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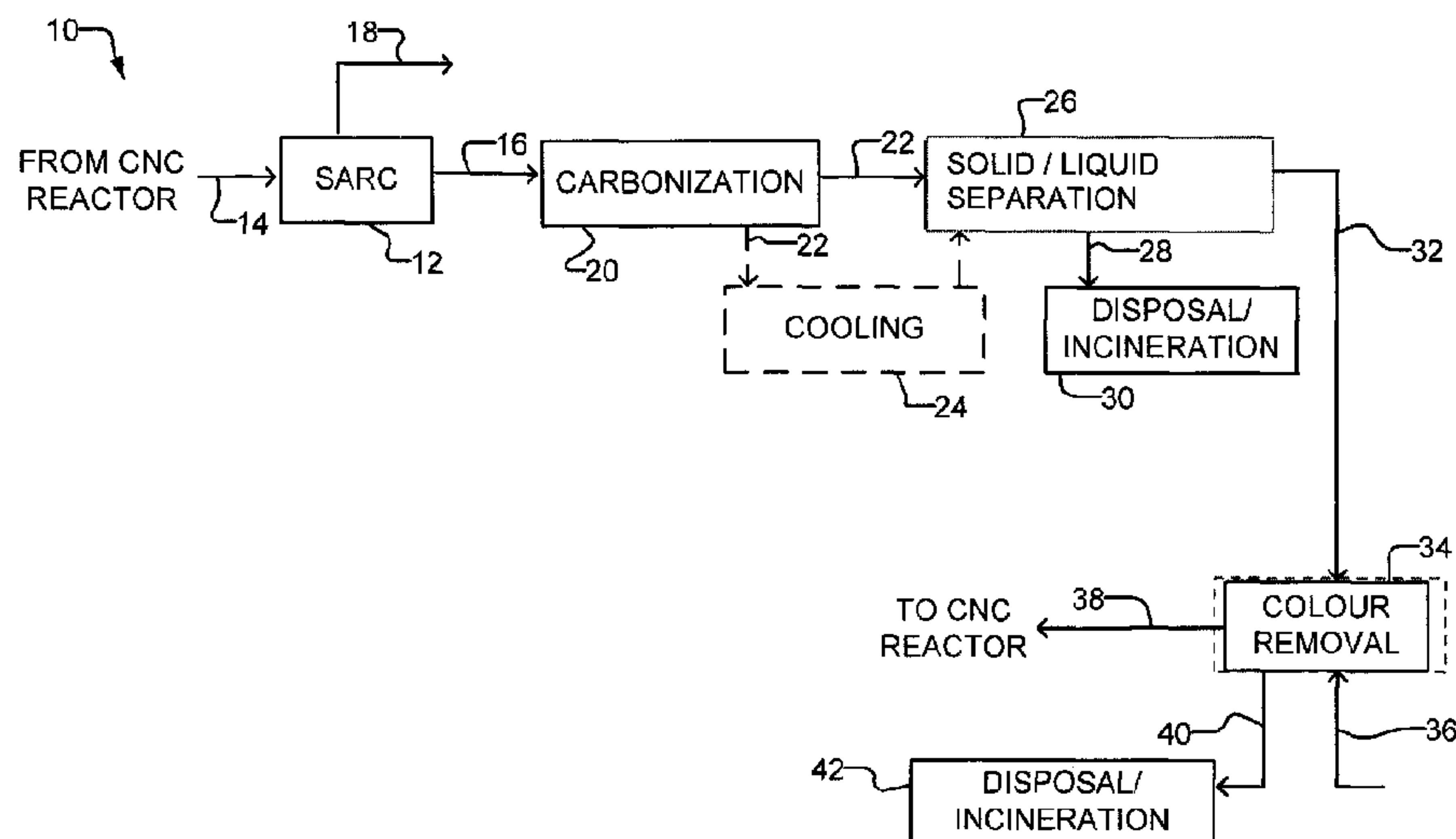
(71) Demandeur/Applicant:  
NORAM ENGINEERING AND CONSTRUCTORS LTD.,  
CA

(72) Inventeurs/Inventors:  
LOCKHART, JAMES M., CA;  
BUCHI, STEVEN D., CA

(74) Agent: OYEN WIGGS GREEN & MUTALA LLP

(54) Titre : RETRAIT D'HYDRATES DE CARBONE DISSOUTS D'UNE SOLUTION D'ACIDE SULFURIQUE

(54) Title: REMOVAL OF DISSOLVED CARBOHYDRATES FROM A SULFURIC ACID SOLUTION



(57) Abrégé/Abstract:

A method of removing dissolved carbohydrates from a sulfuric acid solution, in particular a sulfuric acid solution with dissolved sugars from a process for making cellulose nano crystallites (CNC), so that the acid solution can be recycled for use in the CNC process or other applications. The sulfuric acid solution is held at an elevated temperature to carbonize the carbohydrates and form a carbonized solid, and the carbonized solid is then removed from the sulfuric acid solution. Optionally, the method includes the steps of increasing the concentration of the sulfuric acid solution, and exposing the purified sulfuric acid solution to a colour removal treatment.

