

Process for Detoxification of High Strength Wastewater

Field of Invention

- 5 The present invention describes an anaerobic detoxification process for high strength wastewater so that it may then be more effectively biologically treated subsequently.

Background

- 10 The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

Rapid industrialization has led to the generation of high strength wastewater in large quantities. Such wastewaters can be complex in their nature due to the presence of large numbers of organic and inorganic compounds and these may be inhibitory. Major sources of such wastewaters include those from the petroleum based industry, agro-food industry, pesticides, chemical and pharmaceutical industry, plastics, paper and pulp processing, and dyes and paints manufacturing. The contaminants generated in these industrial processes can include electron-withdrawing compounds, such as azo dyes, chloronitrobenzenes, nitroaromatics, halogenated aliphatics/aromatics and metalloids, which may inhibit or remain unaffected during conventional aerobic wastewater treatment (Van der Zee F.P., and Cervantes F.J., (2009) *Biotechnol. Adv.*, 27:256-277).

- 25 Inhibitory compounds present in industrial effluents can be even more detrimental to anaerobic treatment processes due to their effect on the microbial metabolic pathways (Chen *et al.*, (2008) *Bioresour. Technol.*, 99:4044–4064; Bulich *et al.*, (1982) *Process Biochem.*, 17:45-47) and therefore wastewater treatment plant performance can be compromised with lower chemical oxygen demand (COD) removal efficiencies (Chelliapan *et al.*, (2006) *Water Res.*, 40 (3), 507-516) and possibly even complete process failure eventually (Rodgers and Brunce, (2001) *Water Res.*, 35:2101-2111; Van der Zee *et al.*, (2001) *Biotechnol. Bioeng.*, 75:691-701). Minimization of such potential threats to the wastewater process requires pre-treatment of the influent. The commonly used pre-treatment methods are advanced oxidation processes such as ozone, UV catalytic oxidation, hydrogen peroxide or their combinations (Munter *et al.*, (2001). *Proc. Estonian Acad. Sci. Chem.*, 50: 59–80). Several inventions related to detoxification of solutions and wastewater

containing contaminants such as inorganic cyanides and/or organic nitriles, nitrite ions, phenol derivative or phenol and formaldehyde have been published (see US patent numbers 4,340,490, 3,970,554 and 4,280,914). However, due to the inherent limitations of these various physical, chemical and photochemical approaches, other technologies such as biological pre-treatment (detoxification) continue to be investigated.

Wastewater treatment by anaerobic biological processes has attained significant attention due to possibility of energy recovery in the form of methane. Anaerobic technologies such as the upflow anaerobic sludge blanket (UASB), the anaerobic sequencing batch reactor (AnSBR), and the anaerobic filter (AN) have shown potential to treat high-strength industrial wastewaters. Under anaerobic conditions, contaminants in the wastewater undergo reductive transformation (Field et al., (1995). *Anton. Leeuw. Int.J.G.*, 67:47- 77.). Anaerobic microorganisms are reported to be involved in degradation of a wide range of pollutants (Harwood et al., (1999). *FEMS Microbiol. Rev.*, 22:439-458). The inhibitory effect of wastewater might be drastically reduced if the toxic substances are subject to mineralization or biotransformation by microorganisms (Sierra-Alvarez et al., (1994). *Wat. Sci. Tech.*, 29(5-6): 353-363). However, reductive transformation of many different recalcitrant compounds proceeds very slowly due to electron transfer limitations and can lead to the collapse of anaerobic bioreactors before the inhibitory effects can be adequately mitigated.

The proposed invention is a cost effective, rapid detoxification method where microorganisms can effectively detoxify high strength wastewater under reductive conditions and the resulting metabolites can be further used as substrate by microbes. In one non-limiting example, the subsequent processing may be by anaerobic microbes for energy generation in the form of methane.

Summary of Invention

In a first aspect of the invention, there is provided a method of decontaminating high strength wastewater comprising inhibitory compounds, said process comprising the steps of:

- (a) mixing at least one high strength wastewater with at least one secondary sludge to form a blended slurry having a total chemical oxygen demand (TCOD) loading of up to 4g TCOD/g volatile suspended solids/day; and
- (b) adding the blended slurry to a detoxification reactor under anaerobic conditions that optionally comprises a microbial population of anaerobic bacteria and facultative anaerobic bacteria to provide a detoxified effluent.

