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(54) Title: PROCESS FOR THE TREATMENT OF A WASTE WATER

(57) Abstract: Process for the treatment of a waste water feed containing organic contaminants comprising the steps of (a) subjecting the waste water feed to a freeze-concentration treatment thereby producing at least a brine stream and a water stream having a reduced content of organic contaminants; and (b) subjecting this water stream to a reverse osmosis treatment thereby producing a purified water stream as the permeate and a relatively contaminated water stream as retentate.

PROCESS FOR THE TREATMENT OF A WASTE WATER

The present invention relates to a process for the treatment of a waste water, in particular waste water from industrial processes containing at least hydrocarbons and salts.

The treatment or purification of waste water originating from industrial processes and containing at least hydrocarbons and salts (organic and/or inorganic) normally is a relatively expensive procedure. Environmental legislation nowadays puts stringent demands on the purification of waste water streams from industrial processes, particularly when the purified waste water is to be released into the environment. Accordingly, the choice of a purification method for industrial waste water is bound by practical, environmental and economic considerations.

One industrial process, wherein a relatively large amount of waste water is produced is the styrene monomer/propylene oxide (SM/PO) production process. In general such SM/PO process involves the steps of:
(i) reacting ethylbenzene with oxygen or air to form ethylbenzene hydroperoxide, (ii) reacting the ethylbenzene hydroperoxide thus obtained with propene in the presence of an epoxidation catalyst to yield propylene oxide and 1-phenyl ethanol, and
(iii) converting the 1-phenyl ethanol into styrene by dehydration using a suitable dehydration catalyst. In the last step water is produced. In addition to this reaction water organic by-products such as aliphatic and aromatic hydrocarbons, aldehydes, ketones, alcohols, phenols and organic acids are produced in the course of the entire process. The by-products are separated from the main

products with the aid of clean water and the organic acids are neutralized using a basic aqueous solution, such as an aqueous sodium (bi)carbonate and/or sodium hydroxide solution. Furthermore, additional water is introduced with the air in the step (i) and as steam in step (iii) of the above process.

The waste water from an SM/PO production plant typically contains a total of from 1.0 to 3.5 wt% of non-salt organic compounds and from 3.0 to 6.0 wt% of organic salts. It may further contain up to 2.0 wt% of sodium carbonate and sodium bicarbonate and/or traces of sodium hydroxide, depending on the basic solution used in the neutralization of organic acids.

The input of clean water to an SM/PO plant can be up to tens of thousands kg per hour, while the output of waste water is normally about 50% higher than the input of clean water. The waste water cannot be discharged without additional purification treatment. As has already been indicated above, however, the choice of a suitable purification treatment is limited due to all sorts of practical, environmental and economic considerations.

Another well known method for producing propylene oxide, which also produces substantial amounts of waste water, is the co-production of propylene oxide and methyl tert-butyl ether (MTBE) starting from isobutane and propene. This process is well known in the art and involves similar reaction steps as the SM/PO process described above. In the epoxidation step tert-butyl hydroperoxide is reacted with propene forming propylene oxide and tert-butanol. Tert-butanol is subsequently etherified with methanol into MTBE, which is used as an additive in motor fuels.

Other examples of industrial processes producing large waste water streams are the production of KA oil (a mixture of cyclohexanone and cyclohexylalcohol) by oxidation of cyclohexane and the production of phenol and acetone by oxidising cumene.

In GB-A-2,252,052 further information is given about prior art methods for treating waste water and about typical compositions of SM/PO waste water streams. The purification process disclosed in GB-A-2,252,052 involves freeze-concentration combined with salts-removal, whereby the waste water is separated into an at least two-fold concentrated waste product, salt crystals and a purified melt water product.

The method disclosed in GB-A-2,252,052, however, still leaves room for improvement. More specifically, it has been found that the melt water produced in the freeze-concentration process may still contain a too high an amount of organics, in particular in terms of chemical oxygen demand (COD) and in terms of specific species, especially phenol. Accordingly, the present invention aims to provide a method for further reducing the organics level in waste water streams produced in production processes for propylene oxide, but also applicable to waste water streams of a much wider range of industrial processes.