**Abstract**

A method of removing dissolved carbohydrates from a sulfuric acid solution, in particular a sulfuric acid solution with dissolved sugars from a process for making cellulose nano crystallites (CNC), so that the acid solution can be recycled for use in the CNC process or other applications. The sulfuric acid solution is held at an elevated temperature to carbonize the carbohydrates and form a carbonized solid, and the carbonized solid is then removed from the sulfuric acid solution. Optionally, the method includes the steps of increasing the concentration of the sulfuric acid solution, and exposing the purified sulfuric acid solution to a colour removal treatment.

## Removal of Dissolved Carbohydrates from a Sulfuric Acid Solution

### Field of the Invention

This invention pertains to processes for removing dissolved carbohydrates from sulfuric acid solutions.

### Background of the Invention

Sulfuric acid is used in many industrial applications, including the production of cellulose nano crystallites (CNC). In this process the sulfuric acid becomes diluted but is not consumed to any significant degree. It is desirable to re-concentrate the acid to the original inlet concentration such that the acid can be re-used in the CNC reactor. This is accomplished by feeding the spent acid to a sulfuric acid re-concentrator (SARC) unit.

However, the spent sulfuric acid contains dissolved carbohydrates formed from the hydrolysis of the cellulose. These carbohydrates are mainly sugar monomers and oligomers (primarily glucose ( $C_6H_{12}O_6$ ), but also others from the residual hemicellulose fraction) and some degradation products such as furfural ( $C_5H_4O_2$ ). These carbohydrates must be substantially removed from the acid for it to be re-used in CNC production and many other applications.

Additionally, in the presence of a strong acid, such as sulfuric acid, residual carbohydrates may also undergo a number of complex dehydration and polymerization reactions to form larger species, which may precipitate and are often coloured.

The dehydration of the sugar molecules is known as carbonization and is dependent on the temperature for a given sulfuric acid concentration. In general, as the acid concentration increases, the temperature required for the reaction to occur decreases. Carbonization leads to darkening of the product acid, causing product colour and quality issues for the CNC. If this happens within the sulfuric acid re-concentrator unit it can also cause undesirable fouling of heat exchanger surface area and foaming.

There are several conventional and commercially available techniques for the separation of neutral sugars from acids. These include nano-filtration, ion exchange and



chromatography. However, these involve disadvantages such as high capital cost and production of a concentrated sugar stream, still containing significant levels of acid, which must be dealt with at considerable additional cost. These conventional techniques also often involve dilution of the acid and/or sugar stream, requiring later removal of the water through additional evaporation.

### **Summary of the Invention**

The invention provides an improved method of removing dissolved carbohydrates from a sulfuric acid solution, in particular a sulfuric acid solution with dissolved sugars from a process for making CNC, so that the acid solution can be recycled for use in the CNC process or other applications.

According to one aspect of the invention, there is provided a method of removing dissolved carbohydrates from a sulfuric acid solution, comprising the steps of holding the sulfuric acid solution at an elevated temperature to carbonize the carbohydrates and form a carbonized solid, and removing the carbonized solid from the sulfuric acid solution.

According to a further aspect of the invention, there is provided a method of removing dissolved carbohydrates from a sulfuric acid solution, comprising the steps of increasing the concentration of the sulfuric acid solution, holding the sulfuric acid solution at an elevated temperature to carbonize the carbohydrates and form a carbonized solid, removing the carbonized solid from the sulfuric acid solution to produce a purified sulfuric acid solution, and exposing the purified sulfuric acid solution to a colour removal treatment to remove colour from the sulfuric acid solution.

Further aspects of the invention and features of specific embodiments are described below.

### **Brief Description of the Drawings**

Figure 1 is a schematic block diagram of the purification process according to one embodiment of the invention.

Figure 2 is a graph showing the absorbance spectra of sulfuric acid solutions treated with various colour removal materials.

Figure 3 is a graph showing the absorbance spectra of a sulfuric acid solution treated with colour removal material in accordance with Example 3.