In certain embodiments of the invention, the detoxified effluent may subsequently be treated in an anaerobic reactor to generate biogas. Additionally or alternatively, the detoxified effluent may subsequently be treated in an aerobic reactor for polishing of the wastewater.

- 5 In further embodiments of the invention, the at least one secondary sludge may be a biosludge obtainable from an aerobic stage of a wastewater treatment plant.

In certain embodiments, a ratio of the at least one high strength waste water to the at least one secondary sludge in the blended slurry may be from 1:1 to 5:1. For example, the ratio of
10 the at least one high strength waste water to at least one secondary sludge in the blended slurry may be from 2:1 to 5:1 (e.g. from 2.5:1 to 4:1, such as 3:1).

In certain embodiments the high strength wastewater may:

- 15 (i) comprise organic and/or inorganic inhibitory compounds; and/or
(ii) be a high strength industrial wastewater.

In yet further embodiments of the invention, no additional chemicals may be added. In additional or alternative embodiments of the invention, one or more of UV light, ultrasound, steam treatment, milling, and grinding may be applied to the high strength water and/or at
20 least one secondary sludge in a pre-treatment step before step (a).

In yet still further embodiments of the invention, the detoxification reactor step:

- (i) may have a hydraulic retention time of from 1 to 5 days; and/or
(ii) may have a pH of from 4 to 7.5 (e.g. about 5.5); and/or
25 (iii) may maintain a reaction temperature of from 30 to 60°C.

In certain embodiments of the invention, the blended slurry may have a total chemical oxygen demand (TCOD) loading of from 1g TCOD/g volatile suspended solids/day to 4g TCOD/g volatile suspended solids/day (e.g. 2.2g TCOD/g volatile suspended solids/day). In
30 additional or further embodiments of the invention, the blended slurry may have a soluble chemical oxygen demand to TCOD ratio of from 0.3:1 to 0.95:1 (e.g. 0.5:1 or 0.8:1).

In certain embodiments of the invention, when the detoxification reactor comprises a microbial population of anaerobic bacteria and facultative anaerobic bacteria, the microbial
35 population of anaerobic bacteria and facultative anaerobic bacteria may be generated by the processes described hereinabove, followed by the return of biomass to the detoxification

reactor following a clarification step conducted on the detoxified effluent before further processing of said effluent.

Drawings

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Figure 1 depicts a schematic diagram of a detoxification reactor upstream from a single stage anaerobic digestion process.

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Figure 2 is a graph depicting the volatile fatty acid (VFA) profile in: a mesophilic detoxification reactor with 5 days HRT (MDR-HRT-5); a thermophilic detoxification reactor with 5 days HRT (TDR-HRT-5); and feed.

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Figure 3 is a graph depicting the CH_4 generation in a single stage anaerobic reactor following the detoxification step in: a mesophilic reactor following mesophilic detoxification reactor with 20 days HRT (MM(MDR)-20d); and a mesophilic reactor following thermophilic detoxification reactor with 20 days HRT (MM(TDR)-20d).

Description

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As noted above, this invention relates to a method for detoxifying high strength wastewater (e.g. high strength industrial wastewater) containing organic inhibitory compounds. The reaction is carried out in an anaerobic/facultative reactor which does not need to have balanced acidogenesis and methanogenesis and where biotransformation of the compounds is carried out by anaerobic or facultative microorganisms (in the absence of oxygen) and in the presence of certain redox mediating compounds inherent in the feed stream. Secondary sludge is blended with the wastewater to mitigate the inhibitory effect of the wastewater and for nutrient balancing. This detoxification reactor protects the downstream reactor(s) (which may be anaerobic) from inhibition. Surprisingly, there is no need to add any outside agents to the reactor and the process (e.g. ozone, peroxide, UV light or sonication), as would be expected based upon conventional knowledge.

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Thus, there is provided a method of decontaminating high strength wastewater comprising inhibitory compounds, said process comprising the steps of:

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- (a) mixing at least one high strength wastewater with at least one secondary sludge to form a blended slurry having a total chemical oxygen demand (TCOD) loading of up to 4g TCOD/g volatile suspended solids/day; and

- (b) adding the blended slurry to a detoxification reactor under anaerobic conditions that optionally comprises a microbial population of anaerobic bacteria and facultative anaerobic bacteria to provide a detoxified effluent.