Accordingly, the present invention relates to a process for the treatment of a waste water feed containing organic contaminants, which process comprises the steps of

(a) subjecting the waste water feed to a freeze-concentration treatment thereby producing at least a brine stream (i.e. a concentrated waste product) and a water stream having a reduced content of organic contaminants; and

(b) subjecting this water stream to a reverse osmosis treatment thereby producing a purified water stream as the permeate and a relatively contaminated water stream as retentate.

The waste water to be treated by the present process should preferably have a chemical oxygen demand of at least 500 mg/l, preferably of at least 1000 mg/l, and a phenol content of at least 10 mg/l. Chemical oxygen demand (COD) is a measure of the oxygen required to oxidise all of the oxidisable materials in the sample. It is a good measure of how polluted a water sample is, because many species can be present in a water sample, each at low levels but in total contributing a significant amount of pollution. COD is determined by automated analysers, which mix a certain amount of an oxidising agent, such as oxygen, and optionally a catalyst to oxidise the compounds present in the sample. The carbon dioxide thus generated is measured, often by infra-red analysers, and reported in units of mg oxygen (O_2) consumed per litre water or in ppm O_2. Typical waste water discharge specifications are 100 mg/l COD, as this is considered to be close to the level that is naturally present in water from decaying organic material.

Step (a) of the process according to the present invention is the freeze concentration process as described in GB-A-2,252,052. This process typically produces at least a brine stream and a water stream having a reduced content of organic contaminants. Salt crystals may also be produced depending on the salt concentration of the waste water feed and on the ratio of purified water and brine produced in the freeze concentration unit. Accordingly, step (a) suitably comprises the steps of:

(a1) cooling the waste water feed to form a freeze concentrate comprising the brine stream, possibly salt crystals and water having a reduced content of organic contaminants in the form of ice crystals;

(a2) separating the ice crystals from the freeze concentrate and converting the ice crystals into the water stream to be further treated in step (b); and

(a3) removing the salt crystals, if present, from the remaining freeze concentrate yielding the brine stream and a salts stream.

Step (a1) will normally involve the formation of ice crystals by crystallisation upon cooling of the waste water. Such crystallisation is suitably performed in two separate units: a nucleation unit followed by a growth unit. In the nucleation unit the waste water is cooled until small ice crystals are formed. Typically, the temperature in the nucleation unit is from -5 to -20 °C. The slurry containing the small ice crystals is then passed to the growth unit, wherein the temperature is higher than the melting temperature of small ice crystals but lower than the melting temperature of larger ice crystals. As a result, small ice crystals will melt and larger ice crystals will grow in the growth unit. Typical temperatures in the growth unit are from -3 to -18 °C. The size of the ice crystals will normally range from 0.2 mm to 0.8 mm.

In step (a2) the ice crystals are separated from the freeze concentrate once their size and quantity is sufficiently large. Preferably, such separation is achieved by means of filtration followed by washing the crystals in a packed bed wash column, but other separation techniques like centrifuging of the slurry may be applied as well. In such packed bed wash column the ice crystals-containing slurry is introduced under pressure and the crystal-free concentrate is filtered off at the lower end of the vertical column. This concentrate is suitably recycled to the waste water feed. The washed ice crystals are removed at the upper end of the wash column and melted to yield the purified water stream. Further details are described in GB-A-2,252,052.

If a sufficiently large amount of salts (mainly organic salts) is present in the waste water, these salts tend to precipitate and crystallize when the waste water is cooled and concentrated in step (a1). The salt crystals thus formed are separated from the ice crystals as described in step (a3) yielding the brine stream and a salts stream. Since the ice crystals are larger and less dense than the salt crystals such separation can be effectively achieved by filtration or centrifugation. The brine and the salt crystals, if any, formed in step (a) are suitably incinerated.

In step (b) of the process according to the present invention the melt water stream from step (a), i.e. the water stream having a reduced content of organic contaminants, is subjected to a reverse osmosis treatment thereby producing a purified water stream as the permeate and a relatively contaminated water stream as retentate (also sometimes referred to as concentrate). Suitably, said melt water stream is passed through a reverse osmosis unit comprising at least one reverse osmosis element in which the actual membrane is arranged.