## 5 Detailed Description

In one embodiment, the process of the invention starts with a sulfuric acid solution with dissolved sugars, resulting from a process for the production of CNC. The acid solution has become diluted during the CNC process and accordingly has a concentration lower than that of fresh acid solution for use in the CNC process. For example, the acid solution may  
10 have become diluted from about 60-65 wt.% down to about 15-25 wt.%.

### *Acid Concentration*

As an optional step in the process, the sulfuric acid solution with dissolved sugars can be concentrated prior to further treatment steps, to increase the concentration of the solution to  
15 a concentration suitable for use in the process for producing CNC. This is done by evaporation, using a single effect or multi-effect evaporator.

To avoid undesirable carbonization in the concentrator itself we have found that it is preferable to minimize the coincident temperature/concentration as well as the exposure  
20 time. This can be done in a single effect operating at deep vacuum. However, at higher capacities it is often desirable to improve steam economy, so a multiple-effect evaporator can be configured which avoids the problematic higher concentration and temperature combinations by using either a fully, or partially, feed and steam forward arrangement. The sulfuric acid solution and steam are fed into the first vaporization unit, and the sulfuric acid  
25 solution is processed through the series of vaporization units to concentrate the sulfuric acid solution by evaporation of water. Undesirable carbonization is avoided by reducing the pressure and thus evaporation temperature of the more concentrated acid.

### *Carbonization*

30 Although carbonization is undesirable during evaporation we have found that it can be used positively at the desired point in the carbohydrate-removal process. The sulfuric acid solution with dissolved sugars (whether re-concentrated or not), is thermally treated, i.e., heated and held at the elevated temperature for a residence time sufficient to carbonize the



bulk of the sugars to create a carbonized solid material. Direct steam injection, concentrated product recycle and/or careful design of the heating system is required to avoid fouling of exchanger surfaces due to carbonization.

- 5 Greater removal of sugars during the carbonization step occurs at higher acid concentrations and at higher temperatures. The acid concentration may be greater than 50 wt.%, and preferably in the range of 55-65 wt.%, for best integration back into the CNC process. The temperature to which the acid solution is heated may be at least 80°C, alternatively at least 100°C, or at least 120°C, or at least 150°C. The residence time during  
10 which the acid solution is held at an elevated temperature is at least 1 hour, alternatively at least 4 hours, alternatively at least 5 hours, or at least 6 hours.

The carbonization step can be done before, during or after the optional concentration step depending on the starting concentration. The carbonized solid material is then removed by  
15 conventional solid/liquid separation techniques such as filtration, centrifugation or settling, leaving a purified acid solution.

The carbonized solids may be washed and safely disposed of or burned to recover energy and thus offset the operating costs of the process.

20

#### *Colour Removal*

Residual coloured compounds may have an effect on the whiteness of the CNC product when the purified acid solution is recycled for use in the CNC process, and accordingly their removal from the acid solution is often desirable. As an optional step following thermal  
25 treatment and filtration, the purified acid solution is treated with a colour removal method, such as granular activated carbon, resin and/or nano-filtration, etc., to remove colour compounds formed in the carbonization process.

In some embodiments of the invention, the process also includes the application of one or  
30 more conventional techniques for the separation of neutral sugars from acids. These include nano-filtration, ion exchange and chromatography. Nano-filtration would typically be employed at the incoming, dilute, acid concentration while ion exchange and chromatography would typically be employed after some acid concentration; however, all

three would normally require further acid concentration afterwards due to low incoming concentration and/or additional dilution that occurs during purification. The carbonization technique could also be used as a pre-treatment method upstream of any of these techniques to provide bulk sugar removal.

5

### *The Embodiment of Figure 1*

An embodiment of the process for the removal of dissolved sugars is schematically illustrated in Figure 1, in which the process includes the steps of acid concentration, carbonization and colour removal. In the process 10, a sulfuric acid re-concentrator 12 has a sulfuric acid feed 14, received from a CNC process. The output from the sulfuric acid re-concentrator 12 is a concentrated acid stream 16 and a condensate (water) stream 18. The concentrated acid stream 16 is heated and fed to carbonization unit 20, in which the acid is held for a suitable residence time at elevated temperature. The carbonized acid stream 22 is then optionally cooled 24 (as indicated by broken lines in Figure 1), and subsequently clarified by removal of the solids filtered in the solid/liquid separation unit 26. The isolated carbonized solids 28 from the solid/liquid separation unit 26 are sent for disposal or incineration 30. The suspended solids-free acid product stream 32 from the solid/liquid separation unit 26 is, optionally, pumped to a colour removal unit 34. The colour removal unit 34 comprises, for example, activated carbon beds, fed by an activated carbon stream 36. The colour removal unit 34 produces a purified acid stream 38 which is recycled to the CNC reactor or other application. Spent activated carbon 40 from the colour removal unit 34 is sent for disposal or incineration 42, or alternatively, is regenerated.

