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(54) Titre : TRAITEMENT DE FLUX DE DECHETS D'ALDEHYDES AQUEUX
(54) Title: TREATMENT OF AQUEOUS ALDEHYDE WASTE STREAMS

(57) Abrégé/Abstract:

A process for the reduction of the concentration of aldehyde(s) and/or ketone(s) in an aqueous waste stream comprises the steps of treating an aqueous waste stream with an effective amount of an organic polyamine base. In addition, a process of making a polyester or polyol comprises treating the aldehyde(s) and/or ketone(s) with organic polyamine base compounds to remove at least 50 % of the aldehyde(s) and/or ketone(s) from the aqueous waste stream. Further, a process of making poly(trimethylene dicarboxylate) comprising reacting 1,3-propanediol with at least one dicarboxylic acid or lower dialkyl esters thereof comprises treating the aqueous waste stream using a nitrogen-containing base selected from the group consisting of organic polyamines and inorganic ammonium compounds.

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(54) Title: TREATMENT OF AQUEOUS ALDEHYDE WASTE STREAMS

(57) **Abstract:** A process for the reduction of the concentration of aldehyde(s) and/or ketone(s) in an aqueous waste stream comprises the steps of treating an aqueous waste stream with an effective amount of an organic polyamine base. In addition, a process of making a polyester or polyol comprises treating the aldehyde(s) and/or ketone(s) with organic polyamine base compounds to remove at least 50 % of the aldehyde(s) and/or ketone(s) from the aqueous waste stream. Further, a process of making poly(trimethylene dicarboxylate) comprising reacting 1,3-propanediol with at least one dicarboxylic acid or lower dialkyl esters thereof comprises treating the aqueous waste stream using a nitrogen-containing base selected from the group consisting of organic polyamines and inorganic ammonium compounds.

TITLE

TREATMENT OF AQUEOUS ALDEHYDE WASTE STREAMS

FIELD OF THE INVENTION

This invention concerns a process for the treatment of wastewater streams containing aldehyde(s) and/or ketone(s), in particular, alpha, beta-ethylenically unsaturated aldehydes such as acrolein.

TECHNICAL BACKGROUND OF THE INVENTION

The toxicity of aldehyde(s) and/or ketone(s), especially alpha, beta-ethylenically unsaturated aldehyde(s) and/or ketone(s), to biological waste treatment systems, even in low concentrations, has been recognized by those skilled in the art. A review article on this problem is presented by V. T. Stack, Jr. in Industrial and Engineering Chemistry, Volume 49, No. 5, page 913 (1957). Stack reports that of these compounds, acrolein has the most toxic effect on biological waste treatment processes. Wastewaters containing alpha, beta-ethylenically unsaturated aldehyde(s) and/or ketone(s) must be treated to reduce the concentration of these substances to very low levels before the waste water may be further treated by a biological system. Failure to adequately pretreat the wastewater streams results in the biomass being in danger of being killed or inhibited to a very low level of activity.

Encyclopedia of Polymer Science and Technology (John Wiley & Sons, Inc., 1964), Volume 1, page 173, states that waste acrolein should be disposed of by pouring into dilute sodium bisulfate or sodium hydroxide solutions. Kirk-Othmer Encyclopedia of Chemical Technology (Third Edition, John Wiley & Sons, Inc., 1978), Volume 1, page 290, teaches that sodium bisulfite or dilute aqueous sodium hydroxide addition renders dilute aqueous streams biodegradable.

Treatment of waste streams containing alpha, beta-ethylenically unsaturated aldehyde(s) and/or ketone(s) are known in the art. U.S. Patent No. 3,923,648 discloses a method for the disposal of such wastewaters comprising contacting them with sufficient base to render the pH of the wastewaters alkaline, maintaining the alkaline wastewaters at a temperature of about 25°C to 100°C for at least about 15 minutes and then degrading the wastewater in a biological system containing active biomass. The preferred base is an alkali metal hydroxide. Use of other bases is also disclosed, including alkaline earth hydroxides, alkali metal alkoxides, quaternary ammonium hydroxides, ammonium hydroxide, soluble organic amines such as methylamine, ethylamine, dimethylamine, triethylamine, and the like, and alkanolamines including monoalkanolamines, dialkanolamines, trialkanolamines, N-monoalkylmonoalkanolamines, and N,N-dialkylalkanolamines and the like.