Reverse osmosis is well known in the art. In general, a reverse osmosis element will comprise a high pressure compartment and a low pressure compartment separated by a reverse osmosis membrane. The water to be purified is normally pumped at a certain feed rate and at a certain pressure into the high pressure compartment. The pressure of the contaminated water entering this compartment should be sufficiently above its osmotic pressure to cause a permeate fraction to flow through the membrane. This permeate fraction is then collected in the low pressure chamber, where it is recovered at a lower pressure than the pressure at which it entered the high pressure compartment. The permeate, which is the purified water, is continuously or periodically withdrawn from said low pressure compartment. The retentate is continuously or periodically withdrawn from the high pressure chamber for further treatment, which may include incineration. Preferably, however, the retentate is entirely or partly recycled to the waste water feed for the freeze concentration unit (i.e. the feed for step (a)). At least part of the retentate can also be re-used as wash water in the process in which the waste water was originally produced.

The entire reverse osmosis treatment carried out in step (b) may involve passing the water to be purified through one or more reverse osmosis elements as described above. Such elements may be arranged in parallel and/or in series. Depending on the size and capacity of the reverse osmosis element and on the amount of water to be treated it is, for instance, possible to use two to ten rows of elements arranged in parallel, whereby each row of elements consists of two to ten elements arranged in series. It will be understood that the number and arrangement of reverse osmosis elements is entirely dependent on the amount of waste water to be treated and the size and capacity of the elements used. The reverse osmosis elements may be preceded by one or more prefilters to remove larger particles (e.g. greater than 10 µm) from the contaminated water feed. A pressure increasing pump may also be installed before the reverse osmosis element(s) to bring the pressure of the water at the required level.

The reverse osmosis treatment is preferably carried out under such conditions that the COD of the permeate is 100 mg/l or less, preferably 50 mg/l or less and more preferably 10 mg/l or less. Operation to achieve levels below 5 mg/l is also possible. Preferred conditions to be applied in the reverse osmosis treatment include a temperature in the range of from 2 to 60 °C, more preferably 5 to 40 °C and most preferably 10 to 30 °C. The pressure of the water feed entering the high pressure compartment should anyhow be sufficiently high to cause a permeate fraction to flow through the membrane into the low pressure compartment in sufficiently high amounts. The pressure of the feed entering the high pressure compartment will normally be less than 60 bar and suitably will be in the range of from 3 to 50 bar, more suitably 5 to 35 bar, most suitably 10 to 30 bar. The pressure at which the permeate leaves the low pressure compartment will normally be at least 1 bar lower than the pressure of the water feed entering the high pressure compartment. This pressure differential suitably ranges from 1 to 30 bar. A maximum pressure differential of 20 bar is even more preferred, while in a very much preferred embodiment the pressure differential is from 2 to 10 bar. The absolute pressure of the permeate leaving the low pressure compartment will normally be between 0.1 and 50 bar, suitably between 0.5 and 35 bar, while pressures from 1 to 30 bar are preferred. Very good results have been achieved at pressures of 5 to 25 bar.

The actual reverse osmosis unit used in carrying out the method of the present invention may be of usual and known design and construction. The membrane used may be any reverse osmosis membrane known to be useful in treating contaminated water. One type of membranes that has been found to be particularly suitable are the high rejection membranes, which are for instance used for desalination of seawater.

As has been indicated above, the process of the present invention is particularly useful for treating a waste water feed originating from a process for the production of propylene oxide via the co-oxidation of isobutane or ethylbenzene, i.e. a process for the co-production of respectively tert-butyl alcohol (usually etherified into methyl tert-butyl ether) or styrene on the one hand and propylene oxide on the other hand. The waste water treatment according to the present invention is also very useful for waste water streams produced in processes like the production of KA oil (a mixture of cyclohexanone and cyclohexylalcohol) by oxidation of cyclohexane and the production of phenol and acetone by oxidising cumene. These oxidation processes are well known in the art and both produce large water streams contaminated with organic acids.

The present invention is illustrated by the following examples without limiting the scope of the invention to these specific embodiments.