In an exemplary embodiment of the process 10, the acid feed 14 is centrifuge centrate comprising 25.6 wt.% sulfuric acid and 2 wt.% sugars. The concentrated acid stream 16 from the sulfuric acid reconcentrator 12 comprises 54.9 wt.% sulfuric acid and 4.3 wt.% sugars. The carbonization unit 20 holds the heated acid at about 150°C for 5 hours. The filtrate stream 32 from the filtration unit 26 comprises 56.2 wt.% sulfuric acid and 2.0 wt.% sugars. The carbonized solids 28 comprise 20 wt.% acid and have a dry LHV of 8360 BTU/lb. The colour removal unit 34 operates at 45°C. The purified acid stream 38 comprises 56.6 wt.% sulfuric acid and 1.3 wt.% sugars. The spent activated carbon stream 40 comprises 20 wt.% acid.



## Examples

### Example 1

Samples of sulfuric acid solution with dissolved sugars from a CNC process were subjected to thermal treatment to carbonize the sugars. The tests were conducted at a range of acid concentrations from 10.6 to 60.4 wt.%, temperatures from 80 to 160°C, and durations from 0.5 to 18 hours.

#### Tests 1-7

A glass pressure tube was charged with the feed solution and immersed in a temperature-controlled oil bath. The solutions were heated to the target temperatures and incubated until blackening occurred, or for a desired length of time. For the initial tests the temperature was maintained for 1 hour incubations at increasingly higher target temperatures until darkening of the feed was observed. Later tests were held for longer incubation periods. The material was then cooled to ambient temperature and filtered through a 1.5 µm pore-size glass microfiber filter to remove dark solids. The solids were rinsed with deionized (DI) water and dried in a 105°C oven.

#### Test 8

The feed solution was heated in three segments of 6 hours. After each heating period the sample was cooled, filtered, and a sample of the filtrate was extracted to be tested for carbon oxygen demand (COD). A clean pressure tube was then charged with the remaining filtrate and heating was continued.

#### Test 9

The concentrated acid was heated in a 1L round bottom flask using a temperature controlled oil bath. The flask was equipped with a condenser and the system was open to atmosphere. The acid was heated to 150°C for 6 hours one day and 7 hours the following day. Black solids were removed by filtration using a 1.5 µm pore-size glass-fibre filter. The conditions and results of the nine tests are summarized in Table 1.



Table 1

Test #	H <sub>2</sub> SO <sub>4</sub> (wt.%)	Carbonization Conditions		COD removed (%)
		Temperature (°C)	Duration (hrs)	
1	10.6	100	1	4.9%
		120	1	
		150	1	
2	28.4	80	1	11.9%
		120	1	
3	20.8	80	0.5	14.6%
		120	1	
		150	1	
4	52.0	80	1	26.6%
		100	2	
5	55.3	120	4	51.1%
6	55.3	120	5	60.6%
7	60.4	150	12	72.7%
8.1	20.8	160	6	35.2%
8.2		160	6	-16.4%
8.3		160	6	2.2%
8 total	20.8	160	18	26.3%
9	57.23	150	13	54.6% (69.4% after activated carbon treatment)

The tests show that greater removal of sugars (as COD) occurred at higher acid concentrations and temperatures. COD removal was greatly increased at acid concentrations above 50 wt.%, as seen in Tests 4 & 5.

COD was still being removed after 4 hours of heating, as shown by Tests 5 and 6. The bulk COD was removed in the first six hours of heating, as shown in Test 8, whereas further heating (Tests 8.2 and 8.3) showed no appreciable additional removal.

### Example 2

Tests were conducted using filtrate from Test 9 of Example 1 to determine the effectiveness of colour removal of several commercially available absorption media, including granular activated carbon (GAC), ion exchange resin and adsorbent resins. The results are set out in Table 2.

Table 2

Sample	Material	Dosage (g/mL)	Dosage (wt%)	Colour of Treated acid
1	HYDRODARCO 3000	40.2	2.73	Yellow/brown
2	SEPABEADS SP850	40.8	2.79	Dark brown
3	SEPABEADS SP825L	40.1	2.75	Light brown
4	DIAION HP20	39.7	2.70	Light brown
5	DIAION HP2MGL	39.9	2.75	Dark brown
6	DIAION HP21	40.3	2.75	Brown

- 10 HYDRODARCO is a trademark of Cabot Corporation. SEPABEADS and DIAION are trademarks of Sigma-Aldrich Co.