U.S. Patent No. 5,459,229 discloses a process for the preparation of a 1,3-propanediol based polyester in which an aqueous acrolein-containing waste stream is treated with a sufficient quantity of base to increase the pH to above 7.5 for a time effective to lower the acrolein content, followed, optionally, by dilution and biotreatment. The base utilized is preferably an inorganic base, most preferably sodium hydroxide.

JP 01-094994 teaches a method of removing aldehydes from a solution with a basic ion exchange resin. The ion exchange resin is a solid that is contained in vessel (e.g., a tower).

One objective of the present invention is to provide a more efficient and effective treatment to reduce the levels of alpha, beta-ethylenically unsaturated aldehyde(s) and/or ketone(s) in waste water streams.

SUMMARY OF THE INVENTION

According to the invention, a process for the reduction of the concentration of aldehyde(s) and/or ketone(s) in an aqueous waste stream comprises the steps of (a) contacting an aqueous waste stream with an effective amount of a organic polyamine base; and (b) maintaining said contacted waste stream at essentially ambient temperatures for a sufficient length of time to afford at least a 50% reduction in the concentration of said aldehyde(s) and/or ketone(s).

The invention is also directed to a process of making a polyester or polyol, comprising (a) making the polyester or polyol, (b) forming an aqueous waste stream comprising aldehyde(s) and/or ketone(s), and (c) treating the aldehyde(s) and/or ketone(s) with an organic polyamine base compounds to remove at least 50% of the aldehyde(s) and/or ketone(s) from the aqueous waste stream. Preferably, the aldehyde(s) and/or ketone(s) is (are) selected from the group consisting of acrolein, methacrolein (methacrylaldehyde), crotonaldehyde, 2,4-hexadienal, acetaldehyde and methyl vinyl ketone.

The invention is further directed to a process of making poly (trimethylene dicarboxylate) comprising (a) reacting 1,3-propanediol with at least one dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalic acid and isophthalic acid, and lower dialkyl esters thereof, to yield the poly (trimethylene dicarboxylate) and a waste stream comprising acrolein, and (b) treating the aqueous waste stream using a nitrogen-containing base selected from the group consisting of organic polyamines and inorganic ammonium compounds so that at least 50% of the acrolein is removed from the aqueous waste stream. Preferably, the poly (trimethylene dicarboxylate) is poly (trimethylene terephthalate) and the dicarboxylic acid is terephthalic acid. Preferably, the nitrogen-containing base is selected from the organic polyamines. Preferably, the ratio of 1,3-propanediol:dicarboxylic acid is 50:1 to 0.1:1.

The preferred organic polyamines are organic diamines, organic triamines and organic tetramines. Preferred organic diamines include hexamethylene diamine, 2-methyl pentamethylenediamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,5-dimethyl hexamethylene diamine, 2,2-dimethylpentamethylene diamine, 5-methylnonane diamine, dodecamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, 2,2,7,7-tetramethyl octamethylene diamine, meta-xylylidene diamine, paraxylylidene diamine, diaminodicyclohexyl methane, C_2-C_{16} aliphatic diamines optionally substituted with one or more alkyl groups, and N-alkyl, and N'N-dialky derivatives thereof. Most preferred is hexamethylenediamine.

Of the ammonium compounds, preferred is ammonium carbonate.

The process further comprises removing the at least 50% of the aldehyde(s) and/or ketone(s) (e.g., acrolein) as an insoluble reaction product with the base.