5 When used herein, "high strength wastewater" refers to any wastewater that has a high total chemical oxygen demand (TCOD) and/or a high soluble chemical oxygen demand (SCOD). A high TCOD and/or SCOD may refer to a TCOD and/or a SCOD that is greater than that produced by residential waste water. For example the TCOD and/or SCOD may be greater than 300 mg/L, such as greater than 1,000 mg/L.

10 As noted hereinbefore, the high strength wastewater may comprise organic and/or inorganic inhibitory compounds that may prevent the wastewater from being treated in a conventional treatment system. One advantage of the current method is that these inhibitory compounds do not prevent the detoxification of the wastewater and hence allows said wastewater to be
15 further treated.

When used herein, "secondary sludge" refers to the excess sludge produced from any secondary biological treatment process. Non-limiting examples of secondary sludges that may be suitable for use in the current invention may be produced from a clarifier and
20 dissolved air floatation. Other secondary sludges that may be mentioned herein include thickened sludge with after belt press/decantation may also be suitable for use in the process described herein. In certain embodiments of the invention that may be mentioned herein, the secondary sludge may be a biosludge obtainable from an aerobic stage of a wastewater treatment plant.

25 As noted above, the process of step (b) may involve the use of a detoxification reactor that contains a microbial population of anaerobic bacteria and facultative anaerobic bacteria to provide a detoxified effluent. As should be noted, the presence of this population of anaerobic bacteria is optional and so these bacteria do not need to be present in the
30 detoxification reactor. However, when such bacteria are present, they may be introduced as a seed population of bacteria from any suitable source. In a non-limiting example, the seed population may be obtained by depositing a mesophilic anaerobic sludge into the detoxification reactor. Alternatively or additionally, the microbial population of anaerobic bacteria and facultative anaerobic bacteria may be generated by a first run of the above
35 process in the absence of any bacteria (or in the presence of a seed population), followed by the return of biomass to the detoxification reactor following a clarification step conducted on the detoxified effluent before further processing of said effluent.

The main features of the process are as follows.

- The pre-treatment detoxification reactor can effectively detoxify/biotransform inhibitory organic compounds present in high strength wastewaters.
- Wastewater may be blended with biosludge from a wastewater treatment plant's aerobic stage to provide a supplementary carbon source and so help mitigate the inhibitory effect on the detoxifying microbial consortium.
- The detoxification step is performed by an anaerobic microbial consortium maintained (or selected for) in the pre-treatment detoxification reactor using the reduction-oxidation (redox) mediating compounds inherent in the waste stream so that no external redox mediating chemicals are required. Also, the macromolecules released due to hydrolysis of the biosludge supplement may help protect the microbes involved in the detoxification process from toxic shock.
- The detoxified stream from the pre-treatment described above can then be fed to any appropriate anaerobic reactor for enhanced methane production and COD reduction.

The detoxified effluent may subsequently be treated by any suitable treatment step. Potential subsequent treatment steps may include, but are not limited to, treatment in an anaerobic reactor to generate biogas and/or treatment in an aerobic reactor for polishing of the wastewater.

The high strength wastewater may be a high strength industrial wastewater. When used herein "high strength industrial wastewater" means that the high strength wastewater originates from an industrial source.

In yet further embodiments of the invention, no additional chemicals may be added. In additional or alternative embodiments of the invention, one or more of UV light, ultrasound, steam treatment, milling, and grinding may be applied to the high strength water and/or at least one secondary sludge in a pre-treatment step before step (a).

The detoxification reactor step:

- (i) may have a hydraulic retention time of from 1 to 5 days; and/or
- (ii) may have a pH of from 4 to 7.5 (e.g. about 5.5); and/or
- (iii) may maintain a reaction temperature of from 30 to 60°C.

As noted above, step (a) of the process involves providing a blended slurry of a high strength wastewater and at least one secondary sludge. It will be appreciated that any suitable blend ratio of high strength wastewater to at least one secondary sludge may be used, as determinable by a person skilled in the art. Particular ratios that may be mentioned include a ratio of 1:1 to 5:1, from 2:1 to 5:1 and from 2.5:1 to 4:1, for example a ratio of 3:1 (high strength wastewater to at least one secondary sludge). Additionally or alternatively, the blended slurry may have a soluble chemical oxygen demand to TCOD ratio of from 0.3:1 to 0.95:1 (e.g. from 0.5:1 or 0.8:1). In further additional or alternative embodiments, the blended slurry may have a total chemical oxygen demand (TCOD) loading of from 1g TCOD/g volatile suspended solids/day to 4g TCOD/g volatile suspended solids/day (e.g. 2.2g TCOD/g volatile suspended solids/day).