Example

Waste water from a commercial SM/PO process was treated in a freeze concentration process as described in GB-A-2,252,052 and as outlined above in steps (a1) through (a3). The purified water was recovered in the form of ice crystals. These ice crystals were melted and passed into a reverse osmosis unit at a temperature of 15 °C.

The reverse osmosis unit consisted of a prefilter for removing particles having a diameter above 10 μm from the water feed, followed by a pump to increase the pressure of the water feed (to 23 bar) and after the pump three reverse osmosis elements arranged in parallel. The membrane used in the reverse osmosis units was the SWHR 30 membrane ex DOW FilmTec. Each membrane had a surface of 7.5 m^2 and was arranged in the reverse osmosis element in a spirally wound fashion.

The water was fed to the reverse osmosis unit at a flow rate of 1.2 m^3 per hour. The flux through each membrane amounted 27 litre per m^2 of membrane per hour. The pressure differential across the membrane in each reverse osmosis element was 3 bar. From each reverse osmosis element 200 litres/hour of permeate were recovered.

The experiment was run for five subsequent days in a once-through mode, i.e. without any recycle of retentate.

Table 1 indicates the COD of the original waste water, of the purified water after freeze concentration and of the further purified water after reverse osmosis. Also indicated are the concentrations of sodium, ethylbenzene (EB) and phenol of the purified water from the freeze concentration unit (i.e. the feed to the reverse osmosis unit) and of the permeate obtained after the reverse osmosis treatment. All values given are average values determined over five days of measurements.

Table 1 Waste water treatment

	Waste water	after freeze concentration	after reverse osmosis
COD (mg/l)	137	15.8	2.5
Na^+ (mg/l)	17	9.1	0.47
EB (µg/l)	6,000	81	9
phenol (µg/l)	10,000	8	<5

From Table 1 it is clear that the reverse osmosis treatment significantly reduces COD and phenol content of the purified water from the freeze concentration unit and hence further increases the quality of the purified water.

CLAIMS

1. Process for the treatment of a waste water feed containing organic contaminants comprising the steps of
(a) subjecting the waste water feed to a freeze-concentration treatment thereby producing at least a brine stream and a water stream having a reduced content of organic contaminants; and
(b) subjecting this water stream to a reverse osmosis treatment thereby producing a purified water stream as the permeate and a relatively contaminated water stream as retentate.

2. Process as claimed in claim 1, wherein the waste water feed has a chemical oxygen demand of at least 500 mg/l, preferably of at least 1000 mg/l, and a phenol content of at least 10 mg/l.

3. Process as claimed in claims 1 or 2, wherein the freeze concentration treatment comprises the steps of:
(a1) cooling the waste water feed to form a freeze concentrate comprising the brine stream, possibly salt crystals and water having a reduced content of organic contaminants in the form of ice crystals;
(a2) separating the ice crystals from the freeze concentrate and converting the ice crystals into the water stream to be further treated in step (b); and
(a3) removing the salt crystals, if present, from the remaining freeze concentrate yielding the brine stream and a salts stream.

4. Process as claimed in any one of claims 1-3, wherein the brine stream formed in step (a) is incinerated.

5. Process as claimed in any one of claims 1-4, wherein in step (b) the water stream having a reduced content of

organic contaminants is passed through a reverse osmosis unit comprising at least one reverse osmosis membrane.

6. Process as claimed in claim 5, wherein the reverse osmosis treatment is carried out under such conditions that the chemical oxygen demand of the permeate is 100 mg/l or less, preferably 50 mg/l or less and more preferably 10 mg/l or less.

7. Process as claimed in claim 6, wherein the reverse osmosis is carried out at a temperature in the range of from 5 to 60 °C.

8. Process as claimed in any one of claims 1-7, wherein the retentate produced in step (b) is at least partly recycled to the waste water feed for the freeze concentration treatment.

9. Process as claimed in any one of claims 1-8, wherein the retentate produced in step (b) is at least partly re-used as wash water in the process in which the waste water was originally produced.

10. Process as claimed in any one of claims 1-9, wherein the waste water feed originates from a process for preparing propylene oxide via the co-oxidation of isobutane or ethylbenzene.

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/EP 00/06037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/22 C02F1/44 C02F9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F B01D C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, PAJ, EPO-Internal, COMPENDEX, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A		8,9

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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