The waste streams to be treated normally contain 1-10,000 ppm (preferably 1-3,000 ppm) of the aldehyde(s) and/or ketone(s) (e.g., acrolein). Preferably, the treatment is carried out for a sufficient time to remove 80-100% of the aldehyde(s) and/or ketone(s) (e.g., acrolein). Preferably, the treatment time is 1 minute to 1 hour.

The treated waste stream preferably contains 0-500 ppm of the aldehyde(s) and/or ketone(s) (e.g., acrolein).

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a process for treating aqueous "waste water" streams containing aldehyde(s) and/or ketone(s), particularly alpha, beta-ethylenically unsaturated aldehyde(s) and/or ketone(s) which are toxic to biological waste treatment systems, using selected nitrogen containing base compounds to treat said waste waters.

Preferred nitrogen containing base compounds include organic polyamines, defined herein as organic amines comprising two or more amine groups, preferably diamines such as hexamethylene diamine, 2-methyl pentamethylenediamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,5-dimethyl hexamethylene diamine, 2,2-dimethylpentamethylene diamine, 5-methylnonane diamine, dodecamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, 2,2,7,7-tetramethyl octamethylene diamine, meta-xylylidene diamine, paraxylylidene diamine, diaminodicyclohexyl methane, C_2-C_{16} aliphatic diamines which may be substituted with one or more alkyl groups, and N-alkyl, and N'N-dialky derivatives thereof. The most preferred diamine is hexamethylene diamine. Other nitrogen containing bases containing more than 2 amine groups are also useful in the present invention. These include triamines, for example bis hexamethylene triamine, tetramines and other polyamines.

Another preferred class of nitrogen-containing base compounds is inorganic ammonium salt, preferably ammonium carbonate.

A specific advantage that accrues to the use of the process of this invention, particularly when hexamethylene diamine is used to treat acrolein-containing waste streams, is that an insoluble solid reaction product separates from the reaction system. This allows the bulk removal of acrolein and the reaction product and the resulting carbon load from the waste stream before said waste stream is fed to the optional subsequent biological treatment. This process also eliminates the toxicity associated with the acrolein reaction products in waste streams.

The temperature utilized for the treatment is not critical. The application of this process to an industrial waste stream takes place at the existing waste stream temperature, from about 0°C to 65 °C, defined herein as “essentially ambient conditions”. The treatment is usually carried out for a sufficient time to remove at least 50% by weight of the aldehyde(s) and/or ketone(s), preferably about 80-100%, and more preferably about 99-100%. The treatment time is normally up to 1 day, preferably up to 2 hours, more preferably about 1 minute - about 1 hour, and most preferably about 2 - about 30 minutes.

Alpha, beta-unsaturated aldehyde(s) and/or ketone(s) treatable by the process of the present invention include acrolein, methacrolein (methacrylaldehyde), crotonaldehyde, 2,4-hexadienal, acetaldehyde and methyl vinyl ketone. Other aldehydes such as acetaldehyde can also be similarly treated.

The treatment process of the present invention is especially useful for the treatment of waste aqueous streams containing acrolein resulting from the manufacture of 1,3-propanediol and polyesters and polyols derived therefrom, e.g. poly(trimethylene naphthalate). Of these, a preferred application is to waste streams resulting from the manufacture of 1,3-propanediol based polyesters, most specifically to waste streams resulting from the manufacture of poly(trimethylene terephthalate) (3GT).

The ratio of 1,3-propanediol:dicarbboxylic acid is preferably 50:1 to 0.1:1 weight percent, preferably about 5:1 - about 1:1.

The preparation of 3GT polyester resins involves the reaction of excess 1,3-propanediol with terephthalic acid or a lower dialkyl ester of terephthalic acid at elevated temperature. The ratio of 1,3-propanediol:terephthalic acid or a lower dialkyl ester of terephthalic acid is preferably about 50:1 to about 0.1:1 weight percent, more preferably about 5:1 - about 1:1, and most preferably about 3:1. The temperature is up to about 270°C, preferably about 180 - about 270°C. The major toxic by-products of this reaction, acrolein and allyl alcohol, are contained in solution in the distillate. The waste stream from 3GT, normally the ratio of acrolein formed:1,3-propanediol starting material is about 1 - about 10,000 ppm, more preferably about 1 - about 3,000 ppm. Although the amounts of these byproducts are low, it is desirable to further reduce the level of byproducts in the distillate, especially for preparing 3GT polyester from terephthalic acid and excess 1,3-propanediol.