15 The absorbance spectra of samples 1 to 6 are shown in Figure 2. It was concluded that the Cabot HYDRODARCO 3000 granulated activated carbon was most effective at removing the colour from the concentrated acid.

20 Activated carbon loading of about 40 g/L is higher than what would be expected in an commercial process. This is due to the fact that the lab testing was performed as a single stirred batch, whereas a continuous commercial process would be carried out in a multi-stage packed column. The staging benefit of using a column would provide at least an order of magnitude reduction in required loading.

### Example 3

A 498.5g batch of hydrolysate containing 57 wt.% H<sub>2</sub>SO<sub>4</sub> was prepared, heated to

160°C and held at temperature for a total of 13 hours. COD was reduced by 54.6% after filtration. This material was subjected to two stages of colour removal using Hydrodarco 3000 as indicated in Table 3 below, which reduced the colour of the final material to a pale yellow with an absorbance spectrum as shown in Figure 3.

5

Table 3

	<b>Filtrate Mass (g)</b>	<b>HD3000 Mass added (g)</b>	<b>Dosage (g/L)</b>	<b>Dosage (wt%)</b>
Step 1	498.52	17.25	50.62	3.46
Step 2	From 1 above	15.41	45.22	3.09
Final / Total	428.43	32.66	95.84	6.55

The colour removal step further reduced the COD (from 54.6% to 69.4% COD removed).

10

#### Example 4

Samples of the dried carbonized solids from Example 1 were subjected to calorific testing to determine their heating value. The dry Higher and Lower heating values were determined to be 8680 and 8360 BTU/lb respectively.

15

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the scope thereof.



**CLAIMS:**

1. A method of removing dissolved carbohydrates from a sulfuric acid solution, comprising the steps of:
  - (a) holding the sulfuric acid solution at an elevated temperature to carbonize the carbohydrates and form a carbonized solid; and
  - (b) removing the carbonized solid from the sulfuric acid solution.
2. A method according to claim 1, where the sulfuric acid solution is received from a CNC production process.
3. A method according to claim 1 or 2, further comprising increasing the concentration of the sulfuric acid solution before step (a).
4. A method according to any one of claims 1-3, wherein the concentration of the sulfuric acid solution in step (a) is at least 50 wt.%.
5. A method according to any one of claims 1-4, wherein the concentration of the sulfuric acid solution in step (a) is in the range of 55 to 65 wt.%.
6. A method according to any one of claims 1-5, wherein the elevated temperature is a temperature of at least 80°C.
7. A method according to any one of claims 1-5, wherein the elevated temperature is a temperature of at least 100°C.
8. A method according to any one of claims 1-5, wherein the elevated temperature is a temperature of at least 120°C.
9. A method according to any one of claims 1-5, wherein the elevated temperature is a temperature of at least 150°C.

10. A method according to any one of claims 1-9, wherein step (a) is done for a residence time of at least 1 hour.
11. A method according to any one of claims 1-9, wherein step (a) is done for a residence time of at least 4 hours.
12. A method according to any one of claims 1-9, wherein step (a) is done for a residence time of at least 5 hours.
13. A method according to any one of claims 1-9, wherein step (a) is done for a residence time of at least 6 hours.
14. A method according to any one of claims 1-13, further comprising exposing the sulfuric acid solution to a colour removal treatment after step (b) to remove colour from the sulfuric acid solution.
15. A method according to claim 14, wherein the colour removal treatment comprises activated carbon treatment.
16. A method according to claim 14, wherein the colour removal treatment comprises nano-filtration.
17. A method according to claim 14, wherein the colour removal treatment comprises treatment with a resin.
18. A method according to any one of claims 1-17, wherein step (b) is done by filtration.
19. A method according to any one of claims 1-17, wherein step (b) is done by centrifugation.
20. A method according to any one of claims 1-19, wherein the carbohydrates comprise sugars.

21. A method according to claim 3, wherein increasing the concentration of the sulfuric acid solution is done by:

- (i) providing a forward feed multiple-effect evaporator;
- (ii) feeding the sulfuric acid solution and steam into a first vaporization unit of the multiple-effect evaporator; and
- (iii) processing the sulfuric acid solution through the other vaporization units of the multiple-effect evaporator to concentrate the sulfuric acid solution by evaporation of water therefrom.