The method for detoxification includes feeding the wastewater blended with biosludge into a reactor which can exclude air. In certain embodiments that may be mentioned herein, this process may be conducted with:

- a microbial population comprising anaerobes and facultative bacteria (e.g. already in a reactor, or selected for in the process itself), otherwise known as an active microbial consortium;
- a reactor holding a slurry comprising the wastewater, the supplementary sludge, and the active microbial consortium;
- a hydraulic retention time (HRT) of 1-5 days depending on the nature of the wastewater;
- a total COD (TCOD) loading which can be up to 4g TCOD/g volatile suspended solid (VSS)/day;
- a pH of the detoxification reactor between 4 to 7.5 with an optimal at about 5.5;
- a reaction temperature ranging from 30-60 °C.

Additionally and alternatively, and as a non-limiting example, the detoxification method/process, according to this invention, may involve:

- feeding the wastewater blended with biosludge into an anaerobic reactor with a microbial population comprising of anaerobes and facultative bacteria. The reactor holds a slurry comprising the wastewater, the supplementary sludge and the active microbial consortium;
- providing a hydraulic retention time (HRT) of 1-5 days depending on the nature of the wastewater;

- providing a total COD (TCOD) loading which can be up to 4g TCOD/g volatile suspended solid (VSS) per day;
- providing pH of the detoxification reactor between 4 to 7.5 with an optimal at about 5.5;
- providing a reaction temperature ranging from 30-60 °C.

Effluent from the detoxification processes above can be further treated in an anaerobic reactor for generation of methane and/or an aerobic reactor for polishing.

Some advantages of this invention include that the detoxification of wastewater may be achieved with no supplementary chemicals (such as, ozone or peroxide). The anaerobic process downstream of the detoxification process has higher rate of methane generation and increased COD removal efficiency. This detoxification process is also more rapid than conventional anaerobic detoxification processes. The pre-treated effluent is at a low redox potential and will not compromise the downstream anaerobic process. The metabolites from this detoxification process that are not further degraded in the anaerobic process would also likely be more readily stabilised by an aerobic polishing stage.

A possible treatment plan for the detoxification of a high strength industrial wastewater followed by methane generation is described in Figure 1.

In the embodiment shown in Figure 1, high strength industrial wastewater is first blended with secondary sludge and is fed into the pre-treatment detoxification reactor (100) to reduce inhibition. The detoxification unit may or may not be followed by a clarifier (110) for liquid-solids separation depending on need for biomass return to Reactor 100 and on the design of Reactor 200. The supernatant from clarifier 110 is fed to a single stage anaerobic reactor for biogas generation (Reactor 200). The single stage anaerobic reactor is followed with a degassing unit (210) which separates the biogas (220) and the effluent is fed to the second clarifier (230) for liquid-solids separation and the biomass is returned to the methane reactor. The effluent from clarifier 200 may undergo further treatment prior to discharge as treated wastewater (240).

The invention is intended to be used for the detoxification of high strength industrial wastewaters containing inhibitory compounds. The technology can be used to protect an anaerobic microbial consortium from toxic shock which can lead to anaerobic reactor failure.

The detoxified metabolites present in the pre-treated wastewater can be further used as substrate for energy generation.

Example

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A case study was conducted for the detoxification of high strength wastewaters using mesophilic (35°C) and thermophilic (55°C) conditions in continuous stirred tank lab-scale anaerobic reactors with intermittent feeding and on a wash-out basis. The feed used in the study included two industrial high strength wastewaters containing toxic compounds (WW/1 and WW/2) blended with two biosludges (SL/1 and SL/2) at a blending ratio of 1/8 SL/1 : 1/8 SL/2 : 3/8 WW/1 : 3/8 WW/2. The blending was performed for two minutes using a common household blender to provide the feed used in the example below. The detoxified compounds were subsequently used for biogas generation in a mesophilic reactor.

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The anaerobic seed sludges used in this study were collected from a mesophilic anaerobic digester in a local municipal sewage treatment plant treating primary and secondary sludges. The various process parameters for detoxification of high strength industrial wastewaters used in this example are summarized in Table 1.

