Annex 6 - Overview literature review - Dioxane removal from waste water

First literature search on dioxane removal was done.
See patents and publications.
There is a patent from P&G (not yet granted) which deals with the removal of dioxane from an aqueous surfactant composition by means of two steps process:
1) filtering the initial feed supply through the nanofilter to form a retentate and a filtrate, and
2) subjecting the filtrate to reverse osmosis. The reverse osmosis concentrate is further processed to destroy dioxane by advanced oxidation processing, Fenton reaction, photo-Fenton reaction, activated carbon adsorption, catalyst processing, alcohol dehydration reaction, ozone treatment, ultra-violet/TiO_2 treatment, incineration, or a combination thereof.
In their example they mention a dioxane content below 15 ppm.

University of California published a paper using membrane treatment processes, including microfiltration and reverse osmosis prior to ultraviolet-based advanced oxidation process (based on persulfate and monochloramine oxidating agents). See process scheme.

Annex 6A - Patents

Annex 6A - Publications

Annex 6C - Process scheme - Treatment 1,4-dioxane containing waste water

Annex 6A - Patents

#	Patent	Company	Technology	Year	Patent Status	Claims or Highlights
1	DE3740695C2	REWO CHEM WERKE	Absorption	1987	Withdrawn	- Process for removing 1,4-dioxane from aqueous alkyl polyglycol ether sulfate solutions - Remoal of dioxane by menas of zeolites (molecular sieves)
2	US4285881A	VISTA CHEMICAL COMPANY	Steam stripping	1980	Expired	- Dioxane removal from ether sulfate by menas of falling film evaporator - Dioxane content < 10 ppm
3	US20130220935A1	DOW GLOBAL TECHNOLOGIES	Adsorption	2012	Withdrawn	- Removal of dioxane from water using carbonaceous adsorbents - Dioxane content < 3 ppb - Adsorbent is regenerable in place with low pressure steam
4	EP2904082B1	THE CHEMITHON CORPORATION	Steam stripping	2012	Active in NL, DE, BE, FR, GB BR, CN, US, IN, JP, KR, MX, SG, MY, ID	- Removing dioxane from an aqueous alkoxylated fatty alcohol sulfate paste by means of wiped film evaporator - Dioxane content < 20 ppm
5	US4375437	GAF CORPORATION	Sparging	1981	Expired	- Dioxane removal from a phosphate ester surfactant by means of sparging with N2 or air. Vaccum distillation is also claimed - Dioxane content < 10 ppm
6	US4405799A	GAF CORPORATION	Absorption	1981	Expired	- Removing dioxane from an alkoxylated product waste gas by contacting said gas with an acid having a pKa < 5 (acid can be in liquid form or deposited on a porous support like silica or activated carbon) where dioxane is complexed with the acid in a non-volatile form which is readily disposable
7	CN112707522A	Jiangsu Zanyu Technology Co	Adsorption	2020	Examining	- Removal of dioxane from atty alcohol polyoxyethylene ether sodium sulfate by means of two steps adsorption process using 1) ion exchange resins and 2) activaded carbon
8	CN210473080U	Nanjing Duoyuan Bioengineering Co	Vaccum drying	2019	Active in CN	- Dioxane removal from water soluble ethoxylated lanolin by means of vaccum dryer (the separated dioxane and water vapor form an azeotrope, which is collected by a vacuum condense)
9	US20140263098A1	ABRAMS RICHARD KERFOOT WILLIAM B	Oxidation	2013	Withdrawn	- Removal of dioxane from an aqueous solution by means of exposing the aqueous solution to gaseous ozone (present as micro or nano-bubbles) - Dioxane content < 1 ppb
10	CN103480163A	ZANYU TECH GRP CO LTD JIAXING ZANYU TECH	Vaccum drying with centrifugation	2013	Active in CN	- Removal of dioxane from ethoxylated alkyl sulfate by means of a centrifugal spray dedioxan device
11	CN202113620U	HUNAN LICHEN INDAL	Vaccum drying with cyclone	2011	Expired	- Removal of dioxane from fatty alcohol polyoxyethylene ether sulfate by means of a jet-type dedioxanization device
12	CN101690875B	ZANYU TECH GRP CO LTD	Vaccum spray	2009	Active in CN	- Preparation of fatty alcohol polyoxyethylene ether sulfate with low 1,4-dioxane content. The fatty alcohol ether sulfate is neutralized prior entering the vaccum tube spray. The neutralization system involved in the present invention has more materials that circulate and stay, which can increase the amount of water and facilitate the removal of 1,4-dioxane
13	CN104710019A	EAST CHINA UNIV OF SCI & TECH SHANGHAI ACADEMY OF ENVIRONMENTAL SCIENCES	Biodegradation	2015	Active in CN	- Removal of chlorinated hydrocarbons and dioxane from waste water by means of a zero-valent iron-activated sludge coupling treatment method. Microorganisms are lactic acid bacteria (Lactococcus), iron reducing bacteria (Ferribacterium), dechlorination bacteria (Dehalobacter) and sulfate reducing bacteria (Desulfovibrio)
14	KR1020100113312A (patent is in Korean)	KOLON CORP	Reverse Osmosis	2010	Withdrawn	- Removal over 85% is claimed.
15	US20210269328A1	THE PROCTER & GAMBLE CO	Nanofiltration and Reverse Osmosis	2020	Examining in US Published in CN	- Removal of dioxane from an aqueous surfactant composition - Two steps process: 1) filtering the initial feed supply through the nanofilter to form a retentate and a filtrate, and 2) subjecting the filtrate to reverse osmosis - The reverse osmosis concentrate is further processed to destroy the contaminant by advanced oxidation processing, Fenton reaction, photo-Fenton reaction, activated carbon adsorption, catalyst processing, alcohol dehydration reaction, ozone treatment, ultra-violet/TiO2 treatment, incineration, or a combination thereof