22. A method of removing dissolved sugars from a sulfuric acid solution from a CNC production process, comprising the steps of:

- (a) increasing the concentration of the sulfuric acid solution;
- (b) holding the sulfuric acid solution at an elevated temperature to carbonize the carbohydrates and form a carbonized solid;
- (c) removing the carbonized solid from the sulfuric acid solution to produce a purified sulfuric acid solution; and
- (d) exposing the purified sulfuric acid solution to a colour removal treatment to remove colour therefrom.

23. A method according to claim 22, wherein the elevated temperature is a temperature of at least 80°C.

24. A method according to claim 22, wherein the elevated temperature is a temperature of at least 100°C.

25. A method according to claim 22, wherein the elevated temperature is a temperature of at least 120°C.

26. A method according to claim 22, wherein the elevated temperature is a temperature of at least 150°C.

27. A method according to any one of claims 22-26, wherein step (a) is done for a residence time of at least 1 hour.



28. A method according to any one of claims 22-26, wherein step (a) is done for a residence time of at least 4 hours.
29. A method according to any one of claims 22-26, wherein step (a) is done for a residence time of at least 5 hours.
30. A method according to any one of claims 22-26, wherein step (a) is done for a residence time of at least 6 hours.
31. An apparatus for removing dissolved sugars from a sulfuric acid solution, comprising:
- (a) means for thermal treatment of the sulfuric acid solution, whereby the sulfuric acid solution is heated and held at an elevated temperature for a residence time to form a carbonized solid; and
  - (b) means for removing the carbonized solid from the sulfuric acid solution.
32. An apparatus according to claim 31, wherein the means for removing the carbonized solid comprises one of a filter and a centrifuge.
33. An apparatus according to claim 31 or 32, further comprising means for increasing the concentration of the sulfuric acid solution.
34. An apparatus according to claim 33, wherein the means for increasing the concentration of the sulfuric acid solution comprises a forward feed multiple-effect evaporator.
35. An apparatus according to any one of claims 31-34, further comprising means for removing color from the sulfuric acid solution after removal of the carbonized solid.
36. An apparatus according to claim 35, wherein the means for removing color comprises one of activated carbon, a filter and a resin.