The treated (i.e., after treatment) aqueous waste streams may have about 0 - about 500 ppm, preferably about 0 - about 50 ppm, and most preferably about 0 - 10 ppm, of aldehyde(s) and/or ketone(s) (e.g., acrolein).

The invention is illustrated in the following examples, wherein all percentages are by weight unless otherwise indicated.

EXAMPLES

EXAMPLE 1

Treatment of acrolein with 10% water solution of hexamethylenediamine (HMD)

To a screw cap vial containing 10% of hexamethylenediamine in water solution (mixture of 0.1 g of hexamethylenediamine and 0.9 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table I.

EXAMPLE 2

Treatment of acrolein with 1% water solution of hexamethylenediamine

To a screw cap vial containing 1% of hexamethylenediamine in water solution (mixture of 0.01 g of hexamethylenediamine and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table I.

EXAMPLE 3

Treatment of acrolein with 0.2% water solution of hexamethylenediamine

To a screw cap vial containing 0.2% of hexamethylenediamine in water solution (mixture of 0.002 g of hexamethylenediamine and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table I.

EXAMPLE 4

Treatment of acrolein with 0.076% water solution of hexamethylenediamine

To a screw cap vial containing 0.076% of hexamethylenediamine in water solution (mixture of 0.76 mg of hexamethylenediamine and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table I.

As shown in Table I, the present process is effective to treat acrolein with an aqueous solution of hexamethylenediamine. Acrolein concentration is reduced to 7 ppm from initial 2000 ppm in 5 minutes, and further down to 4 ppm in 15 minutes when a 1% hexamethylenediamine solution is utilized at room temperature. The effect is still observed even with lower concentrations of HMD solution (0.2%).

TABLE I

Acrolein Concentrations (ppm) in HMD Solution vs. Time (min.) at Room Temperature

Time (min.)	10 wt% HMD	1 wt% HMD	0.2 wt% HMD	0.076 wt% HMD
0	2000	2000	2000	2000
5	7	7	30	226
15	5	4	6	149
25	3.7	4		111
35		3.7		90

EXAMPLE 5

Treatment of acrolein with 10% water solution of ammonium carbonate ($(NH_4)_2CO_3$)

To a screw cap vial containing 10% of ammonium carbonate in water solution (mixture of 0.1 g of ammonium carbonate and 0.9 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table II.

EXAMPLE 6

Treatment of acrolein with 1% water solution of ammonium carbonate

To a screw cap vial containing 10% of ammonium carbonate in water solution (mixture of 0.01 g of ammonium carbonate and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table II.

EXAMPLE 7

Treatment of acrolein with 0.2% water solution of ammonium carbonate

To a screw cap vial containing 0.2% of ammonium carbonate in water solution (mixture of 0.002 g of ammonium carbonate and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table II.

EXAMPLE 8

Treatment of acrolein with 0.064% water solution of ammonium carbonate

To a screw cap vial containing 0.064% of ammonium carbonate in water solution (mixture of 0.64 mg of ammonium carbonate and 1.0 g of water), 2 mg of acrolein was injected to spike the acrolein concentration to 2000 ppm. The vial was allowed to stand at room temperature. The vial was sampled periodically and analyzed by gas chromatography with solid phase micro-extraction. The results are shown in Table II.

As shown in Table II, acrolein can also be treated effectively by an aqueous solution of ammonium carbonate. Acrolein concentration is reduced to 3 ppm from initial 2000 ppm in 25 minutes with 10% of ammonium carbonate solution. The effect is still very significant with lower concentrations of ammonium carbonate solution (1%).