Annex 6A - Publications

#	Author	Tehcnology	Year	Abstract
1	Universit of California Similar paper here	Membrane treatment (nnaofiltration, reverse osmosis) and Oxidation	2018	A sequential combination of membrane treatment and UV-based advanced oxidation processes (UV/AOP) has become the industry standard for potable water reuse. Chloramines are used as membrane antifouling agents and therefore carried over into the UV/AOP. In addition, persulfate (S2O82–) is an emerging oxidant that can be added into a UV/AOP, thus creating radicals generated from both chloramines and persulfate for water treatment. This study investigated the simultaneous photolysis of S2O82– and monochloramine (NH2Cl) on the removal of 1,4-dioxane (1,4-D) for potable-water reuse. The dual oxidant effects of NH2Cl and S2O82– on 1,4-D degradation were examined at various levels of oxidant dosage, chloride, and solution pH. Results showed that a NH2Cl-to-S2O82– molar ratio of 0.1 was optimal, beyond which the scavenging by NH2Cl of HO•, SO4•–, and Cl2•– radicals decreased the 1,4-D degradation rate. At the optimal ratio, the degradation rate of 1,4-D increased linearly with the total oxidant dose up to 6 mM. The combined photolysis of NH2Cl and S2O82– was sensitive to the solution pH due to a disproportionation of NH2Cl at pH lower than 6 into less-photoreactive dichloramine (NHCl2) and radical scavenging by NH4+. The presence of chloride transformed HO• and SO4•– to Cl2•– that is less-reactive with 1,4-D, while the presence of dissolved O2 promoted gaseous nitrogen production. Results from this study suggest that the presence of chloramines can be beneficial to persulfate photolysis in the removal of 1,4-D; however, the treatment efficiency depends on a careful control of an optimal NH2Cl dosage and a minimal chloride residue.
2	Yokohama Research & Development Center , Mitsubishi Heavy Industries	Oxidation and Electrolisis	2007	In this paper, applicability of ozonation combined with electrolysis as an advanced oxidation process for the removal of 1,4-dioxane from synthetic wastewater, has been studied. The combined process easily decomposed 1,4-dioxane, and two byproducts were detected in treated water. Although bicarbonate alkalinity was a strong radical scavenger, its influence was abated by air-stripping of carbon dioxide at the anodic compartment of the reactor. Free chlorine produced through anodic oxidation of chloride ion accelerated the COD removal from wastewater, despite the fact that this ion acted as a weak radical scavenger. The combined process was demonstrated to be applicable to the treatment of wastewater containing high concentration of bicarbonate alkalinity and chloride ions.
3	Seoul National University	Sonification	2006	This research investigates the effect of adding oxidants such as Fe0, Fe2+ and S2O82− in the sonication of 1,4-dioxane (1,4-D). The results indicate that the degradation pattern of 1,4-D kinetically could be divided into three steps (initiation, acceleration, and stabilization), with the first two steps predominating. The initiation step agreed with zero order rate model, while the acceleration step was the pseudo-first order. In the presence of HCO3− as a radical scavenger, the degradations of 1,4-D and TOC were suppressed, indicating that OH radical is an important factor in the sonolysis, especially at the acceleration step. The overall degradation efficiency of 79.0% in the sonolysis of 1,4-D was achieved within 200 min. While Fe0, Fe2+ and S2O82− were individually combined with sonication, the total degradation efficiency of 1,4-D increased 18.6%, 19.1% and 16.5% after 200 min, respectively. The addition of oxidants not only increased the rate constant in the acceleration step, but also changed the kinetic model from zero to pseudo-first order at the initiation step. The addition of oxidants such as Fe2+, Fe0 and S2O82− in the sonication of 1,4-D also improved the mineralization of 1,4-D. However, the degradation efficiencies of 1,4-D and TOC were not statistically different (p=0.709, ANOVA) with different oxidants such as Fe2+, Fe0 and S2O82−.