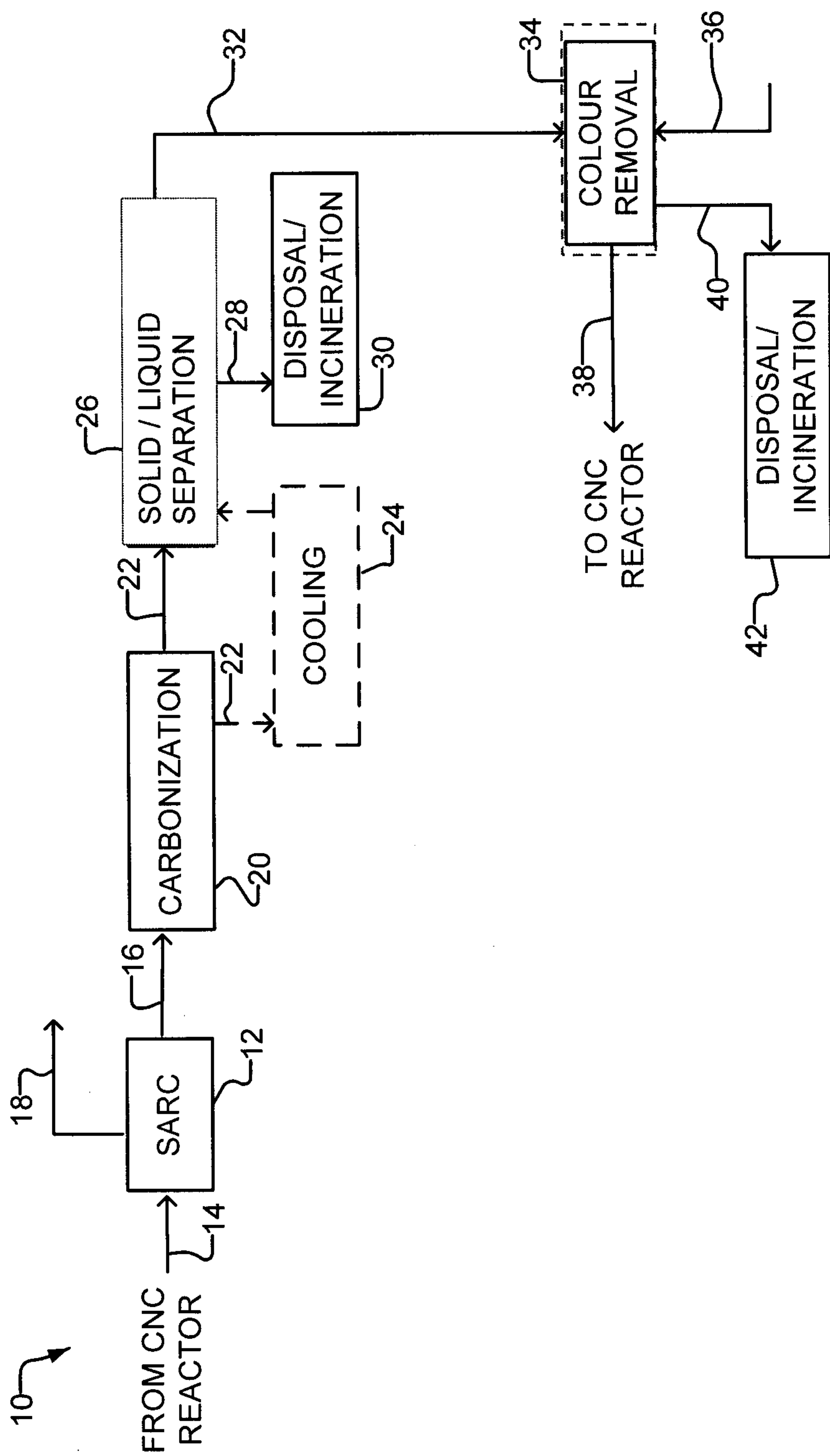


FIG. 1

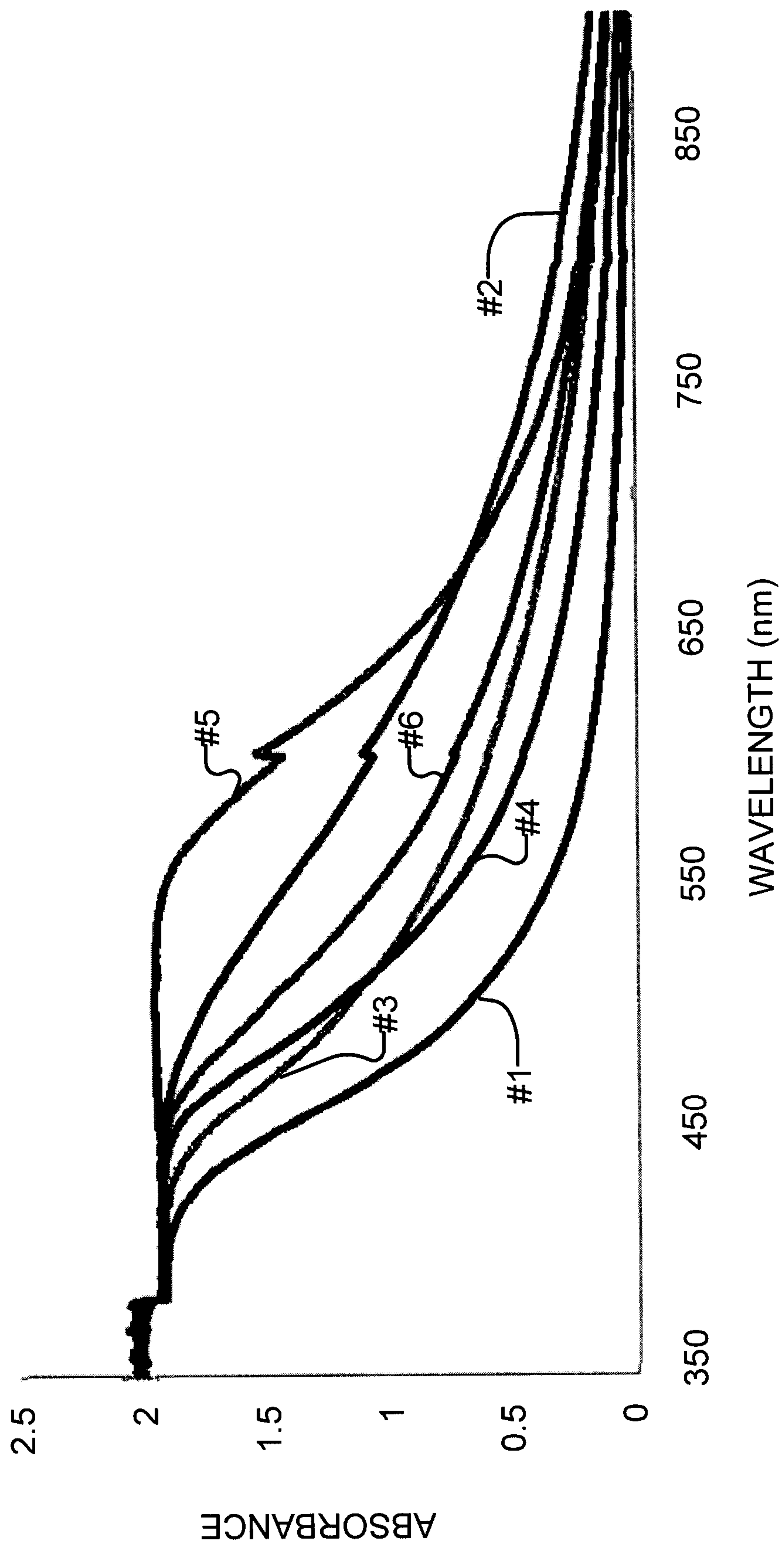


FIG. 2