TABLE II

Acrolein Concentrations (ppm) in Ammonium Carbonate Solution
vs Time (min.) at Room Temperature

Time	10 wt%	1 wt%	0.2 wt%	0.064 wt

(min.)	NH_4CO_3	NH_4CO_3	NH_4CO_3	NH_4CO_3%
0	2000	2000	2000	2000
5	115	513	1362	1857
15		50	359	1536
25	3	22	114	1077
35	2.7	12	47	855
45		9	26	680
55		4	16	538
125				180

CLAIMS

1. A process for the reduction of the concentration of aldehyde(s) and/or ketone(s) in an aqueous waste stream, said process comprising the steps of

(a) contacting the aqueous waste stream with a water solution comprising an effective amount of an organic polyamine base; and

(b) maintaining the contacted waste stream at about 0°C to 65°C for a sufficient length of time to afford at least a 50% reduction in the concentration of the aldehyde(s) and/or ketone(s).

2. A process of making a polyester or polyol, characterized by (a) making the polyester or polyol, (b) forming an aqueous waste stream comprising aldehyde(s) and/or ketone(s), and (c) treating the aldehyde(s) and/or ketone(s) with a water solution comprising an organic polyamine base compound(s) to remove at least 50% of the aldehyde(s) and/or ketone(s) from the aqueous waste stream.

3. The process of any of claims 1-2 wherein the aldehyde(s) and/or ketone(s) is (are) selected from the group consisting of acrolein, methacrolein (methacrylaldehyde), crotonaldehyde, 2,4-hexadienal, acetaldehyde and methyl vinyl ketone.

4. The process of any of claims 1-2 wherein the aldehyde(s) and/or ketone(s) include acrolein and at least 50% of the acrolein is removed from the aqueous waste stream.

5. A process of making poly (trimethylene dicarboxylate) characterized by (a) reacting 1,3-propanediol with at least one dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalic acid and isophthalic acid, and lower dialkyl esters thereof, to yield the poly (trimethylene dicarboxylate) and a waste stream comprising acrolein, and (b) treating the aqueous waste stream using a water solution comprising a nitrogen-containing base selected from the group consisting of organic polyamines so that at least 50% of the acrolein is removed from the aqueous waste stream.

6. The process of claim 5 wherein the poly (trimethylene dicarboxylate) is poly (trimethylene terephthalate) and the dicarboxylic acid is terephthalic acid.

7. The process of any of claims 1-6 wherein the organic polyamine is selected from the group consisting of organic diamines, organic triamines and organic tetramines.

8. The process of claim 7 wherein the organic polyamine is an organic diamine selected from the group consisting of hexamethylene diamine, 2-methyl pentamethylenediamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,5-dimethyl hexamethylene diamine, 2,2-dimethylpentamethylene diamine, 5-methylnonane diamine, dodecamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, 2,2,7,7-tetramethyl octamethylene diamine, meta-xylylidene diamine, paraxylylidene diamine, diaminodicyclohexyl methane, C_2-C_{16} aliphatic diamines optionally substituted with one or more alkyl groups, and N-alkyl, and N'N-dialky derivatives thereof.

9. The process of claim 8 wherein the organic polyamine is hexamethylenediamine.

10. The process of any of the preceding claims wherein the process further comprises removing the at least 50% of the aldehyde(s) and/or ketone(s), or the acrolein, as an insoluble reaction product with the base.

11. The process of any of the preceding claims, wherein the waste streams to be treated contains 1-10,000 ppm of the aldehyde(s) and/or ketone(s), or the acrolein; the treated waste stream contains 0-500 ppm of the aldehyde(s) and/or ketone(s), or the acrolein; the treatment is carried out for a sufficient time to remove 80-100% of the aldehyde(s) and/or ketone(s), or the acrolein; the treatment time is 1 minute to 1 hour; the ratio of 1,3-propanediol:dicarboxylic acid is 50:1 to 0.1:1.