Parameter	MDR-SRT-5 (Mesophilic Detoxification)	TDR-SRT-5 (Thermophilic Detoxification)
Working volume	4.0 L	4.0 L
SRT	5 days	5 days
Temperature	35°C	55°C
pH	6.0±0.4	6.0±0.4
Source of seed	Mesophilic anaerobic sludge	Mesophilic anaerobic sludge
Solids in mixed	MLSS 12.28, MLVSS 8.98	MLSS 12.73, MLVSS 9.65
Feed COD	TCOD 100 g/L, SCOD 80 g/L	TCOD 100 g/L, SCOD 80 g/L
TCOD loading	2.2 g TCOD/g VSS/day 20 g TCOD/ L reactor / day	2.07 g TCOD/g VSS/day 20 g TCOD/ L reactor / day
SCOD loading	1.78 g SCOD/g VSS/day 16 g SCOD/ L/ day	1.65 g SCOD/g VSS/day 16 g SCOD/ L/ day
Feeding program	CSTR with intermittent feeding, 800ml/day	CSTR with intermittent feeding, 800ml/day

Table 1

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The supporting data for the process for detoxification of high strength wastewater and its subsequent use to produce biogas are shown in Figures 2 and 3.

5 The detoxification process was carried out in anaerobic reactors where primarily the biotransformations of the toxic compounds were carried out. There may or may not be a significant change in the VFA concentration during the detoxification process as shown in Figure 2. No significant amount of biogas generation was recorded during this step. Subsequently, when the detoxified feeds were treated in mesophilic single stage anaerobic reactors (HRT 20 days, working volume 10L) significantly high volume of biogas was
10 generated as shown in Figure 3.

Claims

1. A method of decontaminating high strength wastewater comprising inhibitory compounds, said process comprising the steps of:
 - (a) mixing at least one high strength wastewater with at least one secondary sludge to form a blended slurry having a total chemical oxygen demand (TCOD) loading of from 1g to 4g TCOD/g volatile suspended solids/day;
 - (b) adding the blended slurry to a detoxification reactor under anaerobic conditions that optionally comprises a microbial population of anaerobic bacteria and facultative anaerobic bacteria to provide a detoxified effluent; and
 - (c) wherein the detoxified effluent is subsequently treated in an anaerobic reactor to generate biogas.
2. The method of Claim 1, wherein the detoxified effluent is subsequently treated in an aerobic reactor for polishing of the wastewater.
3. The method of any one of the preceding claims, wherein a ratio of the at least one high strength waste water to at least one secondary sludge in the blended slurry is from 1:1 to 5:1.
4. The method of Claim 1 or Claim 2, wherein the ratio of the at least one high strength waste water to at least one secondary sludge in the blended slurry is from 2:1 to 5:1
5. The method of Claim 4, wherein the ratio of the at least one high strength waste water to at least one secondary sludge in the blended slurry is from 2.5:1 to 4:1, such as 3:1.
6. The method of any one of the preceding claims, wherein the high strength wastewater comprises organic and/or inorganic inhibitory compounds.
7. The method of any one of the preceding claims, wherein the high strength wastewater is a high strength industrial wastewater.
8. The method of any one of the preceding claims, wherein no additional chemicals are added.
9. The method of any one of the preceding claims, wherein the detoxification reactor step has a hydraulic retention time of from 1 to 5 days.

10. The method of any one of the preceding claims, wherein the detoxification reactor step has a pH of from 4 to 7.5.
11. The method of any one of the preceding claims, wherein the detoxification reactor step maintains a reaction temperature of from 30 to 60°C.
12. The method of any one of the preceding claims, wherein the blended slurry has a total chemical oxygen demand (TCOD) loading of from 2.2g TCOD/g volatile suspended solids/day.
13. The method of any one of the preceding claims, wherein when the detoxification reactor comprises a microbial population of anaerobic bacteria and facultative anaerobic bacteria, the microbial population of anaerobic bacteria and facultative anaerobic bacteria is generated by the process of any one of Claims 1 to 10, followed by the return of biomass to the detoxification reactor following a clarification step conducted on the detoxified effluent before further processing of said effluent.
14. The method of any one of the preceding claims, wherein the method may comprise a pre-treatment step of the high strength water and/or at least one secondary sludge before step (a), which pre-treatment step may comprise one or more of UV light, ultrasound, steam treatment, milling, and grinding.
15. The method of any one of the preceding claims, wherein the at least one secondary sludge may be a biosludge obtainable from an aerobic stage of a wastewater treatment plant.
16. The method of any one of the preceding claims, wherein the blended slurry has a soluble chemical oxygen demand to TCOD ratio of from 0.3:1 to 0.95:1.