# Absorbance spectra of final treated acid

## Test 9

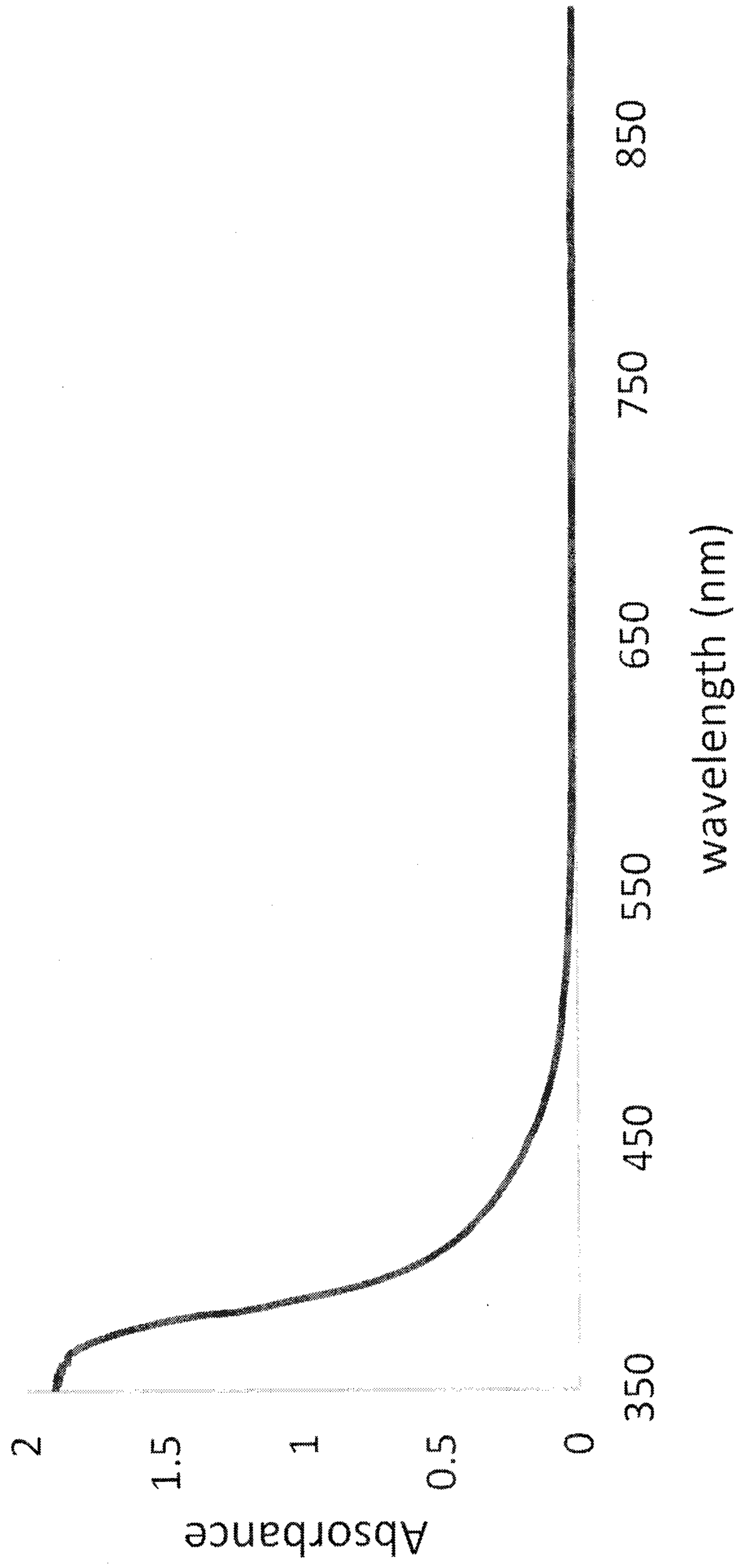


FIG. 3

