 0.1% | 7.5% |

**Figure 5.** Process flow diagram and mass balance for the proposed integrated process of purification of fumaric acid from SSL-based fermentation broth. FA: fumaric acid; AC: activated carbon.

## 4. Conclusions

The developments described in this paper provide an efficient, simple, and cost-effective process of obtaining polymer-grade fumaric acid from complex raw materials, namely spent sulfite liquor. The developed process is based on simple precipitation and adsorption operations and low-cost chemicals with low environmental burden. Further, the dual use of activated carbon for removing contaminants and for capturing fumaric acid from dilute streams, tuned by adjusting the pH of the streams, proved to be an innovative and highly effective way to obtain the product with the required specifications while maximizing yields. The capability of the produced fumaric acid to be employed as the raw material for polymerization creates an opportunity for the application of this bio-based dicarboxylic acid as a substitute to materials from non-renewable sources, and to the valorization of complex waste streams of industrial origin.

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**Author Contributions:** Diogo Figueira, João Cavalheiro and Bruno Sommer Ferreira conceived and designed the experiments; Diogo Figueira and João Cavalheiro performed the experiments; Diogo Figueira and Bruno Sommer Ferreira analyzed the data; Diogo Figueira, João Cavalheiro and Bruno Sommer Ferreira wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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