4	Florida State University	Water-film plasma and Biodegradation	2019	In this work a water film non-thermal plasma reactor is combined with an aerobic biological reactor to treat water contaminated by 1,4-dioxane. The plasma reactor converted 1,4-dioxane to organic products including ethylene glycol, ethylene glycol monoformate, ethylene glycol diformate, 1,4-dioxan-2-one, 1,4-dioxan-2-ol, and formic, oxalic, glycolic, and methoxyacetic acids. The detection of these organic products led to a proposed novel 1,4-dioxane degradation pathway. The plasma reactor primarily utilized OH radicals formed directly from water to degrade 1,4-dioxane at an energy efficiency comparable to, but with a reaction rate over three orders of magnitude higher than that in other advanced oxidation processes (AOPs), which might be due to the significant local OH radical production. The concentration and composition of the organic products exiting the plasma reactor varied with hydraulic retention time (HRT) and affected the following biological treatment time. At the optimum HRT for the plasma reactor (i.e., 1 s), ~25% of 1,4-dioxane was mineralized to CO2, and ~75% was converted to organic products, which were further degraded in the following biological reactor.
5	Pohang University of Science and Technology	Oxidation	2018	In this study, we investigated the performance of nanoscale zerovalent iron (nZVI) in the presence of the common oxidants, persulfate (PS), peroxymonosulfate (PMS) and hydrogen peroxide (HP), for the removal of 1,4-dioxane (1,4-D) and As(III) in contaminated waters. PS/nZVI showed the highest removal of both 1,4-D and As(III), followed by HP/nZVI and PMS/nZVI in order. The removal increased as the oxidant dosage increased, whereas only As(III) removal was enhanced with increasing nZVI dosage. The maximum removal occurred at pH 3 and only PS/nZVI could remove As(III) as the pH increased from 3 to 7. Radicals such as radical dotOH and SO4radical dot− were produced from the oxidant/nZVI system and the radicals contributed more to the removal of 1,4-D than As(III). The removal of As species was significantly influenced by nZVI dissolution, which consequently caused adsorption and co-precipitation as the main removal mechanisms. For environmental applications, the PS/nZVI system efficiently treated a real groundwater contaminated by 1,4-D and As(III), respectively. The basic knowledge gained from this study could help in selecting a proper oxidant to use with nZVI to purify surface and groundwaters contaminated by organic and inorganic contaminants at the same time.
6	Federal University of Santa Catarina Brazil	Oxidation	2020	1,4-Dioxane is a synthetic cyclic ether traditionally used as a chlorinated solvent stabilizer. It is a small molecule and recalcitrant compound that is difficult to remove by conventional processes and in this regard, there is a need for the development of new technologies. In this study, an innovative CuO-coated ceramic membrane (CM) reactor system that can be used to oxidize 1,4-dioxane dissolved in surface water by catalytic ozonation was developed. The effect of the thickness of the CuO deposited on the ceramic membrane surface on the permeability, fouling resistance, 1,4-dioxane removal, and toxicity was evaluated. The efficiency of the hybrid ozonation coupled to the use of a CuO-coated CM in 1,4-dioxane removal and the antifouling properties were assessed from TOC and 1,4-dioxane removal kinetics data. Reusability in four cycles was also tested. The performance of the CuO-coated CM remained stable during the four cycles of the reusability test. The ceramic membrane coated with CuO particles coupled with ozonation is appropriate for 1,4-dioxane degradation in the aqueous phase (45% efficiency, rate constant increased by a factor of 2.98 compared with the uncoated-hybrid process) and fouling removal (60 min to recovery the permeate flux).
7	Hanyang University	Biodegradation?	2019	The purpose of this study was to completely remove low levels of 1,4-dioxane, a controlled substance with high solubility, low degradability, and high hazard level, from water using a specific microbe-immobilized carrier. A cell-entrapped carrier based on polyethylene glycol diacrylate was prepared using enriched culturing of Candidatus Saccharibacteria, using 1,4-dioxane as the only carbon source in activated sludge. When the 1,4-dioxane concentration was 5 mg/L, the cell-immobilized carrier process removed up to 0.026 mg/L of 1,4-dioxane at a hydraulic retention time (HRT) of 6 h, but the activated sludge process was removed up to 0.12 mg/L at an HRT of 20 h. The mollifying effect created by internal recirculation was less effective than that of HRT. This technology could be a cost-effective alternative to advanced oxidation process for the treatment of landfill leachate and groundwater contaminated with 1,4-dioxane.

Annex 6C - Process scheme - Treatment 1,4-dioxane containing waste water

University of California published a paper using membrane treatment processes, including microfiltration and reverse osmosis prior to ultraviolet-based advanced oxidation process (based on persulfate and monochloramine oxidating agents). See scheme below.